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Microemulsion Applications in Carbonate Reservoir Stimulation

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Abstract

Carbonate reservoir stimulation involves the injection of reactive fluids, most commonly hydrochloric acid (HCl), into the porous media to enhance the permeability and increase hydrocarbon production. This process results in the formation of highly conductive flow channels, or wormholes, and relies on the deep penetration of reactive fluids into the formation to maximize stimulation success. However, the rapid rate of reaction of HCl with the carbonate rock often limits the depth of live acid penetration. The reaction is mass transfer limited under typical reservoir conditions. As a result, the acid diffusion and convection rates significantly influence the success of the treatments. Microemulsions prepared with HCl as the dispersed phase offer a solution to significantly reduce the effective diffusivity and, hence, increase the depth of stimulation. This chapter presents the results of laboratory studies of carbonate dissolutions using acid microemulsions and highlights case histories of industry applications using macroemulsions for carbonate reservoir stimulation.

Keywords: microemulsion, emulsified acid, reservoir stimulation, carbonate acidizing, fracture acidizing, retarded acid, diffusion coefficient, rotating disk, wormhole, Damköhler number

1. Introduction

Microemulsion technologies have various applications in the oil and gas industry including improved fluid recovery and relative permeability enhancement in drilling and stimulation applications [1–4], displacement and cleanup of oil-based muds [5], and enhanced oil recovery

[6, 7]. Microemulsion properties such as ultralow interfacial tension, large interfacial area, and the ability to solubilize both aqueous and oil-soluble compounds leverage these applications. When used in reservoir stimulation treatments to improve fluid recovery and relative permeability effects, microemulsions are generally used as an additive to the main treating fluid, with a low concentration of a microemulsion being dispersed in the main oil- or aqueous-based fluid. For example, aqueous hydrochloric acid (HCl) treating fluids containing microemulsion additives have been used to enhance stimulation effectiveness by reducing the surface tension and fluid leak-off rates into the porous media during carbonate acidizing treatments [4].

Microemulsions have also been investigated as the main treating fluid for use in carbonate acidizing treatments. For this application, acid microemulsions are formulated with HCl as the dispersed phase, and the microemulsion property of most interest is the well-known ability to reduce the mobility of the dispersed phase. Acid microemulsions were initially studied to improve the success of carbonate acidizing for Danian chalk reservoirs in the North Sea [8]. Later studies evaluated microemulsion properties including the effective diffusivity of the dispersed acid phase and their overall applicability for carbonate acidizing [9, 10]. The use of acid microemulsions as the main treating fluid during carbonate acidizing is the focus of this chapter.

Acidizing is a reservoir stimulation technique commonly used to increase the near-wellbore flow capacity of petroleum production and injection wells. In carbonate reservoirs (comprised of limestone and/or dolomite), the technique involves the injection of acid, typically hydrochloric acid (HCl), into the reservoir to dissolve the formation rock and materials that plug the pore space. The dissolution removes resistances to flow and creates highly conductive flow channels, thereby allowing oil or gas to flow more readily. The key parameter governing channel formation is the Damköhler number which is the ratio of the rate of reaction of the acid with the porous medium to the rate of convective transport of the acid through the rock [9–11]. When the Damköhler number is high, such as would be the case for low acid flow rates or high acid reaction rates, the acid will not penetrate very deep into the rock, resulting in face dissolution and little if any penetration and dissolution into the formation. For the case of low Damköhler numbers, such as high acid flow rates or low rates of acid reaction, the acid dissolves the porous medium relatively uniformly at the expense of large volumes of acid. At intermediate Damköhler numbers, highly conductive flow channels or wormholes are formed, which can efficiently penetrate deep into the formation. This dissolution phenomenon can be easily characterized by laboratory core flood experiments in which HCl is injected into carbonate porous media.

The success of carbonate acidizing treatments relies on the formation of wormholes that penetrate deep into the formation. However, the treatments are often constrained by the very rapid rate of reaction between HCl and carbonate rock, which results in limited depth of live acid penetration and ineffective flow capacity of the acid-dissolution channels [9–17]. The rapid HCl-carbonate rock reaction is limited by the rate of mass transfer of acid to the rock surface (diffusion limited) under common reservoir conditions [18, 19]. This means that the dissolution process can be controlled by changing the rate of convection and/or the rate of acid diffusion. In treatment cases where the injection rate cannot be increased owing to pressure drop

considerations, the effectiveness of the treatment can be controlled based on the Damköhler number by reducing the acid reaction rate. Because the reaction is mass transfer limited, this reduction can be achieved by reducing the acid diffusivity. This governing parameter provides the fundamental premise behind evaluating acid microemulsion systems to reduce the mobility (and the effective diffusivity) of the dispersed acid phase for use in carbonate acidizing.

This chapter focuses on the application of acid microemulsions for carbonate acidizing and highlights the fundamental research by Hoefner and Fogler [9, 10]. This chapter includes an overview of the fundamentals of carbonate acidizing, laboratory procedures to assess performance for carbonate acidizing, characteristics of the microemulsion systems with HCl as the dispersed phase, and laboratory results for microemulsion impact on carbonate acidizing. Although the research presented in this chapter demonstrate the technical benefits of microemulsions with HCl as the dispersed phase for carbonate acidizing, the authors are not aware of actual acidizing applications of such microemulsion systems in the oil and gas industry. A patent describing an acid internal microemulsion for carbonate acidizing was granted in 1989 and has since lapsed [20]. The most similar industry application is the use of acid-internal "macro"emulsions to reduce the diffusivity and improved acid penetration. The last section of this chapter provides an overview of these macroemulsion case histories and highlights limitations that may be an area of interest for future microemulsion research.

2. Fundamentals of carbonate acidizing

Carbonate acidizing treatments can be categorized as either matrix acidizing or fracture acidizing. In matrix acidizing, the acid is injected into the porous rock matrix to create acid-dissolution channels, commonly referred to as wormholes. In fracture acidizing, the acid is injected at high rates and pressures to create hydraulic fractures in the rock, which then retain flow capacity after closing due to the creation of nonuniform acid-etched channels along the fracture faces. In both cases, the success of carbonate acidizing treatments depends on the flow capacity of the created acid-dissolution channels and the depth to which they penetrate into the formation. High flow capacity and deep penetration are the desired outcome. This section provides an overview of the fundamentals of HCl-carbonate rock reaction, the dissolution phenomenon that leads to the formation of acid-dissolution channels, and their impact on carbonate acidizing treatments.

2.1. Acid-rock reaction

The rate of acid-carbonate rock reaction depends on the mineralogical composition of the rock formation. Carbonate reservoirs are composed of limestone ($CaCO_3$) and/or dolomite [$CaMg(CO_3)_2$], which are completely soluble in acid. The dissolution of limestone by HCl is mass transfer limited at temperatures above 0°C [18], while the dissolution of dolomite is mass transfer limited above 50°C [19]. Thus, at temperatures commonly encountered in petroleum reservoirs, the rate of dissolution is highly dependent on the rate at which the acid is

transported to the rock surface by convection and diffusion. The carbonate reaction chemistry is described in more detail elsewhere in the literature [21].

2.2. Dissolution phenomenon

The flow and reaction of fluids in carbonate porous media results in the formation of highly conductive flow channels, referred to as wormholes (**Figure 1**). Wormholes are desirable during matrix acidizing treatments because they are capable of bypassing near-wellbore damage and their conductivity is several orders of magnitude higher than that of the porous medium. Wormholes form because of the rapid and almost complete dissolution of the mineral in HCl and the variability in pore-scale flow rates caused by the natural heterogeneity of the porous medium. The structure of the dissolution channels vary significantly, depending on parameters such as the injection rate, effective diffusion coefficient, and fluid-mineral properties. **Figure 1** illustrates the five main types of dissolution structures:
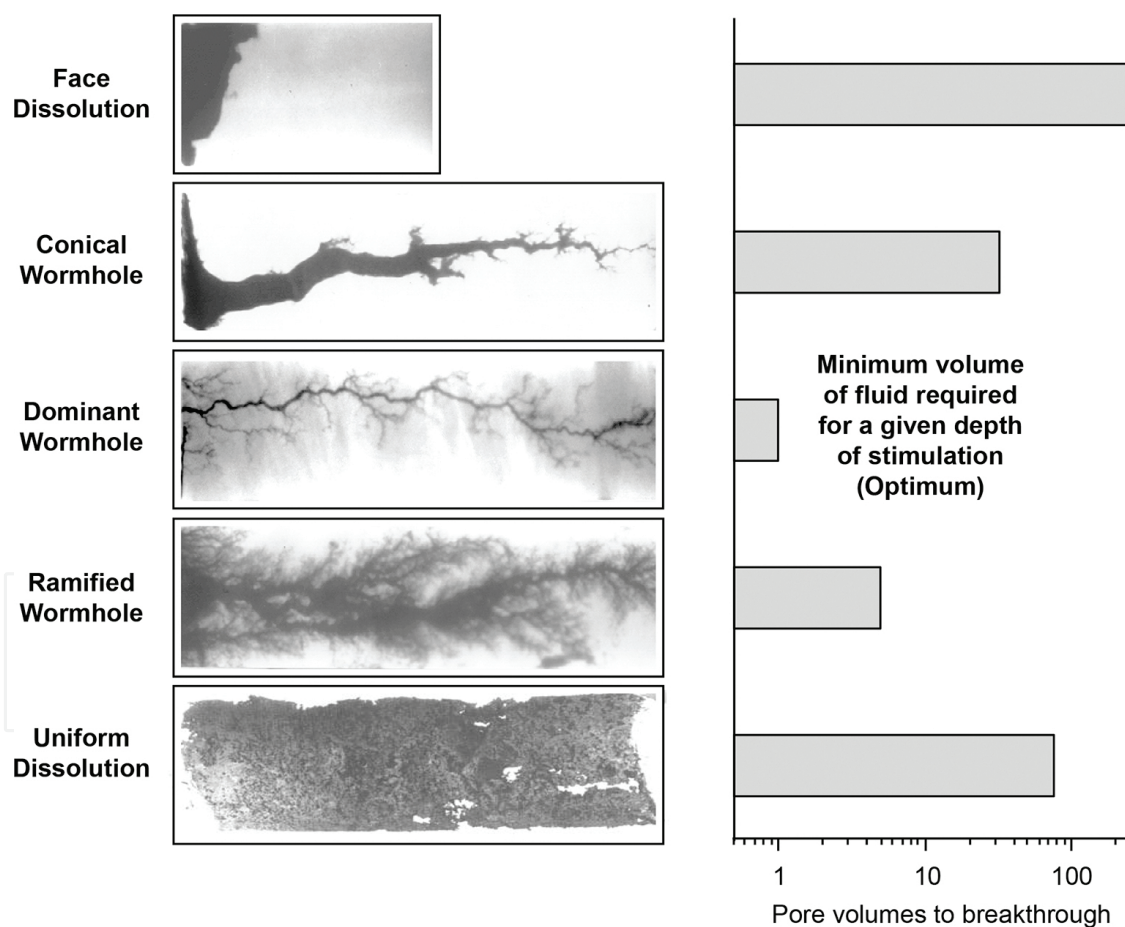

Figure 1. Dissolution structures formed during flow and reaction in carbonate porous media, and corresponding pore volumes of fluid required for breakthrough. (Fluids were injected from left to right during linear coreflood experiments.) The top four images are neutron radiographs of dissolution structures formed during the dissolution of limestone by hydrochloric (HCl) and ethylenediaminetetraacetic acid (EDTA) [11, 22, 23]. The bottom image is a Wood's metal casting of a dissolution structure formed during the dissolution of dolomite by aqueous HCl [10].

1. Face dissolution

2. Conical wormholes

3. Dominant wormholes

4. Ramified wormholes

5. Uniform dissolution

The dissolution structure transforms from face dissolution to uniform dissolution (from top to bottom in **Figure 1**) as the injection rate is increased or the effective diffusion rate is decreased. At low injection rates or high diffusion rates, the reactant is consumed on the inlet flow face of the core, resulting in complete dissolution of the core starting from the inlet flow face. This face dissolution consumes large volumes of reactant and provides negligible depths of live acid penetration. (The required volume of fluid is demonstrated by the bar graph in **Figure 1**, where one pore volume equals the initial porosity times the bulk core volume; and pore volume to breakthrough is the injected pore volume at which the dissolution structure propagates the length of the core.) At slightly higher injection rates or lower diffusion rates, the reactant can penetrate into the porous matrix and enlarge flow channels. However, conical-shaped dissolution channels are formed due to a significant amount of reactant being consumed on the channel walls. At intermediate injection rates, reactant is effectively transported to the tip of the propagating flow channel, where reaction further extends the channel length and creates a dominant wormhole structure. This dominant wormhole structure minimizes the volume of fluid required to achieve a given depth of stimulation and represents the most effective conditions for matrix stimulation. At high injection rates or low diffusion rates, fluid is transported deeper into the porous medium before reaction, resulting in the formation of highly branched or ramified wormholes and an increase in the required volume of fluid. At the extreme of very high injection rates or very low diffusion rates, the reactant is transported to most pores in the medium giving rise to uniform dissolution and inefficient matrix stimulation. Hence, the dominant wormhole structure represents the most effective conditions for matrix stimulation and an optimum injection rate exists for a given fluid-rock system at which a minimum volume of fluid is required to achieve a given depth of wormhole penetration [10, 11, 14–17, 22, 23]. These results demonstrate that the wormhole formation has a significant impact on the success of carbonate stimulation treatments.

The dissolution structure ultimately controls the effectiveness of carbonate acidizing treatment, which has led many investigators to study the dissolution phenomenon. Early investigators recognized the significant influence of mass transfer on wormhole formation in limestone [12, 13]. This influence has served as a basis for many of the theories describing wormhole formation and has led to models of wormhole formation that depend on dimensionless terms such as the Peclet number (ratio of rates of transport by convection to transport by diffusion) [14–16] and the Damköhler number (ratio of the overall rate of dissolution to the rate of transport by convection) [10, 11]. Both dimensionless terms depend on the effective diffusion coefficient and successfully predict wormhole formation for at least a few types of dissolution structures.

The Damköhler number describes the phenomenon of wormhole formation for a wide range of fluid/mineral systems and will be used in this chapter. The Damköhler number, N_{Da}, is defined as the ratio of the overall rate of dissolution to the rate of transport by convection and is given by

$$N_{Da} = \frac{\pi d L \kappa}{q} \tag{1}$$

where q is the flow rate in the wormhole, d and L are the diameter and length of the wormhole, respectively, and κ is the overall dissolution rate constant that depends on the fluid-rock system.

When the overall rate of dissolution is mass-transfer limited, κ is given by

$$\kappa_{mt} = \frac{1.86 D_e^{2/3}}{d} \left(\frac{4q}{\pi L}\right)^{1/3} \tag{2}$$

where D_e is the effective diffusion coefficient, which depends on the fluid system.
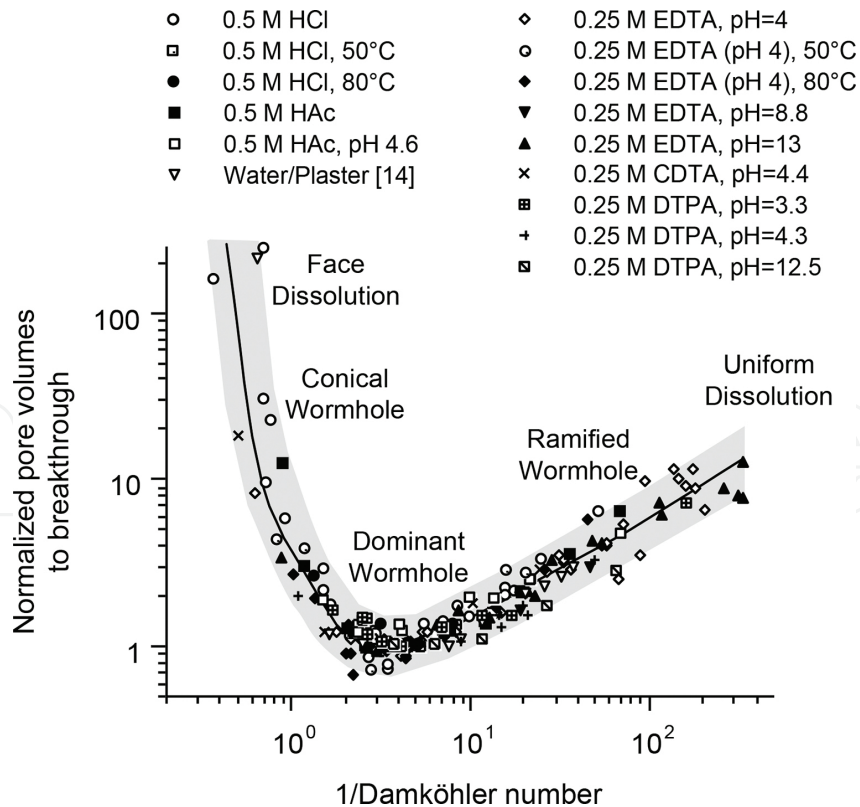

Figure 2. Dependence of the number of pore volumes to breakthrough on the Damköhler number for a wide range of fluid-rock systems (adapted from Ref. [11]).

The Damköhler number captures the balance between convention, diffusion, and reaction that takes place during flow and reaction in porous media and governs the structure of the wormhole channels. This dependency is illustrated in **Figure 2** where the type of dissolution structure and corresponding normalized number of pore volumes to breakthrough is shown as a function of the Damköhler number for a wide range of fluid/rock systems (adapted from Ref. [11]). The data includes aqueous HCl, organic acids [acetic acid (HAc) and formic acid (HFc)], and chelating agents [ethylenediaminetetraacetic acid (EDTA), 1,2-cyclohexane-diaminetetraacetic acid (CDTA), and diethylenetriaminepentaacetic acid (DTPA)], which have varying effective diffusion coefficients and are influenced by reversible or irreversible surface reactions. The results demonstrate the existence of an optimum Damköhler number at which dominant wormhole structures are formed and a minimum volume of fluid is required to achieve a given depth of wormhole penetration. This optimum Damköhler number is observed at 0.29 for several fluid-rock systems and can provide a design basis for optimizing matrix acidizing treatments [11]. A similar dependence on a Damköhler number was demonstrated for acid etching along a fracture face during fracture acidizing [24], and other investigators have highlighted the importance of mass transfer in etching of the fracture face [25, 26]. Hence, both carbonate acidizing approaches are highly dependent on the rate of mass transfer and the effective diffusion coefficient.

2.3. Implications for carbonate acidizing treatments

During matrix acidizing treatments, the low injection rates commonly lead to a Damköhler number higher than 1, where the rapid HCl reaction rate results in face dissolution and an
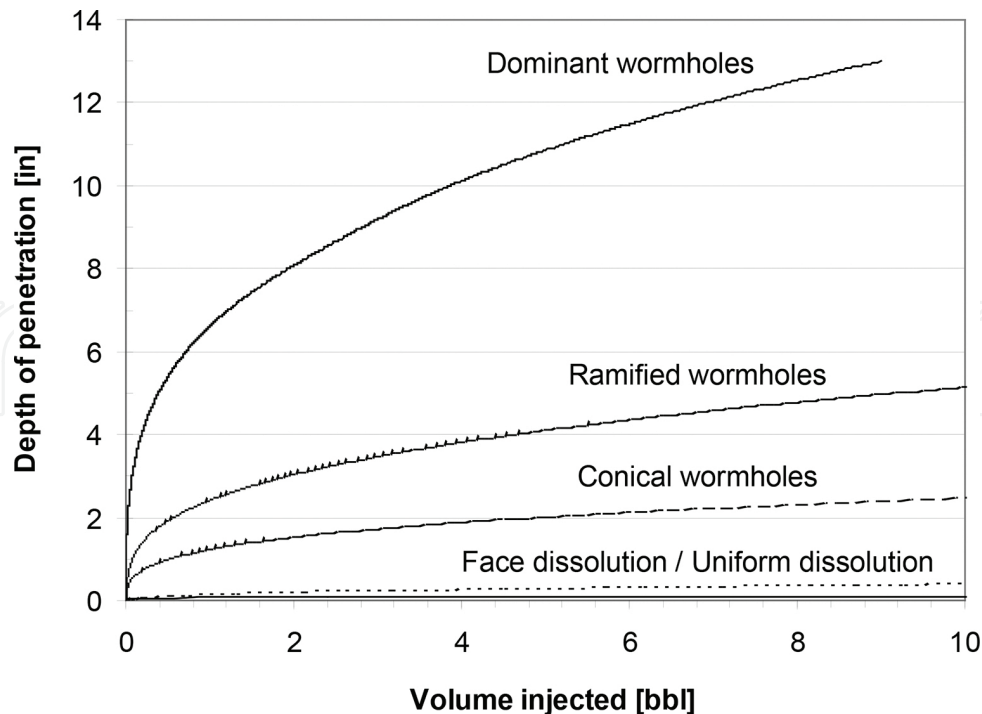

Figure 3. Effects of dissolution structure on the depth of penetration [23]. Copyright 2000, Society of Petroleum Engineers Inc. Reproduced with permission of SPE. Further reproduction prohibited without permission.

ineffective treatment. The impact of the dissolution structure on the effectiveness of matrix acidizing treatments is demonstrated in **Figure 3**, where the depth of penetration into the formation is shown as a function of the volume of HCl injected into limestone at constant Damköhler numbers [23]. When face dissolution occurs, the acid penetrates only a fraction of an inch into the formation. Conical wormholes result in a slight increase to about 2 inches of penetration. Near the optimum Damköhler number, wormhole formation results in effective stimulation as dominant wormholes penetrate over 12 inches into the formation. As the Damköhler number was decreased and the dissolution structure changed to ramified worm-holes and uniform dissolution, the depth of penetration decreased. This trend is consistent with experimental and theoretical results reported by several investigators, who report that wormholes typically penetrate a few feet (0.3–2 m) radially into the formation [12, 13]. At these depths, wormholes stimulate the near-wellbore region (where the majority of flow resistance associated with the radial geometry is manifested) and provide an effective matrix acidizing treatment.

Analogous challenges are encountered during fracture acidizing. Danian chalk reservoirs in the North Sea exhibited poor performance after fracture acidizing due to insufficient acid-etched channel flow capacity and failure of the channels to withstand the closure pressure as a result of low rock hardness [8]. Other investigators demonstrated the effects of acid on rock strength in both chalk formations and competent carbonate formations from laboratory studies and recommended minimizing unnecessary dissolution of the fracture face to better maintain rock strength [26]. These examples demonstrate the common challenges of rapid acid reaction rates resulting in ineffective flow capacity of acid-dissolution channels and the need to reduce the rate of dissolution to enable deeper live acid penetration for both matrix and fracture acidizing treatments in a wide range of carbonate formations.

3. Laboratory methods

Several microemulsion systems (described in the following section) were identified for laboratory study and potential application in the oil and gas industry. Effective acid diffusion coefficients were measured for different surfactant and cosurfactant combinations as a function of acid phase volume using a rotating disk technique while in some cases a NMR self-diffusion technique. Trends in the acid diffusion rate as a function of microemulsion composition (and associated structure) were measured to help optimize the system for a particular application, e.g., to optimize acid strength or temperature stability.

The effectiveness of various microemulsion systems and compositions in increasing rock permeability as a function of distance from the wellbore was studied using core flow experiments relating live acid penetration depth to injection volume and conditions (e.g., injection rate and effective diffusion coefficient). Imaging techniques were then used to characterize the structure of the flow channels created in the rock and in turn relate channel structure to live acid diffusion rate and fluid injection rate. Analyses (including numerical network modeling, which is outside the scope of this chapter) were then used to relate the properties of the acid

system, the injection conditions, and the resulting dissolution channel structure to the overall effectiveness of the acidizing process in increasing permeability away from the wellbore.

3.1. Rotating disk technique for measuring diffusion rates

Acid diffusion rates as a function of microemulsion system and composition were studied using a rotating disk system [27, 28]. Polished marble disks ($CaCO_3$) were partially dissolved by rotation in the acid microemulsion. The measurements were carried out under high inert gas overburden pressure to prevent the evolution of gaseous reaction products that would interfere with hydrodynamics at the surface of the disk. The rate of dissolution was measured by analyzing samples for calcium using atomic absorption spectroscopy. For the diffusion-controlled reaction (rapid reaction between HCl and the limestone rock), the rate of acid transport to the surface of the disk is proportional to the disk rotation speed to the ½ power and to the acid diffusion rate to the ⅔ power [27]. For the apparatus used, correction factors that account for finite disk diameter and reactor volume can be neglected.

The dissolution rate of the carbonate disk was monitored by sampling the liquid concentration for calcium. By measuring the dissolution rate at different disk rotational speeds, an effective acid diffusion coefficient for the microemulsion system can be measured. **Figure 4** shows data for a typical set of experiments. For a mass transfer limited reaction, the dissolution rate plotted against the square root of the disk rotation speed will give a straight line passing through the origin. From the slope, we calculate the effective diffusivity, D_e, for the acid microemulsion system.
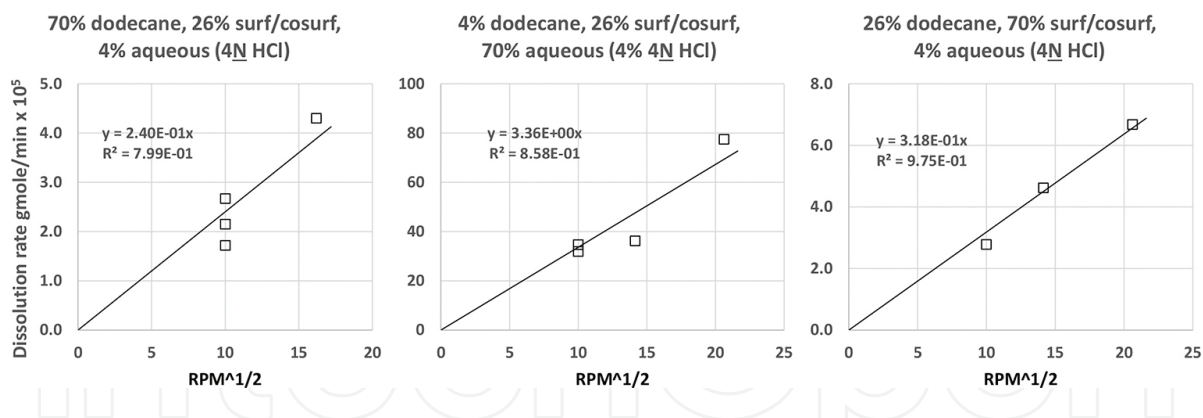

Figure 4. Rotating disk dissolution rate results for three microemulsion formulations.

3.2. Core flow experiments

It is challenging to carry out controlled experiments in actual oil wells. In order to simulate flow and reaction taking place in the rock during acidizing, laboratory "coreflood" experiments are often performed. Core-flooding is a general term and many processes related to petroleum production can be studied using the procedure. Such experiments can be extremely complex, intended to quantitatively represent in situ flow conditions related to hydrocarbon recovery, or they can be simplified to examine one or a few individual effects. In this case, the

acid system such as aqueous HCl or microemulsion is injected axially at a constant rate through cylindrical limestone or dolomite cores and the pressure drop along the length of the core is monitored as the dissolution progresses in the porous medium. Similar to the rotating disk experiments, sufficient backpressure was maintained to prevent gaseous reaction products (CO_2) from evolving in the cores. Coreflood experiments were performed with the cores initially water saturated to eliminate any relative permeability effects associated with an initial oil or gas saturation. Thus, the coreflood experiments were designed to examine the dissolution phenomenon in carbonate cores.

Coreflood experiments were performed to test whether lowering the HCl diffusion rate would allow the microemulsion to achieve deep penetrating, dominant wormhole structures for effective matrix stimulation of carbonate rock. Fluid was pumped at a constant rate axially through 1 inch (2.54 cm) diameter rock cores. The pressure drop across the core was monitored as a function of fluid volume injected. The cell designed to hold the core and simulate reservoir conditions is shown in **Figure 5**. Details of the coreflood experimental procedures and apparatus are described elsewhere in the literature [10, 22, 29].
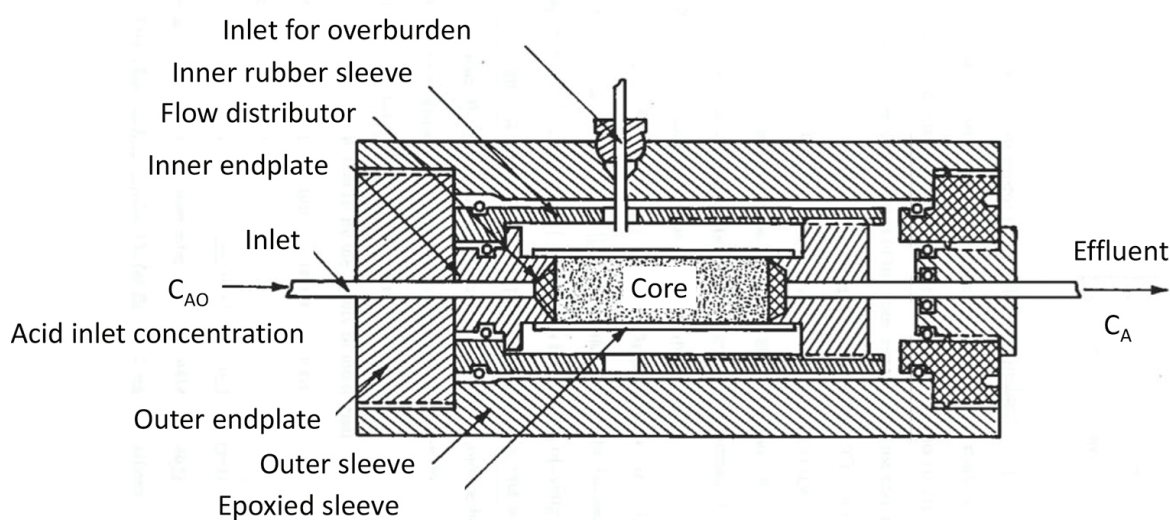

Figure 5. Bi-axial core holder or "Hassler" cell [10]. Copyright© 1988 American Institute of Chemical Engineers.

As the fluid is injected and acid begins to dissolve the rock matrix, the pressure drop associated with the flow begins to decrease, corresponding to an increase in the rock permeability. Results are typically plotted as the ratio of the permeability at any time to the initial permeability as a function of the volume of fluid injected (expressed as porevolumes, where one porevolume equals the initial porosity times the bulk core volume). The pore volume of fluid required to bring about a significant increase in the permeability is a direct measure of the effectiveness of that fluid to stimulate the rock under those treatment conditions. The coreflood experiment provides information relating the effects of parameters such as the fluid injection rate and the acid diffusion rate or reaction rate, as well as properties of the rock such as composition, permeability, and pore size distribution.

Core flow experiments have been conducted over a wide range of core dimensions, rock types (including limestone as well as dolomite), injection rates, and acid diffusion rates for various microemulsion systems.

3.3. Dissolution channel characterization

Imaging techniques were used to evaluate the impact of microemulsion properties (acid diffusion rate) and flow conditions (fluid flow rate) and resulting increase in rock permeability on the structure of the dissolution channels that resulted from the core flow experiments. The earliest technique involved first drying the cores after acidizing, evacuating, and heating in the presence of Wood's metal (a low-melting point mixture of bismuth, lead, tin, and cadmium). The metal was melted and subsequently forced into the channels when the vacuum was released, thus forming a cast of the dissolution channels. The remaining core material was then dissolved in HCl, leaving behind the metal casting of the channel structure. An example is shown in **Figure 1** (bottom image).

Later, a technique involving neutron radiography was used to image the Wood's metal-filled dissolution structures, thereby eliminating the need to dissolve the rock and potential damage to the fine details of the wormhole casting. This technique is ideally suited for imaging structures within consolidated porous media because: (1) the matrix is virtually transparent to thermal neutrons and (2) the cadmium-containing Wood's metal is an excellent neutron absorber and thus provides high contrast between the dissolution channels and the consolidated porous matrix [30]. To image the wormholes, the Wood's metal-filled cores were placed in a beam of thermal neutrons for imaging. Neutron radiography is described in more detail elsewhere in the literature [30, 31].

4. Microemulsions

The fundamental premise behind evaluating microemulsion systems for use in carbonate acidizing is that microemulsions have the well-known ability to reduce the mobility of the dispersed phase, in this case hydrochloric acid, without a proportionate increase in the fluid viscosity. This ability is important because the very rapid HCl-carbonate reaction rate is limited by the rate of diffusion of acid to the rock surface ("diffusion-limited"). One could, in theory, decrease the acid diffusion rate by increasing the fluid viscosity, for example with polymer viscosifiers, but the result would be slower fluid flow through the porous media. Slower fluid flow would in-turn offset the effect of slowing the acid diffusion rate by allowing acid more time to diffuse to the rock surface, as governed by the Damköhler number. It should be emphasized that most matrix acidizing treatments are limited in the rate that the fluid can be injected into a well to avoid fracturing the rock (i.e., the injection rate is often already too low for efficient wormhole formation). In addition, the acid diffusion coefficient increases with increasing temperature, making it even more important to control the acid diffusion rate in high temperature reservoirs. Hence, acid microemulsions provide a potential solution for controlling the acid diffusion rates without significantly reducing the flow rates and in high

temperature reservoirs. This section reviews the characteristics of acid microemulsion systems for use in carbonate acidizing.

4.1. Microemulsion systems

The microemulsion systems that have been investigated for decreasing acid diffusion rates include one using a cationic surfactant, and one using a nonionic surfactant [32, 33]. The cationic system, comprising dodecane, water phase (actually aqueous HCl), butanol, and cetylpyridinium chloride (CPC), was used to demonstrate the capability of the microemulsion system and to understand the relationship between dissolved channel structure and acid effectiveness in increasing rock permeability.

A cationic surfactant was chosen for increased microemulsion stability at higher temperatures, for decreased surfactant adsorption on calcite at low pH, and for surfactant stability in the presence of reaction products. Phase diagrams for the system are shown in **Figure 6**. The lower right comer represents a constant surfactant/cosurfactant weight ratio of 35:65 (corresponding to 10 mole% surfactant). The large enclosed area indicates a one-phase region. The most important factors in choosing the model system are: (1) it can solubilize a significant volume fraction of concentrated HCI, and (2) the one-phase region is extensive to minimize the possibility of viscous surfactant mesophases forming when the microemulsion contacts water or oil already present in the rock.
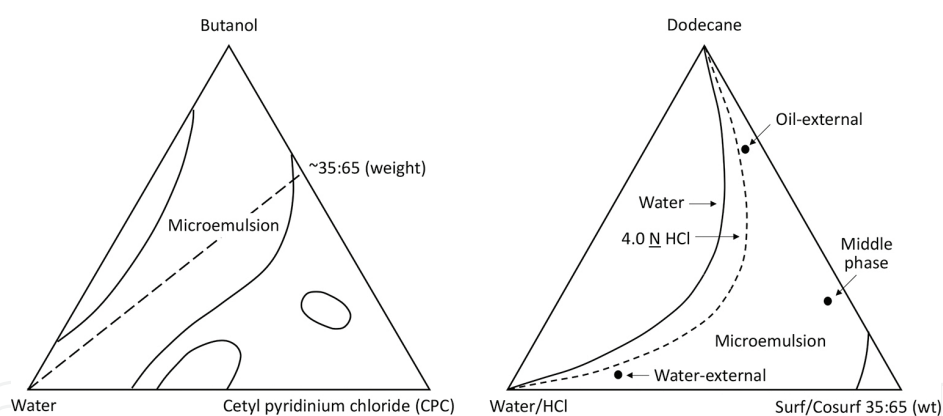

Figure 6. Phase behavior for CPC/dodecane/butanol/water (aqueous hydrochloric acid) system.

The area of the one-phase region near the pure oil corner may represent a reversed micelle structure, while regular micelles (oil-in-water) may exist near the water comer. The center-region may consist of the two micelle types in equilibrium. Reversed micelles are expected to restrict acid mobility (acid diffusivity) to the greatest extent, and so formulations in that region comprised the bulk of the microemulsion studies.

Phase behavior was characterized for the cationic system for cosurfactants ranging from propanol through octanol in order to understand the effects of the cosurfactant chain length. In all cases, the surfactant/cosurfactant ratio was kept at 1:9 molar (corresponding to a 35:65 weight ratio of surfactant to butanol). The butanol system was chosen for further study

because, although lower acid diffusion rates were achieved with pentanol, the isotropic region for butanol was more extensive compared to the longer alcohols.

A nonionic system utilizing mixtures of nonylphenolpolyethoxy alcohol surfactant, naphtha, and aqueous HCl was studied as a potential commercially applicable system. The specific systems involved combinations of surfactants with different numbers of ethoxy head units (Triton brand X-35, N-42, and N-57). The nonionic system had the advantage of significantly lower surfactant cost, no requirement for a cosurfactant, and the ability to solubilize a higher aqueous phase fraction as compared to CPC. A disadvantage of the Triton systems was that the extent of the isotropic region was sensitive to temperature, although by mixing the different surfactants, it was shown that the system could be customized to a broad temperature range and thereby tailored to the specific reservoir temperature of wells to be treated [33].

5. Microemulsions enhancing carbonate reservoir stimulation

The microemulsion systems described in the previous section were evaluated for applications in carbonate acidizing using rotating disk and coreflood experiments.
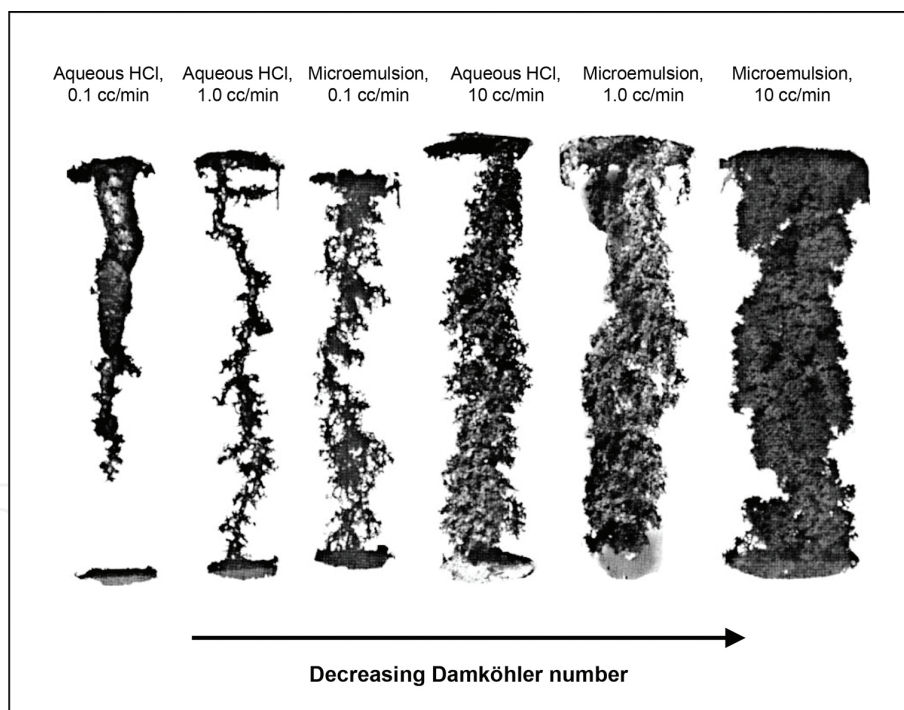

Figure 7. Wormhole structures formed during the flow and reaction of microemulsions and aqueous HCl in limestone, with decreasing Damköhler number from left to right (adapted from Ref. [10]). Copyright© 1988 American Institute of Chemical Engineers.

Rotating disk experiments demonstrated that the dissolution of limestone by acid microemulsion is fully mass transfer limited at 22°C. Data shown in **Figure 4** represent an acid microemulsion formulation near the pure oil corner of the phase diagram that exhibits an acid

diffusion coefficient approximately two orders of magnitude lower than for aqueous HCl. The effective acid diffusion coefficient for the microemulsion system is 8×10^{-7} cm^2/s compared to 4×10^{-5} cm^2/s for aqueous HCl [9, 32]. This significant decrease in the acid diffusion coefficient provides a significant reduction in the rate of acid-rock reaction under mass transfer limited conditions. There is also a relatively insignificant decrease in the reaction rate due to a viscosity effect, as the microemulsion has a viscosity of only about 3 cp. For comparison, gelled acids with viscosities greater than 25 cp at 100 s^{-1} are commonly used as "retarded" acid systems, but they reduce the effective diffusivity by only a factor of two compared to aqueous HCl [34]. Hence, the reduced acid mobility provided by the microemulsion system provides far superior reduction of the acid diffusion coefficient than viscous mechanisms.

The transport and reaction of microemulsions in carbonate porous media during coreflood experiments results in the formation of wormholes as demonstrated in **Figure 7**. The images demonstrate that the acid microemulsion created a dominant wormhole structure at 0.1 cm^3/min (third image). At the same injection rate, aqueous HCl resulted in the formation of an inefficient conical dissolution structure (first image). The improved effectiveness of microemulsions is further illustrated in **Figure 8** for the butanol and pentanol formulations. The pore volumes to breakthrough curve for the microemulsions are shifted by about an order of magnitude to lower injection rates relative to aqueous HCl. Hence, the microemulsions are more effective than aqueous HCl at the low injection rates commonly encountered during carbonate matrix acidizing treatments.
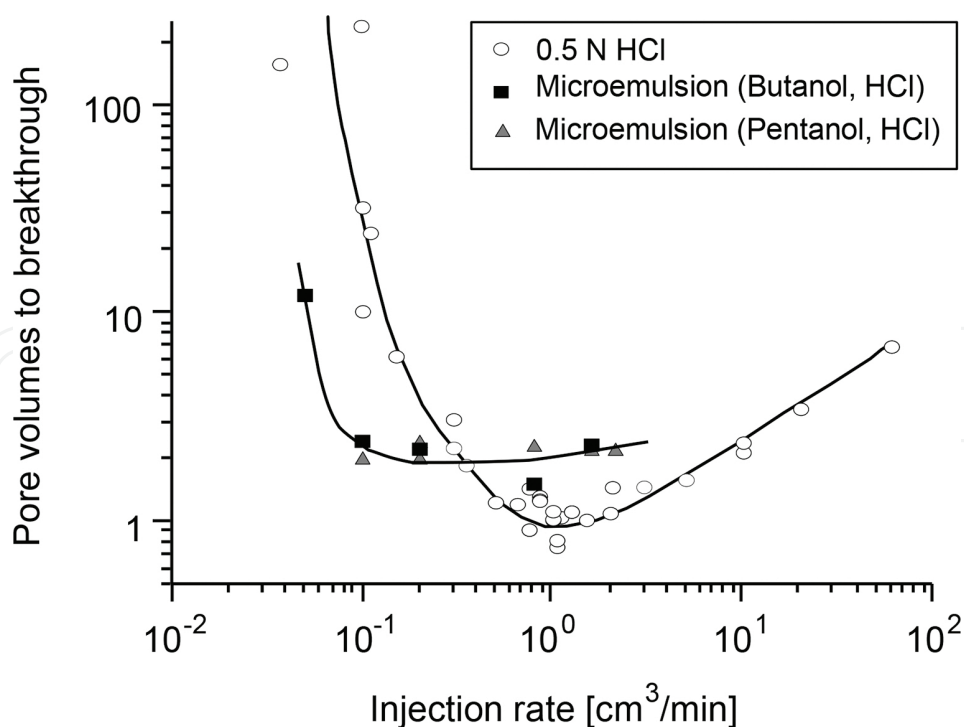

Figure 8. Comparison of stimulation effectiveness for microemulsions and aqueous HCl (data adapted from Refs. [9, 11]).

The improved performance achieved by the acid microemulsion systems at low injection rates is due to the dependence of the dissolution phenomenon on the Damköhler number and the significant reduction in the effective diffusivity of the dispersed acid phase. This dependency is demonstrated in **Figure 9**, where the acid microemulsion systems overlay the performance band observed for the wide range of fluid-rock systems from **Figure 2**, and exhibit the existence of an optimum Damköhler number at which the dissolution process is most effective. Based on these results, acid microemulsions provide useful characteristics for use in carbonate acidizing treatments, particularly at low injection rates and high temperatures where HCl is not effective.
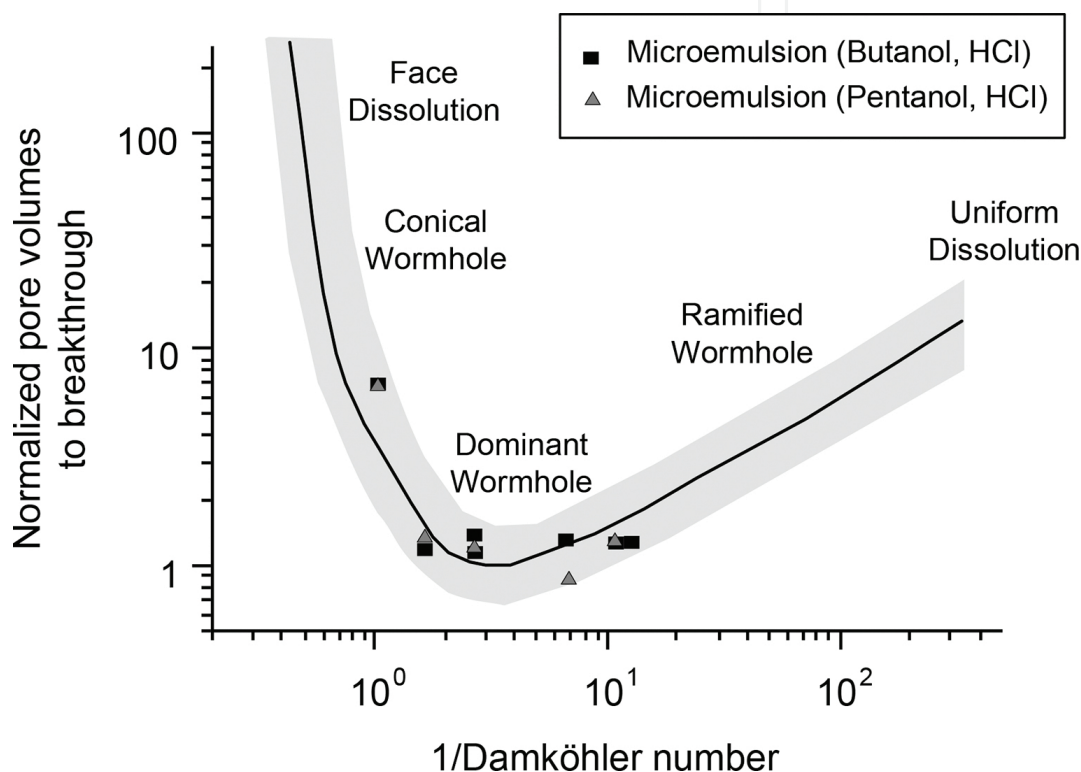

Figure 9. Dependence of the number of pore volumes to breakthrough on the Damköhler number for acid microemulsion systems (data adapted from Ref. [10]). The gray shaded area is the performance band observed for the wide range of fluid-rock systems from **Figure 2**.

6. Industry applications: carbonate acidizing

Microemulsions have numerous properties such as ultralow interfacial tension, large interfacial area, and the ability to solubilize both aqueous and oil-soluble compounds that are valuable for various applications in the oil and gas industry. Carbonate acidizing treatments performed with aqueous HCl as the main treating fluid have contained low concentrations of microemulsion additives to enhance stimulation effectiveness by reducing the surface tension and fluid leak-off rates into the porous media [4]. This chapter highlighted the evaluation of

acid microemulsion systems for use as the main treating fluid to enhance dissolution channel formation and the depth of live acid penetration during carbonate acidizing treatments, where the microemulsion property of most interest is the ability to reduce the mobility of the dispersed acid phase.

Although research demonstrates the technical benefits of acid microemulsion systems, the authors are not aware of actual carbonate acidizing applications of such systems in the oil and gas industry. A patent describing an acid internal microemulsion for carbonate acidizing was granted in 1989 and has since lapsed [20]. Since the early 1990s, the industry has commonly used emulsified acids, formulated as acid-internal "macro"emulsions, to reduce the effective acid diffusivity and improve the depth of live acid penetration [25]. Typical macroemulsion systems prepared with HCl as the dispersed phase have effective diffusion coefficients of about $8 \times 10^{-7} cm^2/s$ at 22°C [34], which is consistent with that measured for the microemulsions systems in this research. Hence, the carbonate dissolution phenomenon is similar for acid microemulsions and macroemulsions.
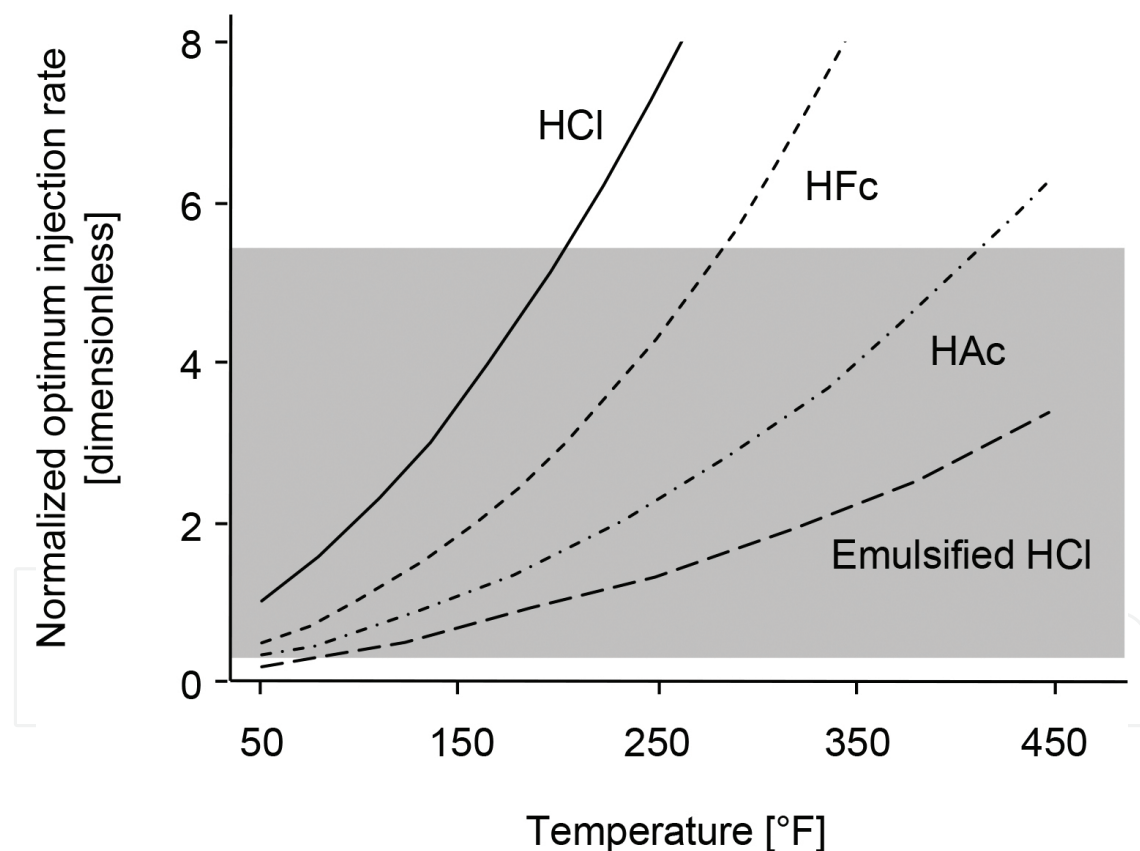

Figure 10. Effect of temperature on the optimum injection rate required to achieve wormhole penetration of 6 inches with various acid systems [23]. (The shaded box represents typical injection rates used in matrix acidizing treatments.) Copyright 2000, Society of Petroleum Engineers Inc. Reproduced with permission of SPE. Further reproduction prohibited without permission.

Macroemulsions are successfully applied in both matrix acidizing and fracture acidizing treatments [25, 35–37]. These case histories demonstrate the use of emulsified acids as the main

treating fluid to increase the depth of stimulation at treatments up to about 176°C. The emulsified acids provide improved stimulation effectiveness over a wider range of injection rates and temperatures compared to aqueous acid systems. This wider operating range is illustrated in **Figure 10**, where the optimum injection rate for the creation of dominate wormhole structures is plotted as a function of reservoir temperature during matrix acidizing treatments [23]. The lines represent the injection rate required to achieve wormhole formation for various acid systems including aqueous HCl, organic acids HFc and HAc, and emulsified HCl. The shaded box represents typical injection rates used in matrix stimulation treatments. The results show that aqueous HCl is unable to achieve effective wormhole formation without requiring excessive injection rates (above the typical ranges that would avoid fracturing the formation). Under the same conditions, emulsified HCl can effectively stimulate the formation even at higher temperatures where aqueous systems would not be effective. The results demonstrate that emulsified acids generate more effective acid dissolution channels under typical treatment conditions, which enables increased hydrocarbon production.

While emulsified acid systems are more effective than aqueous HCl for carbonate acidizing applications, they often require treatments to be pumped at lower than optimal injection rates due to relatively high friction pressures. The emulsified acid viscosities typically vary between 2.5 and 4.5 cp at 800 s^{-1} and 121–176°C, which is an order of magnitude higher than the 0.25 and 0.5 cp viscosity of aqueous HCl over the same temperature range [25]. Viscosities around 3 cp were reported for acid microemulsion systems [9]. Other investigators have reported significantly lower viscosities of about 0.1 cp at 400 s^{-1} for microemulsions [38]. The authors are not aware of friction loss measurements for the flow of acid microemulsion systems under typical oilfield conditions. Therefore, friction studies could be an interesting area for further investigation to assess the potential of acid microemulsions to mitigate this operational limitation and provide a technical advantage over macroemulsion systems commonly used in carbonate acidizing applications.

7. Summary

Microemulsion technologies have unique properties that make them applicable in the oil and gas industry. Of particular value for carbonate acidizing is their ability to reduce the mobility of the dispersed phase, in this case hydrochloric acid, without a proportionate increase in the fluid viscosity. Microemulsions provide effective acid diffusion coefficients that are two orders of magnitude lower than aqueous HCl. This reduction in the diffusion coefficient is important in carbonate acidizing because the rate of dissolution is mass transfer limited, meaning it can be controlled by changing the rate of convection and/or the rate of acid diffusion.

This research evaluated acid microemulsions with respect to the phase behavior, effective diffusivity, and corresponding impact on the dissolution phenomenon occurring during carbonate acidizing. Results demonstrate that acid microemulsions are effective at creating highly-conductive dissolution channels, or wormholes, in carbonate porous media. Further-more, the dissolution structure and corresponding volume of fluid required for a given depth

of stimulation are governed by the Damköhler number for transport and reaction. Due to the significant reduction in the effective diffusivity of the dispersed acid phase and the dependence of the dissolution phenomenon on the Damköhler number, acid microemulsions provide improved performance compared to aqueous acids, particularly at low injection rates and high reservoir temperatures.

Although research demonstrates that acid microemulsions are effective carbonate acidizing fluid systems, the authors are not aware of microemulsions prepared with acid as the dispersed phase being used for treatments in the field. Emulsified acids ("macro"emulsions) are commonly used for carbonate acidizing and provide a similar reduction in the effective diffusion coefficient as observed for acid microemulsions. These macroemulsion systems often constrain operating conditions due to high friction pressures. Friction studies could be an interesting area for future acid microemulsion research.

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