

Effect of Additives on the Acid Dissolution Rates of Calcium and Magnesium Carbonates

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Summary

A rotating-disk instrument was used to measure the dissolution rates of both calcite and dolomite rock samples in HCl solutions. The results of more than 60 experiments are reported in this paper. The effect of common acidizing additives on the rock dissolution rate is measured for different acids containing quaternary amines, polymer, surfactant, mutual solvent, iron-chelating additive, and dissolved iron. Measurements are made at 23 and 50°C for calcite and dolomite marble samples.

Marble samples from Turkey, Greece, and Italy were analyzed to find suitable reference materials. Marble composed of 100% calcite (calcite marble) as well as 91% dolomite (dolomite marble) was used and compared very well with previously published results. Results of rock dissolution rates with common acidizing additives showed significant differences.

- 1.5 vol% cationic acrylamide copolymer decreased the calcite and dolomite dissolution rates significantly. At 1,000 rpm, the calcite dissolution rate with 1.5 vol% polymer and 0.1 M (0.36 wt%) HCl had a value that was 11.4% of the value measured with 0.1 M of HCl alone.

- Polymer changed the acid/rock reaction from mass-transfer-limited to surface-reaction-limited with both calcite and dolomite. This surface effect is possibly caused by polymer adsorption.

- 10 vol% mutual solvent increased the acid dissolution rate by 9% for calcite and by up to 29% for dolomite.

- 5000 mg/L iron (III) resulted in surface deposition of iron (III) hydroxide for both calcite and dolomite. At low rotational speeds, this surface layer had an inhibiting effect on the dissolution rate.

- 2 vol% corrosion inhibitor decreased the calcite dissolution rate by approximately 9%.

- Citric acid at 12 g/L decreased the calcite dissolution rate by an average of 9%, possibly because of the formation of calcium citrate at the surface.

- 0.2 vol% nonionic surfactant had no significant effect on the acid dissolution rate of calcite.

Introduction

The reaction kinetics of acidic fluids and chelating agents with carbonate rocks has been widely studied in the petroleum industry with the rotating-disk instrument.¹⁻⁷ This system allows determining the rock dissolution rate, reaction-rate constants, reaction order, and diffusion coefficients.^{1,8}

Lund *et al.* studied the dissolution of both calcite² and dolomite³ with the rotating-disk instrument. Reaction stoichiometry and adsorption/desorption steps were also reported.^{2,3} Their work showed that at 25°C, the dissolution of calcite is mass-transfer-limited, even at high disk rotational speeds (500 rpm), while at -15.6°C, both mass-transfer and surface-reaction rates limit the dissolution rate. In contrast, Lund *et al.*³ showed that the dissolution of dolomite was surface-reaction-rate-limited at 25°C, even at low disk rotational speeds (100 rpm). As the temperature increased

to 100°C, the dissolution of dolomite approached the mass-transfer limitation, even at relatively high rotational speeds.³

The mass-transfer-limited and surface-reaction-limited regimes are important features of the rotating-disk instrument. Fluid/solid reactions can be described by the sequence of adsorption, surface reaction, and desorption. The slowest step is considered to be the rate-determining step. If the slowest step is the adsorption or desorption of reactants and products to and from the rock surface, then the reaction is mass-transfer-limited. If the slowest step is the surface reaction itself, then the reaction is surface-reaction-limited. Both regimes can occur with the rotating-disk instrument. For a hypothetical example, these two regimes are illustrated in **Fig. 1**. At low rotational speeds, the dissolution rate increases with the disk rotational speed. This is the mass-transfer-limited regime. The dissolution rate increases because the diffusion boundary layer of the rotating disk decreases at high rotating speeds.⁸ At high rotational speeds, the dissolution rate is constant. This occurs because the reaction rate in this regime is limited by the surface reaction rate.

The rotating-disk instrument has been used with a wide variety of rock types to study acid/rock interactions. These include calcite marble (CaCO₃),^{2,6,9} dolomite marble [CaMg(CO₃)₂],^{3,10} Indiana limestone,¹¹ St. Maximin and Lavoux limestones,¹² San Andres dolomite,⁷ Kasota dolomite,⁷ Haute Vallée de l'Aude dolomite,¹³ Bellefonte dolomite,¹⁰ and dolomite reservoir cores.^{14,15} Previous related work has been summarized by Taylor *et al.*¹⁶

Frenier and Hill⁶ studied the effects of acidizing additives on calcite with the rotating-disk instrument. Chelating agents, corrosion inhibitor, nonionic surfactants, and mutual solvent [ethylene glycol monobutyl ether (EGMBE)] were examined for their effect on the dissolution rate of calcite marble at 20 and 65°C. Measurements were made at 600 rpm and 500 psig and showed that some of these additives had an effect on the calcite dissolution rate in 7.5 wt% HCl.

The main objective of this study was to evaluate the effect of a large number of additives on the acid dissolution rates of calcite and dolomite over a wide range of rotational speeds. These additives include corrosion inhibitor, polymer, surfactant, mutual solvent, citric acid, and dissolved iron (III).

Experimental Procedures

Both calcite and dolomite disks were used in experiments with the rotating-disk instrument. Calcite marble (CaCO₃) from Italy, with a trade name of "Acqua Bianca," was obtained as a white, fine-grained rock. Purity was determined by X-ray diffraction (XRD) and elemental analysis, as shown in **Table 1**. Elemental analysis showed that the calcite marble contained more than 99 wt% calcium carbonate. Trace amounts of albite, quartz, and chlorite were identified by XRD analysis. Noncrystalline components are not identified by XRD. Two other types of calcite marble were examined but were not of sufficient purity for further use. They were not pure white in color and showed slightly more impurities by XRD analysis. Taylor *et al.*¹⁶ have shown that low levels of impurities, especially clays, can significantly affect dissolution-rate measurements.

Dolomite marble [CaMg(CO₃)₂] from Greece, with a trade name of "Crystallina," was obtained as a white rock with visible grains. Environmental scanning electron microscopy (ESEM) showed that the dolomite marble consisted of 50- to 100- μ m

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