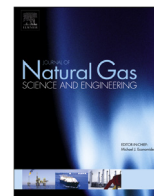




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Stimulation of high temperature carbonate gas reservoirs using seawater and chelating agents: Reaction kinetics

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ABSTRACT

The use of hydrochloric acid (HCl) in gas well stimulation of high temperature reservoirs is currently facing different challenges. These challenges include rapid corrosion of the well tubulars, face dissolution, very high and uncontrolled reaction rate, and formation damage in high clay content and iron-rich reservoirs. In this study, water-soluble diethylene triamine penta acetic acid (DTPA) chelating agent is introduced as alternative to eliminate the risk associated with HCl at high temperatures. In addition, the potential of using seawater to replace fresh water in the stimulation process is explored to save the cost of fresh water transportation to deep offshore oil and gas wells. The effect of seawater on the reaction kinetics of DTPA with carbonate rocks under high pressure and high temperature conditions is investigated using the rotating disk apparatus. The reactions of DTPA solution diluted with fresh water (DTPA/DI) and seawater (DTPA/SW) with carbonate rocks were carried out at the same conditions. In the case of fresh water, the reaction is controlled by the surface reaction regime. Adding HCl to adjust DTPA pH did not turn the reaction into a mass transfer controlled reaction like the case of using HCl alone. The heavy matrix of seawater increased the resistance of ions diffusion, which resulted in a low reaction rate and transformed the reaction into a mass transfer limited regime. Corrosion tests were carried out on production and coiled tubing coupons obtained from the gas wells and the results of the new DTPA/SW formulation is compared to the standard HCl formulation. DTPA showed very low corrosion rate of 0.0034 g/cm² without adding corrosion inhibitors compared to 0.205 g/cm² of 15 wt% HCl with 3% corrosion inhibitors while the industry limit is 0.0244 g/cm² in 6 h. The reaction regime of DTPA chelating agent with calcite is identified to be mass transfer limited in seawater and surface reaction limited in fresh water. The rate expression for the dissolution of Ca²⁺ in DTPA/SW solution is obtained. Coreflooding experiments were performed to determine the optimum injection rate using low permeability Indiana limestone core samples. The optimum injection rate required to stimulate a very deep carbonate gas well was found to be 1.4 bbl/min after scaling up the coreflooding results to field scale. The application of the new DTPA/SW formulation in treating deep gas wells is expected to save the cost of fresh water and eliminate the cost of corrosion inhibitors.

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1. Introduction

In matrix acidizing, the main target is to recover and enhance the permeability of the near-wellbore area by creating high conductivity channels (called wormholes) from the dissolution of carbonate rock matrix. Wormholes enable the hydrocarbon to flow

from the oil reservoir to the wellbore. Wormhole penetration is of interest rather than the wormhole size, because the deeper the acid can go the higher the permeability improvement. At low injection rates, fluid loss to the face of the created wormholes will increase and more face dissolution is expected due to the fast reaction of HCl with carbonate rocks. Face dissolution, asphaltene sludge formation, the need for using costly additives to prevent sludge precipitation are some of the common problems in the stimulation of carbonate formations using HCl. Different HCl alternatives were introduced for well stimulation purposes to avoid or minimize face

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dissolution problems especially in shallow and depleted formations. Fredd and Fogler (1998a, 1998b) and Fredd (1998) investigated the use of different chelating agents on carbonate rock samples and evaluated their ability to create wormholes. They performed linear coreflooding experiments using 4.3 pH 0.25M DTPA chelating agent, and 4 and 13 pH 0.25M Ethylenediaminetetraacetic acid (EDTA). Wang et al. (2009) tested nonaggressive fluid, with a very low corrosion rate compared to HCl, for the stimulation of carbonate reservoirs. They proved that both high and low permeability core could be stimulated by nonaggressive fluid without adding diverting agents.

Freiner et al. (2001) tested 2.5, 4, and 9 pH solutions of Hydroxyethylethylenediaminetriacetic acid (HEDTA) at 300 °F and reported that the pH 4 sodium HEDTA was more effective than the pH 12 in terms of the required volumes to breakthrough. LePage et al. (2009) examined a readily biodegradable poly acidic chelate L-glutamic acid, N, N-diacetic acid (GLDA) as a stand-alone stimulation fluid. They compared GLDA with other chelating agents, including EDTA, HEDTA, NTA and EDG. GLDA was very effective for carbonate rock stimulation compared to other chelating agents and organic acids and it has a thermal stability of the same order as HEDTA. However, using seawater as a base for stimulation fluid in stimulation operations was not fully studied in terms of its effect on the reaction kinetics. Rabie et al. (2014) used seawater to dilute lactic acid and they concluded that the presence of salts (from seawater) reduced the rate of dissolution by lactic acid. Recently, Barri (Barri and Mahmoud, 2015) performed coreflooding experiments using different seawater-diluted chelating agents and proved that the solutions were able to generate wormholes through Indiana limestone core samples.

Among the techniques used to evaluate stimulation fluid efficiencies for matrix acidizing is the rotating disk apparatus (RDA). RDA is used mainly to study the reaction kinetics of stimulation fluids with the reservoir rocks. The rotating disk was first introduced in 1972 (Boomer, 1972) and used to determine the reaction rate, the order of the reaction, and the diffusion coefficient associated with the minerals dissolution (Fredd and Fogler, 1998a; Wang et al., 2009; Lund et al., 1973).

Studying the reaction kinetics of stimulation fluids can minimize the required coreflooding experiments needed to capture the optimum parameters for a stimulation treatment. With the fact that the optimum injection rate to bypass a formation damage of a certain depth changes with the damage depth. Several coreflooding experiments are needed to locate the optimum injection rate for each damage depth. Knowing the nature and limitations of the reaction between the stimulation fluid and a certain rock will facilitate the treatment design for any formation penetration radius. For example, the optimum Damköhler number and injection rate can be reported as a function of the diffusion coefficient of the mass transfer limited reaction.

The previous work that addressed the use of chelating agents as stimulating fluid was limited to room temperature. Currently, no work has been done to study the reaction kinetics of DTPA with carbonate rocks at high pressure and temperature typical of reservoir conditions. In addition, the potential of using seawater to replace fresh water in the stimulation process is explored to save the cost of fresh water transportation to deep offshore gas wells. Therefore, the reaction kinetics of DTPA chelating agent diluted with seawater and deionized water with carbonate samples are studied in rotating disk apparatus at elevated pressure and temperature. The reaction regime is determined and the diffusion coefficient of DTPA; along with the optimum injection rate required to treat deep gas wells are identified for scale up purposes. The corrosion rate of DTPA/SW formulation at high pressure and high temperature (HPHT) conditions is measured using field samples of

tubing coupons. Finally, the effectiveness of stimulations using DTPA and HCl formulations are compared.

2. Materials and methodology

2.1. Rotating disk apparatus

For an acidizing treatment, involving a solid rock and a fluid acid system, the reaction rate determination process is greatly affected by reactant transport to the rock surface and products transport away from the surface. Therefore, the overall reaction consists of three steps as shown in Fig. 1:

- Reactant transfer from the bulk solution to the solid surface.
- Reaction at the solid surface.
- Products transfer from the surface to the bulk solution again.

The slowest step of the three controls the overall reaction kinetics and is referred to as the rate-limiting step. For a reaction system, if the mass transfer process is faster than the surface reaction rate, then the overall reaction is controlled by surface reaction. On the other hand, if the rate of surface reaction is faster than diffusion to the surface, the process is mass transfer limited.

Levich and Newman (Levich, 1962; Newman, 1966) showed that for Newtonian fluids, the rate of mass transfer (R_{MT}) of a reactant to the solid surface in a laminar flow regime induced by a rotating disk geometry is given by the following equation:

$$R_{MT} = \frac{J}{A} = k_m(C_b - C_s) \quad (1)$$

$$k_m = \frac{0.60248 \left(S_c^{-\frac{2}{3}} \right) \sqrt{\nu \omega}}{1 + 0.2980 \left(S_c^{-\frac{1}{2}} \right) + 0.1451 \left(S_c^{-\frac{2}{3}} \right)} \quad (2)$$

where:

- J: Mass transfer flux,
- A: Surface area, cm^2 ,
- C_b : Bulk concentration of the transferred species,
- C_s : Surface concentration of the transferred species,
- k_m : Mass transfer coefficient,
- ω : Disk angular velocity ($2\pi N$, where N is the number of cycles/s), rad/s,
- ρ : Fluid density, gm/cm^3 ,
- μ : Fluid viscosity, $\text{gm}/\text{s}\cdot\text{cm}$,
- ν : Kinematic viscosity (μ/ρ), cm^2/s ,
- D_e : Diffusion coefficient, cm^2/s ,
- S_c : Schmidt number (ν/D_e), dimensionless

Levich (1962) defined the Reynold number for the flow around a rotating disk in the laminar flow regime (Re of the order 10^4 - 10^5) as:

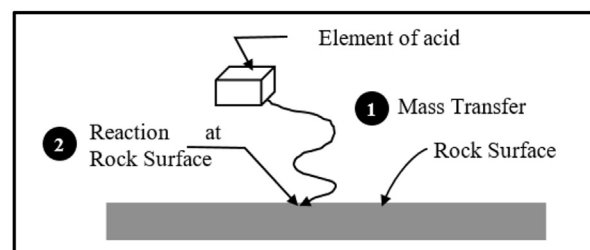


Fig. 1. Acid reaction with rock surface.

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