

Laboratory Evaluation of In-Situ Gelled Acids for Carbonate Reservoirs

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Summary

Three different commercial formulations (A, B, and C) of in-situ gelled acids are compared in detail at temperatures up to 150°F and acid concentrations from 5 to 20 wt% HCl. In-situ gelled acids are said to work by a gelation mechanism that occurs at the rock surface as the acid is spent. These acids contain a polymer, a crosslinker, and a breaker, in addition to other additives. Detailed viscosity measurements of each in-situ gelled acid were made with live, partially neutralized, and spent acid. A new experimental procedure was developed to partially neutralize the in-situ gelled acid with calcium carbonate, and then the apparent viscosity was measured as a function of shear rate in the range 1 to 3,000 s⁻¹. The pH values of these samples varied from 0 to 6. Relative reaction rates with reservoir rock of the three in-situ gelled acids were compared at 100°F. Coreflood experiments were conducted with small acid volumes, so that permeability could be measured before acid breakthrough occurred.

In-situ gelled acids all retarded the reaction of acid with reservoir rock, primarily as a result of the polymer present in the acid formulae.

From viscosity measurements, live in-situ gelled acids A and B behaved more like gelled acids. Their viscosity in live acid was significantly higher than that of Acid C. In spent acid, the viscosity of Acid C was higher than that of Acids A or B. Acid C was most effective at initial HCl concentrations of 5 and 10 wt% at 100 and 150°F. Acids A and B were effective only at an initial HCl concentration of 10 wt% and 100°F.

Coreflood studies showed that the polymer and crosslinker component of in-situ gelled acids irreversibly reduced the permeability of carbonate reservoir rock.

As with any spent acids, mixing spent in-situ gelled acids with seawater resulted in calcium sulfate precipitation for all three of the acid systems.

Introduction

Acid diversion is very important when stimulating vertical wells with long target zones or horizontal wells in carbonate formations.^{1,2} In a heterogeneous formation, the injected acid will flow primarily into the high-permeability zones. This poor acid distribution will reduce the overall efficiency of the stimulation treatment. Increasing the acid viscosity can improve acid diversion in the formation. The use of in-situ gelled acids is a relatively new technique in acid diversion. The viscosity of in-situ gelled acids increases significantly as the injected acid reacts with the reservoir rock. In-situ gelled acids also retard the acid reaction with the formation. These two properties improve treatment efficiency. The viscosity of in-situ gelled acids should break rapidly after the acid is spent to improve well cleanup after the acid treatment.

In-situ gelled acids consist of an acid-soluble polymer, a crosslinker, and a breaker. Some formulations contain a pH buffer. It has been reported that the polymer in this system forms a gel within a narrow pH range.^{3,4} As a result of gel formation, the viscosity of the acid increases in-situ, and acid diversion can be achieved. Ideally, the gelled acid will form wormholes evenly distributed over the entire target zone. This gel will improve acid

placement, provide more uniform damage removal, and control acid fluid loss.^{4,5}

Each type of in-situ gelled acid uses slightly different gelation chemistry. The crosslinker may be iron (III), zirconium compounds, or other polyvalent cationic species.⁶ The behavior of the gelled acid will be determined by temperature, which affects viscosity and acid reaction rate. Dilution of the acid with formation brine will reduce viscosity and the effectiveness of the crosslinking reaction.

When hydrochloric acid is injected into a formation, it has a pH of nearly zero. The pH of the acid increases as the acid reacts with the carbonate rock. At a pH value of approximately 2, it is claimed that the polymer reacts with the iron (III) crosslinker and forms a very viscous gel.^{3,4} At pH 2, the acid concentration has decreased to approximately 0.04 wt%, and it is nearly completely spent. The viscosity of the acid can reach 1,000 mPa·s and is able to divert unreacted acid into other zones in the formation.⁴ As the acid continues its reaction, the pH will rise further. At pH values greater than 4 to 5, the viscosity of the gel is claimed to decrease as the polymer and crosslinker dissociate. A breaker is used to ensure a complete reversal of the crosslinking process by reducing iron (III) to iron (II).⁴ The decreased viscosity of the spent acid is designed to improve its removal from the formation. In comparison, zirconium (IV) crosslinker is claimed to form a viscous gel at pH values of 4 to 5, and the gelation process is reversed by the addition of calcium fluoride. The fluoride ion forms a stable complex with zirconium (IV) to reverse the crosslinking of the polymer.

A comprehensive review of the effectiveness of more than 80 acid treatments of power water injection and salt-water disposal wells was reported by Mohamed *et al.*⁷ These treatments included regular, emulsified, and in-situ gelled acids. It was speculated that severe formation damage can result from the improper use of in-situ gelled acids. Taylor *et al.*⁸ reported a case study of a seawater injection well stimulated with an in-situ gelled acid. When used correctly, in-situ gelled acids improved acid treatment results.^{7,8,9} Woo *et al.*¹⁰ discussed the plugging problems inherent with conventional crosslinked acid gellants. Laboratory studies of in-situ gelled acids were reported by Bazin¹¹ and by Lynn and Nasr-El-Din.¹²

The objectives of this work are to:

1. Determine the relative rate of the reaction of in-situ gelled acid with the reservoir rock.
2. Study the gelation mechanisms of in-situ gelled acid systems using viscosity measurements.
3. Compare the performance of in-situ gelled acids in coreflood experiments.

Experimental Studies

Acid formulae used in this work are listed in **Table 1** for Acid A, **Table 2** for Acid B, and **Table 3** for Acid C. Composition of the additives came from Material Safety Data Sheets supplied by each company. Acids B and C use an iron (III) compound as a crosslinking agent. Acid A uses a zirconium (IV) compound. Acid C was the only one to use a buffer, hydroxyacetic acid, at 2 gal/Mgal. All three of the acids had the same polymer loading (20 gal/Mgal). The three companies claim a useful range of 5 to 28 wt% HCl, but were examined at 5 to 20 wt% HCl in these experiments.

Viscosity measurements were made using a Haake Rheostress RS100 rotational viscometer. Most measurements were made using a double gap sensor system to increase accuracy. Measurement temperature was 100 or 150°F (38 or 65°C). These temperatures cover the range found in power water injection wells and disposal wells in the reservoir studied.

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