

Development and Field Application of a New Measurement Technique for Organic Acid Additives in Stimulation Fluids

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Summary

Formic and acetic acids, with and without HCl, have been used extensively over the last 40 years as stimulation fluids and as acid additives. A measurement method for these organic acids was not previously available for highly contaminated acid stimulation samples that contain high acid concentrations, dissolved oil, suspended solids, and several different acid additives. Citric and acetic acids are also used in acid treatments as iron control agents at temperatures less than 200 and 150°F, respectively. An analytical method using capillary electrophoresis was developed to simultaneously measure the concentrations of formic and acetic acids in stimulation fluids. The developed method was used to evaluate flowback samples from pickle treatments and stimulation treatments of several high-temperature wells.

The following conclusions are made:

- A method for the simultaneous measurement of formic and acetic acids was developed, evaluated, and implemented for acid stimulation samples.
- Citric acid concentration can be determined in certain cases, which are identified in the paper.
- Results of formic and acetic acid concentrations in sandstone and carbonate corefloods were evaluated.
- Flowback samples from pickle treatments and acid fracture treatments were evaluated. Results from treatments of super chrome-13 and low-carbon steel tubing with 15 wt% HCl/ 9 wt% formic acid show that a small decrease in formic acid relative to chloride concentration occurred over time with carbon steel. No significant decrease of formic acid relative to chloride concentration was observed in the flowback of a well with a super chrome-13 completion.

Introduction

Organic acids have been used extensively in acid stimulation treatments in the oil industry. Harris first reported the use of acetic acid for well completion and stimulation in 1961.¹ Formic acid was used with HCl for high-temperature stimulation by Dill and Keeney in 1978.² Acetic acid^{3–13} and formic acid^{6–9,12,14} have been used extensively in stimulation treatments in recent years. The application of organic acids in Saudi Arabia was first reported by Nasr-El-Din *et al.* and Hashem *et al.*,^{8,15} where a mixture of acetic acid (5 wt%) and hydrochloric acid (5 wt%) was successfully used to stimulate water supply and injection wells in a sandstone field in central Saudi Arabia. In addition, citric and acetic acids are frequently used with hydrochloric acid as iron control agents.¹⁶ Acetic and formic acids are used in field treatments at concentrations up to 13 and 9 wt%, respectively.¹⁷ Formic acid is used as a corrosion inhibitor intensifier in wells completed with low-carbon steel tubulars.¹⁸ Even so, the measurement of formic acid concentration in flowback samples has never been reported.

Acetic acid concentration in flowback samples has been reported once using a titration method,¹³ to the best of the authors' knowledge.

To effectively evaluate stimulation treatments using organic acids, it is critical to measure their concentrations in the injected fluids and in the well flowback samples. Analysis of these samples can be difficult because they can contain high concentrations of chemical additives, dissolved solids, suspended solids, and oil. Nasr-El-Din *et al.*¹³ used a titration method to determine acetic acid in the well flowback samples. However, this method is only applicable for high acetic acid concentrations and only measures the concentration of unspent acid.

Methods that have been used to determine the concentration of carboxylic acids in aqueous (nonacid) samples were summarized by Volgger *et al.*¹⁹ Chromatographic methods have usually been used, including gas/liquid chromatography, liquid chromatography using ion exchange, ion-moderated chromatography, reverse-phase chromatography, and ion chromatography. Although these methods can have very low detection limits, they often require extensive sample pretreatment, derivatization steps, and long analysis time.²⁰ In contrast, capillary electrophoresis (CE) is characterized by ease of sample preparation, low cost, and short analysis time.²¹ The theory of capillary electrophoresis has been discussed previously.^{19,22–25} Evans and Beaumont²⁶ have compared capillary electrophoresis methods with ion chromatography (IC). A specific disadvantage of IC is fouling of the expensive anion-exchange column by complex samples. To summarize, no methods have been reported for the determination of formic and acetic acids in flowback samples following acid-stimulation treatments. Based on the literature, it appeared that capillary electrophoresis was likely to be the most suitable method for determination of organic acids in complex samples obtained from acid stimulation treatments.

Several published CE methods for the determination of carboxylic acids were considered for modification to meet the requirements of this work. These included the methods of Volgger *et al.*,¹⁹ Chen *et al.*,²⁰ Wu *et al.*,²¹ Devèvre *et al.*,²² Oehrle,²⁷ Madsen and Lind,²⁸ and Krol *et al.*²⁹ A direct-detection method is preferred because the dynamic range is much greater than with indirect detection and the electrolyte contains fewer components.²⁵ Direct detection methods are compared in **Table 1**.

For the present work, the analytical conditions of Oehrle²⁷ and Krol *et al.*²⁹ were investigated. This decision was based on the simplicity of the electrolyte and the expected detection limit of the method of 1 mg/L. In stimulation fluids, concentrations of acetic and formic acids can range up to 13 and 9 wt%, respectively. This means that field samples can be highly diluted prior to analysis and still contain detectable concentrations of organic acids. This dilution is extremely useful because it is expected to reduce the effect of interferences. Use of an accurate autodiluter introduces very little additional error into the measurements. Typically, with dilutions of 200 to 1, a dual syringe autodiluter will have accuracy $\pm 1\%$ and precision $\pm 0.2\%$.³⁰

The objectives of this work are to: (1) develop and evaluate a method for the determination of formic, acetic, and citric acids in acid stimulation samples, and (2) use this method to determine the concentration of these organic acids in laboratory and field samples.

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