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Reaction of Simple Organic Acids and Chelating Agents with Calcite

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Abstract

Acid stimulation of deep wells is a difficult task, mainly because of high reaction rate and the high corrosion rate induced by strong acids. One way to address these problems is to use simple organic acids and chelating agents. Unlike HCl, the reaction of organic acids with calcite is reversible and the reaction products can precipitate at certain conditions. The precipitant may form on the rock surface and act as a barrier and ultimately, stop the reaction of the acid with the rock. Recently, chelating agents have been introduced as stimulation fluids. The advantage for chelating agents is they can complex with calcite and form water-soluble products.

Different mathematical models were developed to describe reaction of organic acids (both simple organic acids and polycarboxylic acids) with calcite. All of these models were described in detail and compared with each other. The mechanism of calcite dissolution includes acid dissociation, mass transfer and surface reaction. The chelating effect of organic acids/chelating agents were also considered.

Association reactions of acetate ion with calcium ion are important for reactions of acetic acid with calcite. They **cannot** be ignored even at low acetic acid concentrations. Strong inorganic acid HCl can increase the conversion of organic acids. More concentrated CaA^{+} can be obtained because of large amount of calcium ion due to the reaction by HCl and calcite. The order of reaction between organic acid/chelating agents and calcite needs to be more carefully considered rather than one. Proton attack controls the reaction rate of chelating agent with calcite at low pH values. Ligand attack limits the rate at high pH, while water attack can dominantly influence the calcite dissolution at extremely low concentration. The combination of these two attacks affects the reaction rate at moderate pH values. It is difficult to determine the overall diffusion coefficient of reactants or products if multiple types of calcium species are present at moderate pH values. More research is needed to determine the kinetics of the reaction of chelating agents with calcite at low-moderate pH values. The details of adsorption, complexation and desorption are necessary for investigating the mechanism of interfacial reactions of chelating agents and calcite.

Introduction

Hydrochloric acid is commonly used in matrix and acid fracturing treatments in carbonate reservoirs. However, application of HCl in deep wells is a concern because of its high reactivity and sludging tendencies when the acid contacts asphaltic crude oils. In addition, concentrated HCl-based acids are very corrosive to well tubulars. One way to address these issues is to use organic acids. The two main organic acids that are frequently used in the field are formic acid and acetic acid (Harris, 1961; Smith et al., 1970; Chatelain et al., 1976; Dill and Keeney, 1978; Crowe et al., 1988; Fredd and Fogler, 1998; Huang et al., 2000; Nasr-El-Din et al., 2001). These acids are weakly ionized and slow reacting. Acetic and formic acids are less corrosive than mineral acids and can be inhibited.

Nierode and Williams (1971) speculated that the lower rate of dissolution of calcite with simple organic acids was due to limitations associated with the kinetics of the surface reaction, while Chatelain et al. (1976) demonstrated that the dissolution was influenced by the thermodynamics of the reversible reactions. A variety of transport and reaction processes were described on how to influence the rate of calcite dissolution in acetic acid by Fredd and Fogler (1998c). Buijse (2004) developed a new model for acid/calcite spending, which is applicable to strong and weak acids and to acid mixtures. Mixtures of organic acids (acetic and formic acids) have been used to stimulate high-temperature/pressure wells in the Arun limestone field in Indonesia (Van Domelen and Jennings, 1995) and economic comparison between HCl and organic acid blends was made. The base cost of an organic acid blend was higher than that of HCl, however, reductions in inhibition and gelling agent costs resulted in a final acid blend that was both technically and economically more attractive than an HCl-based system. A mixture of 7 wt% HF/5 wt% HAc was used to remove calcium carbonate scales in gas wells in the Merluza field and was shown at least four times more efficient than 10 wt% HAc alone (Da Motta et al., 1998).