JCPT

Measurement of Acid Reaction Rates with the Rotating Disk Apparatus

K.C. TAYLOR
Taylor Industrial Research Inc.
H.A. NASR-EL-DIN
Texas A & M University

Abstract

The authors have published several papers on the rotating disk apparatus (RDA) in recent years. The RDA is used to measure acid reaction rates, reaction order and activation energy of acidizing fluids with carbonate reservoir rock. This paper summarizes the different ways that acid reaction rates are measured, the factors that affect the results and why this is important when modelling acid stimulation treatments in the field.

In particular, experimental procedures used to obtain acid reaction rates vary widely and can produce very different results. These procedures are often not well-documented in the literature. The validity of different experimental procedures are carefully compared in this paper.

In addition to experimental concerns, the reactivity of reservoir rock can also vary widely. It was recently reported that the reactivity of reservoir rock toward acid is strongly affected by mineralogy and by mineral impurities. In particular, clay impurities in calcite rock were found to reduce the dissolution rate by nearly an order of magnitude. Some calcite rocks with clay content as low as 1 wt% showed acid reactivity similar to that of 100 wt% dolomite.

Acidizing additives such as polymers and corrosion inhibitors have been shown to significantly affect the way that acid reacts with the reservoir rock.

Introduction

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 rocks[1-11]. This system allows the determination of rock dissolution rate, reaction rate constants, reaction order and diffusion coefficients[1, 12].

Taylor et al.[13] examined the effects of acidizing additives on acid reaction rates of calcite and dolomite rock. These additives were quaternary amines, polymer, surfactant, mutual solvent, iron chelating agents and dissolved iron (III).

Taylor et al.[14, 15] examined, in detail, the relationship between acid reaction rate and rock mineralogy for a deep, dolomitic gas reservoir. Their results showed that mineralogy significantly affected acid reaction rate, and that clay contents as low as 1 wt% could reduce the apparent reaction rate of limestone reservoir rock by up to a factor of 25.

There has been significant variability in acid reaction rate data of reservoir rocks[11]. These variations have often been attributed to activation energies lower than obtained for pure calcite or dolomite rock[11]. However, several detailed studies have contradicted this claim[8, 16].

Alkattan et al.[8] 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 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[16] 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[16]. 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.

The purpose of this paper is to examine the different ways that acid reaction rates are measured with the RDA and the factors that affect the results. It is proposed that measurement procedures, rock porosity and clay impurities can have a significant impact on RDA measurements.

Experimental Studies

The rotating disk apparatus used in this work was the RDA-100 manufactured by CoreLab Instruments Ltd. All experiments were made under a nitrogen pressure of 6.9 MPa so that carbon dioxide would remain in solution. Separation of carbon dioxide out of solution will adversely affect the way the acid reacts with carbonate rocks, especially when organic acids are used.

The HCl solutions were prepared from concentrated hydrochloric acid (ACS reagent grade) and distilled water. An autotitrator (METTLER DL70ES) was used to accurately measure the HCl concentration of the prepared samples. The titrant, 0.1 M sodium hydroxide, was standardized using potassium hydrogen phthalate ($KHC_8H_4O_4$).

Calcium and magnesium determinations were made using inductively coupled argon plasma emission spectroscopy. Sulphate concentrations were determined using turbidity measurements after mixing with 0.1 N barium chloride solutions.

The Reynolds number, R_e, for flow at the surface of the rotating disk was calculated for rotational speeds up to 1,000 rpm[4]. R_e was well below the transition value of 3×10^5 indicating that the measurements were made in the laminar flow regime[3, 17].

PEER REVIEWED PAPER ("REVIEW AND PUBLICATION PROCESS" CAN BE FOUND ON OUR WEBSITE)

Only page 1 of this paper is provided for copyright reasons. For more information, please contact:

Kevin Taylor, B.Sc., M.Sc. (Chemistry), PChem

Taylor Industrial Research, Inc.

Tel: 250-418-5705 Fax: 250-361-0099

Email: kevin.taylor@industrialresearch.ca Website: www.industrialresearch.ca