

Anomalous Acid Reaction Rates in Carbonate Reservoir Rocks

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Summary

It is generally assumed that the reaction of acid with limestone reservoir rock is much more rapid than acid reaction with dolomite reservoir rock. This work is the first to show this assumption to be false in some cases, because of mineral impurities commonly found in these rocks. Trace amounts of clay impurities in limestone reservoir rocks were found to reduce the acid dissolution rate by up to a factor of 25, to make the acid reactivity of these rocks similar to that of fully dolomitized rock. A rotating disk instrument was used to measure dissolution rates of reservoir rock from a deep, dolomitic gas reservoir in Saudi Arabia (275°F, 7,500 psi).

More than 60 experiments were made at temperatures of 23 and 85°C and HCl concentration of 1.0 M (3.6 wt%). Eight distinctly different rock types that varied in composition from 0 to 100% dolomite were used in this study. In addition, the mineralogy of each rock disk was examined before and after each rotating disk experiment with an environmental scanning electron microscope (ESEM) using secondary and backscattered electron imaging and energy dispersive X-ray (EDS) spectroscopy. Acid reactivity was correlated with the detailed mineralogy of the reservoir rock. It was also shown that bulk anhydrite in the rock samples was converted to anhydrite fines by the acid at 85°C, a potential source of formation damage.

Introduction

A study of acid reaction rates and reaction coefficients of a dolomitic reservoir rock was recently reported by Taylor et al. (2004a). In that work, it was found that reaction rates depended on mineralogy and the presence of trace components such as clays. This paper examines in detail the relationship between acid reactivity and mineralogy of a deep, dolomitic gas reservoir rock. An accurate knowledge of acid reaction rates of deep gas reservoirs can contribute to the success of matrix and acid fracture treatments. Many studies of acid stimulation treatments of the Khuff formation, a deep, dolomitic gas reservoir in Saudi Arabia, have been published (Nasr-El-Din et al. 2001, 2002a, 2002b; Bartko et al. 2003).

It is generally assumed that the reaction of acid with limestone reservoir rock is much more rapid than acid reaction with dolomite reservoir rock during acidizing treatments. However, much of the reported data were obtained with pure limestones, dolomites, and marbles. These include calcite marble (CaCO_3) (Lund et al. 1975; de Rozières 1994; Frenier and Hill 2002), dolomite marble [$\text{CaMg}(\text{CO}_3)_2$] (Lund et al. 1973; Herman and White 1985), Indiana limestone (Mumallah 1991), St. Maximin and Lavoux limestones (Alkattan et al. 1998), Haute Vallée de l'Aude dolomite (Gautelier et al. 1999), Bellefonte dolomite (Herman and White 1985), San Andres dolomite (Anderson 1991), Kasota dolomite (Anderson 1991), and Khuff dolomite reservoir cores (Nasr-El-Din et al. 2002b). The effects of common acid additives on calcite and dolomite dissolution rates were reported in detail (Frenier and Hill 2002; Taylor et al. 2004b; Al-Mohammed et al. 2006). The effects of impurities such as clays on rock dissolution have not been reported.

Lund et al. studied the dissolution of both pure calcite marble (Lund et al. 1975) and pure dolomite marble (Lund et al. 1973) with the rotating disk instrument. According to Lund et al. (1975), at the solid/liquid interface, calcite marble reacts with 1 M HCl approximately 650 times faster than dolomite marble at 25°C. Calcite and dolomite marbles make excellent standards, but do not occur in oil and gas reservoirs.

Alkattan et al. (1998) showed that the dissolution rates of calcite crystals, limestones, and compressed calcite powders were the same within experimental error in the bulk solution pH range of -1 to 3 and at temperatures of 25, 50, and 80°C. The limestones contained less than 1 vol% clays, but one type of limestone (St. Maximin) did contain 16 vol% quartz. This shows that the dissolution rates of pure forms of calcium carbonate are not significantly affected by different mineralogy.

Herman and White (1985) showed that dissolution rates of pure forms of dolomite are not significantly affected by mineralogy. The dissolution rates of dolomites in the form of a single crystal, microcrystalline sedimentary rock, and coarse-grained marble in aqueous carbonate solutions were also found to be similar (Herman and White 1985). The single crystal of dolomite was of hydrothermal origin. The sedimentary dolomite was from the upper Bellefonte formation, Pennsylvania, U.S. It was composed of 80 wt% microcrystalline dolomite (grain size approximately 10 μm), 20 wt% interstitial quartz, and traces of feldspar. The coarse-grained dolomite marble (grain size approximately 100 μm) was from the Fauske formation in Norway and was composed entirely of dolomite.

Anderson (1991) measured acid dissolution rates of Kasota quarried dolomite. Kasota dolomite contained 80 to 90 wt% dolomite, 5 to 10 wt% quartz, 2 to 5 wt% feldspars, and up to 2 wt% calcite. At 49°C, the dissolution rate of the Kasota dolomite was approximately 80% higher in 1 M HCl than the value given by Lund et al. (1973) for dolomite marble. Anderson's results showed that Kasota dolomite was significantly more reactive than dolomite marble.

Anderson (1991) also examined the reactivity of San Andres dolomite samples that contained 80 to 100 wt% dolomite, 0 to 2 wt% calcite, 0 to 10 wt% anhydrite, 0 to 5 wt% gypsum, 0 to 10 wt% quartz, and up to 2 wt% clays. The reaction rate constants of these rocks varied by approximately one order of magnitude. The least reactive samples were similar in reactivity to the Kasota dolomite. Anderson showed that significant variations in reactivity existed, but did not explain or investigate the results.

Gdanski and van Domelen (1999) reported that carbonate reservoir rocks were often significantly less reactive at reservoir conditions than would be expected from reactivity data reported for pure calcite marble and dolomite marble as given by Lund et al. (1973, 1975). Although the implications of these results for acidizing treatments were evaluated, the underlying cause was not addressed. Reaction rate reduction caused by clays will be discussed in this paper that can explain the results reported by Gdanski and van Domelen (1999).

The main objective of the current work is to investigate the impact of mineralogy on reservoir rock reactivity.

Experimental Studies

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 (Boomer et al. 1972; Lund et al. 1975; Anderson 1991; Alkattan et al. 1998; Fredd and Fogler

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