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Reaction of citric acid with calcite

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Abstract

The reaction of citric acid with calcite was investigated using the rotating disk apparatus. The effects of disk rotational speed, system pressure, and presence of magnesium and ferric ions on this reaction were examined. Scanning electron microscope (SEM) was also used to characterize the surface of the calcite disks at the end of each experiment.

The reaction of citric acid and calcite is mass-transfer limited up to 500 rpm. The reaction rate of citric acid–calcite is limited by the precipitation of calcium citrate on the surface, especially at atmospheric pressure. Increasing the system pressure from 1000 to 1500 psi has no significant effect on the dissolution rate of calcite. The diffusion coefficient of 7.5 wt% citric acid in the presence of calcium citrate and calcium ions is $4.5\mathrm{E}-6\,\mathrm{cm}^2/\mathrm{s}$ at 50 °C and 1000 psi. The presence of magnesium ions in citric acid solutions results in higher concentration of calcium ions in solution.

Calcium citrate forms only on the disk surface, but not in the bulk solution. The morphology of the calcium citrate layer is dependent on the rotational speed of the calcite disk. More calcium citrate precipitation occurs at high disk rotational speeds, above 500 rpm, and at system pressures less than 100 psi. Calcium citrate appears to precipitate as feathery aggregates of radiating platy crystals on the surface of calcite.

Keywords: Citric acid; Calcium citrate; Dissolution rate; Rotating disk

1. Introduction

Organic acids have been used to stimulate carbonate reservoirs for more than four decades (Harris, 1961; Chatelain et al., 1976; Crowe et al., 1988; Fredd and Fogler, 1998a,b,c; Fredd, 2000; Huang et al., 2000; Nasr-El-Din et al., 2001). The two main organic acids that are frequently used to stimulate the carbonate reservoirs are formic acid (HCOOH) and acetic acid (CH_3COOH). These acids are less reactive with carbonate rocks than hydrochloric acid (Nierode and Williams, 1971). Acetic and formic acids are less corrosive than mineral acids and can be inhibited. For example, acetic acid can be inhibited against all types of steel at elevated temperatures for extended periods of time (Harris, 1961). They are mostly used in high temperature reservoirs, where the fast HCl spending rate can cause severe tubing corrosion and poorly etched fractures (Crowe et al., 1988).

Organic acids are more expensive than HCl per unit volume of rock dissolved and cannot be used at high concentrations. Typically, the concentrations of acetic and formic acids used are less than 13 and 9 wt%, respectively. This is because the reaction products (especially calcium formate) can precipitate at higher acid concentrations (Robert and Crowe, 2000). In addition, the reaction of organic acids with calcite, $CaCO_3$, is reversible and thermodynamically limited by the presence of the reaction products (Chatelain et al., 1976; Buijse et al., 2004). In other words, the reaction is controlled by the diffusion of the reaction products away from the rock surface (Fredd and Fogler, 1998a; Fredd, 2000). Mixtures of organic acids have been used to stimulate high temperature/pressure wells in the Arun limestone field in Indonesia (Van Domelen and Jennings, 1995) and to remove calcium carbonate scale in gas wells in the Merluza field (Da Motta et al., 1998).

Citric acid ($C_6H_8O_7$) has historically been used in oilfield treatments as an iron-control agent (Hall and Dill, 1988). It is an α-hydroxy carboxylic acid with three carboxylic (–COOH), and one hydroxyl (–OH) groups. Because of its highly stable

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Table 1
Previous studies on reaction kinetics of carbonates using the rotating disk apparatus

Author	Rock type	Reactive system
Lund et al. (1975)	Calcite	HCl
Anderson (1991)	Dolomite	HCl
AlKattan et al. (1998)	Dolomite/limestone	HCl
Fred and Fogler (1998b,c)	Calcite; Calcite	Acetic acid; ethylenediamine tetra acetic acid (EDTA)
Gautelier et al. (1999)	Dolomite	HCl
Conway et al. (1999)	Calcite/dolomite	Straight/gelled/emulsified HCl
AlKattan et al. (2002)	Calcite	HCl
Frenier et al. (2004)	Calcite/dolomite	Hydroxethylaminocarboxylic acid
Taylor et al. (2004a)	Calcite/dolomite	HCl + additives
Taylor et al. (2004b)	Dolomitic reservoir rocks	HCl + additives

complexes with iron, citric acid is commonly used to stabilize iron in spent HCl acids and prevent precipitation of ferric hydroxide in sweet environments (Taylor et al., 1999), and/or iron sulfide in sour conditions (Raju et al., 2005).

Recently, citric acid has been introduced as a stand-alone acid. It was used in an encapsulated form to prevent the acid reaction with the formation until 180 F (Blauch et al., 2003; Burgos et al., 2004). A major concern with using citric acid is that the reaction product (calcium citrate) has low solubility in water (0.0018 mol/1000 g water at 22.8 °C), which decreases further with temperature (Apelblat, 1993).

Citric acid in an encapsulated form was used in the field with mixed results. Blauch et al. (2003) reported positive results and indicated that potential precipitation of calcium citrate was not a major concern. Burgos et al. (2004) noted that encapsulated citric acid did not improve the performance of the acid-fractured well. Calcium citrate precipitation was cited as one of the reasons for poor field results. They conducted a few experiments in an autoclave where calcium citrate was noted on the surface of the calcite particles used. According to Burgos et al. (2004), calcium citrate will precipitate, even when only a small fraction of citric acid was spent. They found that the precipitation of calcium citrate occurs on the calcite surface where the concentration of Ca^{2+} ions and pH value were high.

Al-Khaldi et al. (2005) examined the reaction of citric acid and calcite. Calcium citrate was noted when this reaction occurred at ambient conditions. Coreflood tests indicated that precipitation of calcium citrate caused severe loss of core permeability if the tests were run at atmospheric pressure. The impact of calcium citrate on core permeability diminished at pressures greater than 1000 psi.

The rotating disk apparatus (RDA) has been widely used to study the reaction kinetics of different acids with carbonate rocks, Table 1. It was used in the present study to examine the reaction of citric acid with calcite under dynamic conditions. This work marks the first time the RDA is used to examine this reaction. The objectives of this study are to: (1) examine the reaction of citric acid with calcite using RDA, (2) determine the nature of calcium citrate precipitate and the mechanism of its formation, (3) study the effects of disk rotational speed and system pressure on the morphology of calcium citrate, and (4) investigate the impact of magnesium and iron (III) ions on the calcium citrate layer.

2. Dissociation and chelation chemistry of citric acid

Citric acid (H_3AOH) is a weak organic acid, which ionizes in water stepwise as in Eqs. (1)–(4) (Levien, 1955):

$$H_3AOH \leftrightarrow H_2AOH^- + H^+, \quad (1)$$
$$H_2AOH^- \leftrightarrow HAOH^{2-} + H^+, \quad (2)$$
$$HAOH^{2-} \leftrightarrow AOH^{3-} + H^+, \quad (3)$$
$$AOH^{3-} \leftrightarrow AO^{4-} + H^+, \quad (4)$$

where A is $C_6H_4O_6$. The distribution of the ionic species of citric acid depends on the dissociation constants and the pH value. These constants are more conveniently expressed as pKa values, $pKa = -\log K_a$, K_{a_1} for Eq. (1) $= \frac{[H_2AOH^-]*[H^+]}{[H_3AOH]}$.

The pKa values for citric acid at 25 °C are $pKa_1 = 3.13$, $pKa_2 = 4.76$, $pKa_3 = 6.4$, and $pKa_4 = 11.6$ (Levien, 1955; Maryadele et al., 1976). In typical acid treatments, the pH value ranges from 0 (live acid) to 5–6 (spent acid). Therefore, the reaction given in Eq. (4) is not likely to play a role on the outcome of the acid treatments using citric acid.

Fig. 1 shows the distribution of citric acid species as a function of the equilibrium pH value. As the pH value increases, more citric acid (H_3AOH), di-hydrogen (H_2AOH^-) and monohydrogen ($HAOH^{2-}$) citrate ions are ionized to produce citrate ions (AOH^{3-}), at pH values greater than 6.

The reaction of citric acid with calcite at pH values of 1.8–6 follows Eqs. (5)–(7). A pH value of 1.8 corresponds to 7.5 wt% citric acid at 50 °C, which was used in the present study.

$$2H^+ + CaCO_3 \leftrightarrow Ca^{2+} + H_2O + CO_2\uparrow, \quad pH = 1.8\text{–}4, \quad (5)$$
$$H_2AOH^- + Ca^{2+} \leftrightarrow CaH_2AOH^+, \quad pH = 1.8\text{–}4, \quad (6)$$
$$Ca^{2+} + 2(CaH_2AOH^+)_{(aq)} \leftrightarrow Ca_3(AOH)_{2\,(s)}\downarrow + 4H^+, \quad pH = 6. \quad (7)$$

Based on Eq. (7), it is clear that the precipitation of calcium citrate is dependent on the pH value and can only occur at or