

Measurement of Acid Reaction Rates of a Deep Dolomitic Gas Reservoir

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Abstract

A rotating disk instrument was used to measure acid reaction rates, reaction order, and activation energy of reservoir rock from a deep dolomitic gas reservoir in Saudi Arabia. These values are required to optimize acidizing simulations. Results of more than 50 experiments are reported in this paper. Measurements were made from room temperature to 85° C at rotational speeds of 100 to 1,000 r/min and acid concentrations of 0.05 to 5 M HCl (0.2 to 17 wt%). The results show how acid dissolution rates change as the reservoir rock varied from 3 to 100 wt% dolomite. Factors affecting the measured parameters are discussed in detail. It was found that the reactivity of the rock varied from values expected for pure calcite marble to those expected for pure dolomite marble. At grain densities near 2.72 kg/dm³ (expected for pure calcite), rock dissolution rates varied by more than an order of magnitude, due to rock mineralogy. At grain densities near 2.83 kg/dm³ (expected for pure dolomite), rock dissolution rates were higher than that observed with pure dolomitic marble. Reaction rates depended on mineralogy and the presence of trace components such as clays.

Introduction

An accurate knowledge of acid reaction rates of deep gas reservoirs can contribute to the success of matrix and acid fracture treatments. These parameters are used in simulation models to estimate the optimum acid concentration, pumping rate, and shut-in time of acid treatments. Many studies of acid stimulation treatments of formation K, a deep, dolomitic gas reservoir in Saudi Arabia, have been published⁽¹⁻³⁾. This is the first study of acid reaction rates and reaction coefficients of this important formation.

The rotating disk instrument is widely used in the petroleum industry for kinetic studies of the reaction of acidic fluids and chelating agents with reactive rock⁽⁴⁻¹⁰⁾. This system allows the determination of rock dissolution rate, reaction rate constants, reaction order, and diffusion coefficients^(4,11).

In the rotating disk instrument, a rock disk 3.81 cm (1.5 in.) in diameter is mounted on a spindle using heat-shrink Teflon[®] tubing. The rock disk can be spun at rates up to 1,000 r/min in a Hastelloy[®] B2 reaction vessel. Acid solution is preheated in a Hastelloy[®] B2 acid reservoir and transferred under pressure into the reaction vessel⁽⁴⁾. Small volumes (8 mL) are removed from the reaction vessel every 2 minutes for 20 minutes. Concentrations of calcium and magnesium in the samples are determined by inductively coupled argon plasma emission spectroscopy. From the calcium and magnesium concentrations, and accounting for the loss of acid volume from the reactor, the amount of acid that reacted with the rock can be calculated for each sample⁽⁸⁾. A plot of calculated acid concentration vs. time shows the rate of acid consumption with time.

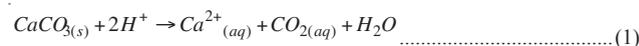
From the slope of this line, and the surface area of the rock disk, the dissolution rate (moles/s•cm²) can be calculated^(6,8).

Test pressure was set at 6.9 MPa so that carbon dioxide would remain in solution. Chatelain et al.⁽¹²⁾ showed that 6.9 MPa was sufficient to keep carbon dioxide in solution for the reaction between organic acids and carbonates. Pressure is not expected to affect the dissolution rate as long as carbon dioxide remains in solution.

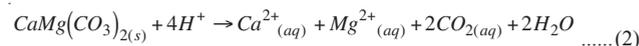
Fluid-solid reactions can be described by the sequence of acid diffusion to the interface, surface reaction, and diffusion of reactants from the interface. The slowest step can be considered the rate-determining step. If the slowest step is the diffusion of reactants and products to and from the surface, then the reaction is mass-transfer-limited. If the slowest step is the surface reaction itself, then the reaction is surface-reaction-limited. In the rotating disk instrument, both of these reaction regimes can occur.

Lund et al. studied the dissolution of both calcite⁽⁵⁾ and dolomite⁽⁶⁾ with the rotating disk instrument. Their work showed that at 25° C, the dissolution of calcite is mass-transfer-limited even at high disk rotational speeds, while at -15.6° C, both mass-transfer and surface-reaction rates limit the dissolution rate. In contrast, Lund et al.⁽⁶⁾ showed that the dissolution of dolomite was surface-reaction-limited at 25° C even at low disk rotational speeds. As the temperature was increased to 100° C, the dissolution process approached diffusion limitation even at relatively high rotational speeds⁽⁶⁾.

The reaction of calcite with HCl in the rotating disk instrument is shown in Equation (1):



The reaction of dolomite with HCl proceeds according to Equation (2):



The rotating disk instrument has been used with a wide variety of rock types to study acid-rock interactions. These include San Andres dolomite⁽¹⁰⁾, dolomite marble [CaMg(CO₃)₂]⁽⁶⁾, calcite marble (CaCO₃)^(5,9), Indiana limestone⁽¹³⁾, Carrara marble⁽¹⁴⁾, and Khuff dolomite reservoir cores⁽¹⁾.

Frenier and Hill⁽⁹⁾ studied the effects of acidizing additives on calcite using the rotating disk instrument. Chelating agents, corrosion inhibitor, non-ionic surfactants and mutual solvent (ethylene glycol monobutyl ether) were examined for their effect on the dissolution rate of calcite marble at 20 and 65° C in the presence of hydrochloric acid. Measurements were made at

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