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Analysis and simulation of rheological behavior and diverting mechanism of In Situ Self-Diverting acid

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ABSTRACT

SDVA acid is one kind of In Situ Self-Diverting acid fluids that are widely used for diverting acid into a low-permeability zone in carbonate reservoir treatment, thus stimulating the production of the heterogeneous reservoir effectively. However, the rheological behavior and diverting mechanism of In Situ Self-Diverting acid (SDVA acid) is so complicated that no models reported can perfectly simulate the acidizing process of SDVA acid, especially in radial flow. In this paper, we study the factors influencing rheological behavior such as pH value, calcium ion concentration and SDVA concentration. An empirical rheological model is developed to describe the relationship between the apparent viscosity of SDVA acid and the coefficient of pH, calcium ion and SDVA. Based on the two-scale continuum models, a numerical model is developed to describe reaction, transportation and diversion of SDVA acid in carbonate rocks for linear flow and radial flow. From the simulation results, the gel region is observed around the wormholes and branches, and this high-resistance region limits the propagation of wormholes more seriously in the radial direction compared to the length direction of linear core. When the acidizing is performed in a single linear core or in a single radial core, the injection pressure drop decreases monotonically versus the injected pore volume of HCl acid. But when SDVA acid is injected, the pressure drop increases initially and decreases afterward. The pressure drop curves from simulations are consistent with experimental results. Finally, we analyze the diversion results in parallel core set-up with different permeability, where the wormhole propagates much longer in the low-permeability core when SDVA acid is injected compared to HCl acid systems and wormhole breaks in high-permeability core firstly no matter which acid systems are used. The curves of diversion flow rate in the parallel core simulation further confirms that the diverting mechanism is simulated successfully for SDVA acid by models developed in this paper.

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1. Introduction

In carbonate reservoirs, acid injection is commonly used to improve or recover productivity [\(Economides and Nolte, 1989\)](#page--1-0). However, in those reservoirs with a huge variety of pore structure or permeability property, acid preferably enters the region with the highest permeability, leaving the damage zone untreated after injection. As a result, magnitude of variance of permeability property inside and between layers continues to increase. Consequently, the effective fluid placement is the key to treatment success for this kind of reservoir.

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A variety of diversion techniques exist in oil field applications, which can be divided into either mechanical or chemical techniques. Mechanical diversion methods mainly include packers or/and bridge plugs, ball sealers and coiled tubing. Chemical diversion methods can be classified into foam acid, in situ cross-linked acid and self-diverting acid [\(Kalfayan and Martin, 2009; Cohen](#page--1-0) [et al., 2010](#page--1-0)). Even though packers or/and bridge plugs and ball sealers are effective, they are time-consuming and expensive and the operation progress is complex. Coiled tubing is applicable to both openhole completion wells and slotted linear completion wells, but has a big disadvantage of pumping rate limitation. Foam is a dispersion of a gas in a liquid with gas being in a noncontinuous phase and liquid is the continuous phase [\(Chang et al.,](#page--1-0) [2007](#page--1-0)). The biggest problem encountered in the application of foam for acid diversion is its stability, which cannot be well ensured, especially in a high-temperature reservoir. In situ cross-linked acids are prepared by adding polymers, cross-linkers, and breakers that use pH to control the crosslinking of polymers and form gel in certain pH ranges where viscosity is increased enormously. The introduction of polymer and cross-linker (Fe³⁺, Zr⁴⁺) will definitely cause damage after flow-back ([Lynn and Nasr-El-Din, 2001; Nasr-El-](#page--1-0)[Din et al., 2002\)](#page--1-0). VES self-diverting acids have been extensively used in matrix stimulation and field application has been very positive ([Cohen et al., 2010; Cesin et al., 2011; Sarma et al., 2012; Jardim](#page--1-0) [Neto et al., 2013](#page--1-0)). Typical VES self-diverting acid solution is usually composed of a viscoelastic surfactant, HCl (usually mass concentration is not more than 20%) and other additives. Commonly used viscoelastic surfactants are amphoteric surfactants ([Nasr-El-Din](#page--1-0) [et al., 2006; Nasr-El-Din and Samuel, 2007; Yu and Nasr-El-Din,](#page--1-0) [2009; Gomaa et al., 2012](#page--1-0)). Amphoteric surfactants are pH sensitive to pH value change. When the pH value is less than isoelectric points, the surfactant is protonated and the net charge of the molecule is positive, and the acid viscosity is very small. As the acid reacts with rocks, the pH is increased to beyond the isoelectric point, the net charge of the molecule becomes zwitterionic, and monomers of the surfactant form rod-like micelles, which impart high viscosity. As the concentration of surfactants, Ca^{2+} and Mg^{2+} increases, these long rod-like micelles get strengthened, which largely increase the viscosity of the system. As a result, in the layers of high permeability which exhibit less resistance and first react with the acid, the high viscosity produced creates a temporary block zone, so the injection profile is changed [\(Al-Ghamdi et al., 2004; Yu](#page--1-0) [and Nasr-El-Din, 2009; Qu, 2011; Song, 2013](#page--1-0)).

Studies have shown that pH value, content of Ca^{2+} and VES are the main factors affecting self-diverting acid viscosity, ([Al-Otaibi](#page--1-0) [et al., 2011; Al-Nakhli et al., 2008\)](#page--1-0), while the effect of Mg^{2+} and Na⁺ on the viscosity of spent acid is much less ([Zhao, 2006; Qu](#page--1-0) [et al., 2012, 2013\)](#page--1-0). The increase of the viscosity of the spent acid will reduce the rate of transfer of H^+ from the bulk solution to the surface of the formation. Moreover, viscoelastic surfactant molecules can absorb on the rock surface and form a barrier that reduces acid reaction with the rock. Finally, viscoelastic surfactant solutions are non-Newtonian fluids and can change the flow pattern close to the surface of the rock. Therefore, the wormhole pattern in VES selfdiverting acid is different from that in HCl. [Tardy et al. \(2007\)](#page--1-0) developed a new set of parameters characterizing the reactive flow of a self-diverting acid, which were used later to model the process. Based on previous studies [\(Hill et al., 1995](#page--1-0)), in In Situ Self-Diverting acid simulation a resistance has been considered in the core that is the barrier blocks VES acid to react with the rock, where a large increase of the apparent viscosity is observed. One paper [\(Liu et al.,](#page--1-0) [2013](#page--1-0)) developed a viscosifying model that described the relationship among the viscosity, pH and the concentration of Ca ion and a model describing the relationship between the reaction rate and the concentration of HCl, and couples them with the linear two-scale continuum model, but the author did not quantify the changes in viscosity with the concentration of Ca ion directly. Another paper ([Bulgakova et al., 2013\)](#page--1-0) investigated the viscoelastic surfactant effect on the HCl and calcite reaction and examined the effects of the surfactant and acid concentrations on the SDVA apparent viscosity and also proposed the semi-empirical rheological model, which describes the relationships between viscosity, rate, and HCl. Another paper [\(Zhang et al., 2013](#page--1-0)) built a VES wormhole model, which simulates acid flow, acid–rock reaction, porosity variation, and acid viscosity variation. For the viscosity variation due to acid–rock reaction, they used a correlation of viscosity as a function of pH, temperature, cation concentration, VES concentration, and shear rate based on experimental results. When the pH value is less than a critical value, viscosity of the acid solution is considered to be a constant value (ignore the influence of each factor on viscosity), but when the pH value is bigger than the critical value, only then different constant values are introduced in viscosity correlations to calculate the viscosity.

2. Rheological modeling for SDVA acid

20 wt% CaCl₂ is used to replace the spent acid of 15 wt% live acid that reacted completely in experiments, and SDVA with different concentration is added into the spent acid in each experiment. Then the corresponding viscosity is measured at $170 s^{-1}$, $20 °C$ in different pH value by adding HCl. From the experimental results shown in Fig. 1(a), no matter how much SDVA concentration the spent acid contains, the corresponding maximum viscosity will become almost constant when the pH value exceeds 2. Similarly, no matter how much the Ca ion concentration the spent acid contains, the corresponding maximum viscosity will also become almost constant when the pH value exceeds 2, as shown in Fig. 1(b) ([Liu](#page--1-0) [et al., 2013](#page--1-0)). In general, the viscosity increases dramatically with SDVA or Ca ion concentration once the pH value exceeded 2. [Chang](#page--1-0) [et al. \(2001\)](#page--1-0) achieved similar results in experiments of VES acid. From Fig. 1, it can be observed that the viscosity of SDVA acid depends on pH, SDVA concentration and Ca ion concentration strongly. In this section, we will fit the functions throughout the experiment results to describe the relationship between viscosity of SDVA acid and pH, SDVA concentration, and Ca ion concentration. Then the functions will be further introduced into the two-scale

Fig. 1. SDVA acid apparent viscosity versus pH obtained from experiments for different SDVA concentrations and Ca ion concentrations ([Liu et al., 2013](#page--1-0)).

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