REACTION OF CITRIC ACID WITH CALCITE

by

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TABLE OF CONTENTS

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ABSTRACT

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This study is the first one to examine the reaction of citric acid with calcite over a wide range of parameters. Its main focus is to study the effects of different parameters such as initial citric acid concentration and temperature on the citric-calcite reaction.

A rotating disk apparatus was used to study the reaction of calcite ($CaCO_3$) with citric acid. Using the rotating disk theory, the calcite dissolution rates in citric acid solutions were evaluated as a function of rotating speed, initial concentration of citric acid, concentration of magnesium (Mg^{2+}) & Iron (Fe^{3+}) ions, temperature, and pressure. In addition, Scanning Electron Microscopy (SEM) technique was used to explore the precipitation mechanism of calcium citrate during the reaction of citric acid with calcite. Using this technique, several factors affecting the precipitation of calcium citrate were identified.

In this research, citric acid was found to be an effective stimulation fluid at pH values < 4, rotational speeds of (100-1,000 rpm), initial citric acid concentration of 1-7.5 wt%, pressure values of 1,000-1,500 psi, and temperatures of 25-50°C. However, SEM analysis has shown that calcium citrate precipitation occurred during the reaction at the calcite disk. The precipitation of calcium citrate was found be function of disk rotational speed, initial citric acid concentration, and the concentration of both Mg^{2+} and Fe^{3+} ions. More calcium citrate precipitated at high rotational speeds and high initial citric acid concentration. The presence of both Mg^{2+} and Fe^{3+} ions minimized the precipitation of calcium citrate.

The rate of calcite dissolution in citric acid was found to be mainly dependent on the rotational speed. In general, at low rotational speeds, below 500 rpm, the calcite dissolution is mainly governed by the mass-transfer rate, while at high rotational speed, above 500 rpm, it is controlled by the surface-reaction rate. The mass-transfer and the surface-reaction mechanism were investigated thoroughly.

Using the rotating disk theory, the overall mass transfer coefficient was determined at various rotational speeds, initial citric acid concentrations, and temperature values. The effective diffusion coefficient of citric as was determined at various citric acid concentrations and various temperature values. In addition, the apparent activation energy of calcite dissolution in mass-transfer regime was found to be **37.9** kJ/mol. Finally, a simplified expression was developed to model the reaction kinetics of citric acid with calcite. The model parameters: reaction order, and activation energy were found to be **0.833** and **63.1** kJ/mol, respectively.

This study highlights the importance of the initial acid concentration, temperature, and calcium citrate precipitation on the citric acid reaction with calcite. Another important outcome is the effect of various key parameters on the performance of citric acid as a stand-alone stimulation fluid at conditions similar to those present in a typical field case.

Findings based on this work provide new insights into the applications, usage, and potential limitations of citric acid. Factors controlling downhole reaction of citric acid with calcite are also disclosed.