

Measurement of Reaction Rate of Gelled Acids and Calcite with the Rotating Disk Apparatus

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Abstract

An investigation has been made to study the reaction kinetics of gelled acids with calcite using a rotating disk apparatus. The rheological experiments revealed that all gelled acids behaved as non-Newtonian shear thinning fluids. With the rotating disk apparatus, the reaction kinetics parameters, activation energy, and effective diffusion coefficients were determined. It was found that the reaction of gelled acid with calcite was mass transfer limited at low polymer concentration and moving toward surface reaction limited at higher polymer concentration. And the diffusion rate marginally decreased, with increasing the polymer concentration.

Keywords

Reaction Rate, Mass Transfer, Surface Reaction, Gelled Acid,
Effective Diffusion Coefficient

1. Introduction

In carbonate formations, acidizing treatments provide not only a means of removing the damage from the wellbore area but also an opportunity to improve the near-wellbore permeability. Gelled acids, which have been widely used to increase the viscosity of acid in the formation, can enhance diversion and achieve deep acid penetration and longer fractures. The reaction rate is used to determine the distance that acid can penetrate from the wellbore at a given pumping rate before it is completely spent [1] [2]. The reaction of gelled acids with calcite in the rotating disk apparatus is shown in Equation (1):



The reaction between acid and rock is a three-step process involving: transport of the H^+ from the bulk solution to the rock surface, reaction at the surface,

transfer of the reaction products away from the surface. The slowest step controls the overall reaction rate [3].

Conway *et al.* [4] found that the acid diffusivity is proportional to temperature and H^+ concentration and inversely proportional to the Ca^{2+} and Mg^{2+} . Lakatos [5] found that the effective diffusion coefficient of H^+ ions increased with increasing HCl content. The correlation predicts lower acid diffusivity. K.C. Taylor [6] showed that cationic acrylamide polymer and the acid rock reaction were to turn from mass transfer limited to surface reaction limited. This is due to polymer adsorption. H.A. Nasr-El-Din [7] studied the effect of polymer concentration, temperature and disk rotational speed on the dissolution rate of calcite using gelled acids. There is no significant change in the dissolution rates when the polymer concentration is higher than a certain value.

Lund *et al.* [8] described the reaction rate by the power-law expression shown in Equation (2):

$$J = K \cdot C_s^m \quad (2)$$

If the surface reaction limits the reaction, the acid concentration on the rock surface is assumed to be equal to the acid concentration in the bulk fluid [9]. And the reaction rate equation can be expressed by Equation (2).

The activation energy, E_a , can be obtained by plotting the log of specific reaction rate from Equation (3) vs. the reciprocal of the temperature in Kelvin. This is done using the Arrhenius equation [10]:

$$K = K_o \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

For non-Newtonian fluids, the viscosity of power-law model fluids, like the gelled acid, can be given by Equation (4) [11]:

$$\mu = k\gamma^{n-1} \quad (4)$$

When the reaction is mass transfer limited, the rate of reaction can be determined directly from the mass-flux equation. Hansford and Litt [12] solved the convective-diffusion equation and introduced modified Reynolds and Schmidt numbers to take into account the shear dependence of the viscosity power law. The model was represented by de Rozières *et al.* [13] as:

$$J = \phi(n) D^{\frac{2}{3}} \left(\frac{k}{\rho}\right)^{\frac{-1}{3(1+n)}} r^{\frac{1-n}{3(1+n)}} \omega^{\frac{1}{1+n}} C_b \quad (5)$$

Equation (5) can be written as:

$$F = D^{\frac{2}{3}} \omega^{\frac{1}{1+n}} \quad (6)$$

where

$$F = \frac{J}{\phi(n) C_b \left(\frac{k}{\rho}\right)^{\frac{-1}{3(1+n)}} r^{\frac{1-n}{3(1+n)}}} \quad (7)$$

Equation (6) shows that plotting F vs. $\omega^{1/(1+n)}$ results in a straight line and the slope of the line is the effective diffusion coefficient raised to the 2/3 power.

The objectives of this work are to 1) study the mass transfer and the reaction-rate kinetics of the reaction of gelled acid with calcite and 2) investigate the effect of acid concentration, polymer concentration, temperature and disk rotational speed on the rate of calcite dissolution.

2. Materials and Methods

2.1. Materials and Chemicals

Rock samples were cut from blocks of Dong Fang Gas Field limestone (>99 wt% calcite) into disks with a diameter of 2.54 cm and a thickness of 2 cm. The purity was determined by X-ray diffraction (XRD). **Table 1** gives the porosity and the permeability of these rocks. Each surface of the disk was polished.

The gelled acid was prepared using ACS grade acid (36.5 wt%), a corrosion inhibitor and an acid-soluble polymer. Deionized water was used to prepare the acid. Corrosion inhibitor was used at 2 wt%. Acid concentration varied from 5 wt% to 20 wt%. Polymer concentration varied from 0.2 wt% to 0.8% wt%.

2.2. Viscosity Measurements

Viscosity measurements for acid were made using a high-pressure/high-temperature (HP/HT) viscometer. The wetted-area of this viscometer was made of Hastalloy C to resist corrosion by the acids. Viscosity was measured as a function of shear rate from 57 to 1020 s^{-1} over a temperature of 50°C. A pressure of 300 psi was applied to minimize evaporation of the sample.

2.3. The Rotating Disk Apparatus

The rotating disk apparatus used in this work was manufactured by Haian Petroleum Instruments Ltd. The calcite disks were fixed in the disk-holder assembly into the reactor vessel using heat-shrinkable Teflon tubing. A new calcite disk was used for each experiment. And every calcite disk was soaked in 0.1N HCl for nearly 30 minutes, then rinsed with deionized water before fix them in the disk-holder assembly [14]. The gelled acid was poured into the reservoir vessel and heated to 30°C - 70°C. Pressurizing the reactor vessel to 1000 psi by compressed N_2 gas is necessary to ensure that the evolved CO_2 is kept in solution and does not affect the dissolution rate [15]. Then the rotational speed was set up to 200 - 1000 rev/min.

For the rotational speed up to 1000 rev/min, the Reynolds number R_e for flow at the reaction surface was calculated. R_e was well below the transition value of 3×10^5 , indicating that the experiments were made in the laminar flow regime [16].

Table 1. Properties of the rock disk.

| Rock Type | Porosity (vol%) | Permeability (md) |
|-----------|-----------------|---|
| limestone | 1 - 7 | 0.1×10^{-3} - 0.9×10^{-3} |

The reaction-rate experimental time was fixed at 5 minutes in order to reduce the influence of reaction surface area on the dissolution rate. During the experiment, acid samples, each of approximately 2 cm³, were taken periodically with time to measure the calcium concentration present in the samples using Inductively Coupled Plasma (ICP). The density of samples was measured using a pair densitometer, model DAM 35. Acid concentration was calculated from the calcium concentration. From the decrease in acid concentration vs. time and the initial surface area of the disk, the dissolution rate was calculated in units of mol/(cm²·s).

3. Results and Discussion

3.1. Viscosity Measurement

The gelled acids were prepared at 0.2, 0.4, 0.6, and 0.8 wt% polymer concentrations. The additives were mixed so that the final acid concentration was 15 wt% HCl. All measurements were performed at 50°C and a shear rate from 57 to 1020 s⁻¹. The effect of changing the shear rate on the apparent viscosity of gelled acid is shown in **Figure 1**, which represents a log-log plot of apparent viscosity vs. shear rate. The apparent viscosity of gelled acid decreased, as the shear rate increased. It can be represented by a straight line, which indicated that all gelled acids can be considered a non-Newtonian shear thinning fluids. The relationship between apparent viscosity and shear rate can be described by the power-law model that can be represented by Equation (4). **Table 2** shows the values for “*k*”, “*n*”, and the correlating coefficient for the acid samples, prepared at 0.2, 0.4, 0.6, and 0.8 wt% polymer concentration. The high correlating coefficient indicates a good correlation of apparent viscosity and shear rate.

Figure 1 shows that the apparent viscosity of gelled acid increased, as the polymer concentration increased. The polymer was made of partially hydrolyzed polyacrylamide. The chains of linear macromolecule were long, soft, and high

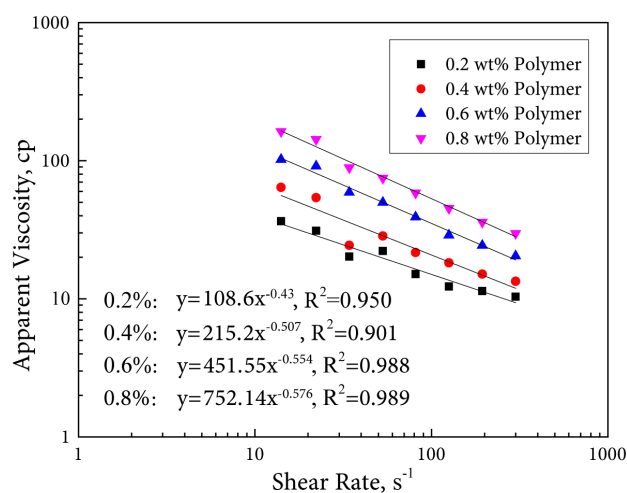


Figure 1. Gelled acid apparent viscosity vs. shear rate for different polymer concentrations.

Table 2. The power-law parameters of gelled acid.

| Sample No. | Polymer Concentration (wt%) | Power Law Constant, k ($\text{g}\cdot\text{cm}^{-1}\cdot\text{s}^{n-2}$) | Power Law Index, n | Correlating Coefficient | $\varphi(n)$ | Density, ρ (g/cm^3) |
|------------|-----------------------------|--|----------------------|-------------------------|--------------|--|
| 1 | 0.2 | 1.086 | 0.57 | 0.950 | 0.653 | 1.044 |
| 2 | 0.4 | 2.152 | 0.493 | 0.901 | 0.655 | 1.046 |
| 3 | 0.6 | 4.5155 | 0.446 | 0.988 | 0.659 | 1.048 |
| 4 | 0.8 | 7.5214 | 0.424 | 0.989 | 0.660 | 1.050 |

molecular weight. The intertwining and friction among the molecular chains resulted in the high apparent viscosity of gelled acid. As the polymer concentration increased, the amounts of linear macromolecule chains increased and the intertwining and friction become more intense, that, in turn, resulted in higher apparent viscosity of gelled acid. However as the shear rate increased, the macromolecule coils untwisted and the linear macromolecule chains broken, which finally result in lower apparent viscosity. As the polymer concentration increased from 0.2 to 0.8 wt%, the power parameter “ n ” reduced from 0.57 to 0.424, which means the influence of shear rate on apparent viscosity is less. When the shear rate was high, there was no significant change in the viscosity of the gelled acid at different polymer concentrations.

3.2. Reaction Kinetics Equation

Plots of the dissolution rate vs. the acid concentration on the rock surface were given at 30°C, 50°C, and 70°C (**Figure 2**). Setting the rotational speed up to 1000 rev/min to ensure the reaction was close to surface reaction limited was necessary. The acid concentration on the rock surface is assumed to be equal to the acid concentration in the bulk fluid. And the specific reaction rate, the reaction order and the activation energy can be calculated by Equation (2) and Equation (3).

The rate of the reaction at 30°C, 50°C, and 70°C could be described by the power-law expression shown in Equations (8)-(10).

$$J = 1.8849 \times 10^{-5} C_s^{0.1722} \quad (8)$$

$$J = 3.2237 \times 10^{-5} C_s^{0.2119} \quad (9)$$

$$J = 6.0401 \times 10^{-5} C_s^{0.2744} \quad (10)$$

The reaction rate significantly increased as the temperature was increased from 30°C to 70°C. The reaction rate of gelled acid with calcite at 70°C was about twice as much as the reaction rate at 30°C. The reaction orders, which indicated the influence of acid concentration on the reaction rate, were 0.1722, 0.2119, 0.2744 at 30°C, 50°C, and 70°C. The higher reaction order indicated the greater influence degree of acid concentration on the reaction rate. As the temperature increased, the apparent viscosity of gelled acid decreased. The high temperature make the barrier that formed by polymer molecules on the rock

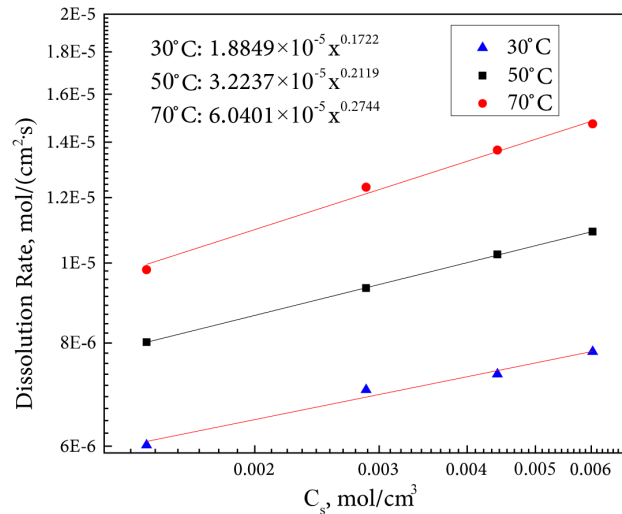


Figure 2. Reaction kinetics equations of gelled acid with calcite at different temperatures.

surface unstable. And there are more and more collision between the acid drop-let and the rock surface. The high temperature also will increase the diffusion rate of H^+ from the bulk solution to the surface of the rock.

3.3. Activation Energy

The Arrhenius equation was used to determine the activation energy E_a and the pre-exponential factor K_0 by plotting the log of specific reaction rate vs. the inverse of the absolute temperature as shown in **Figure 3**.

The activation energy was found to be 25.08 kJ/mol, and the pre-exponential factor was $0.1116 \text{ mol}/(\text{cm}^2 \cdot \text{s}) (\text{mol}/\text{cm}^3)^{-m}$. The activation energy value is comparable to that obtained by Nasr El-Din *et al.* [17], who reported a value of 3.51 kcal/mol (14.6957 kJ/mol) for the reaction of gelled acid and Khuff limestone.

3.4. Effective Diffusion Coefficient

The effect of common acidizing additives on reaction rates were examined by Taylor *et al.* [6]. An acrylamide copolymer decreased the calcite dissolution rates significantly. Polymer changed the acid-rock reaction from mass transfer limited to surface reaction limited. Plots of the dissolution rate vs. rotational speed to the power $1/(1+n)$ are given at different concentration and 50°C (**Figure 4**).

As the polymer concentration increased, the apparent viscosity of gelled acid increased, which will reduce the diffusion rate of H^+ . More and more polymer molecules will adsorb on the surface of the rock and reduce the reaction rate. As the rotational speed increased, the apparent viscosity of gelled acid decreased and mass transfer intensified. From **Figure 4**, it is apparent that, at 50°C, that reaction of gelled acid and calcite is mass transfer limited for 0.2 and 0.4 wt% polymer. With increasing the polymer concentration to 0.6 and 0.8 wt%, the reaction seems to be in the region between mass transfer limited and surface

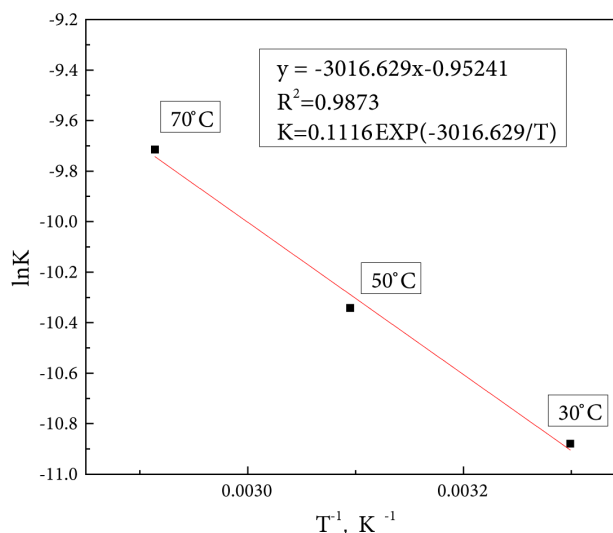


Figure 3. Determination of the activation energy and the pre-exponential constant for the reaction between gelled acid and calcite at 1000 rev/min.

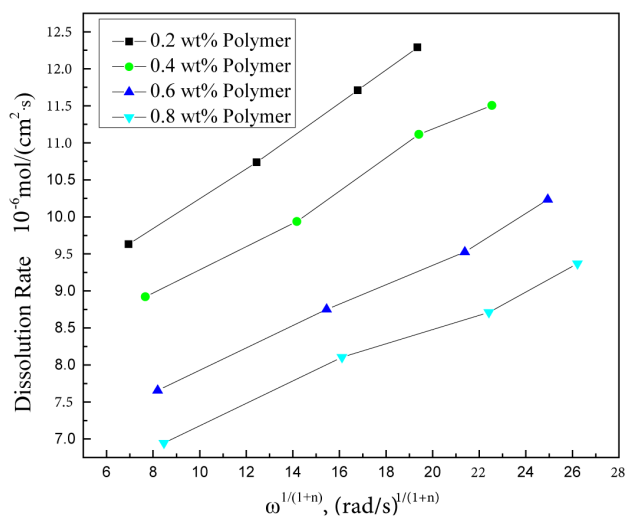


Figure 4. Effect of disk rotational speed on the dissolution rate of calcite in 0.2, 0.4, 0.6, 0.8 wt% polymer and 15 wt% HCl gelled acid at 50°C.

reaction limited. This behavior is best explained by M.A. Sayed [18], where the reaction rate date, as a function of the rotational speed to the power $1/(1+n)$, seems to be follow a plateau, which indicates that the reaction is a surface reaction limited.

The effective diffusion coefficient, D , of H^+ in gelled acid at 50°C, for mass transfer limited reaction, can be determined by Equation (6). The F function was calculated using the density, viscosity date, and $\varphi(n)$ from Table 2. In Figure 5, the F function value were plotted against the disk rotational speed raised to the power $1/(1+n)$. The effective diffusion coefficient was calculated by raising each slope to the power of 1.5.

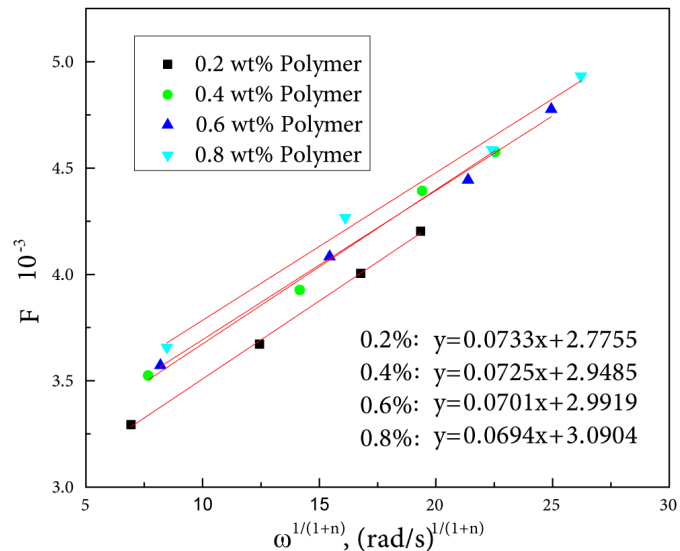


Figure 5. Dissolution as a function of disk rotational speed raised to power $1/(1+n)$ and polymer concentration at 50°C .

The effective diffusion coefficients were found to be 6.2756×10^{-7} , 6.1732×10^{-7} , 5.8692×10^{-7} , 5.7815×10^{-7} cm^2/s at 0.2, 0.4, 0.6, and 0.8 wt% polymer concentration. From the dates, it is clearly that as the polymer concentration increased, the diffusion coefficient decreased, and hence the reaction rate decreased. However, this effect was not significant.

4. Conclusion

The rheology of gelled acids was examined at different polymer concentrations and 50°C . The reaction rate of the gelled acid with calcite was studied using a rotating disk apparatus at 30°C , 50°C , 70°C and for rotational speed ranging from 200 to 1000 rpm. The acid diffusivity in gelled acid with calcite was measured assuming the reaction is a mass transfer limited reaction. Based on the results obtained, the following conclusions can be drawn:

- 1) The viscosity of gelled acid increased, with increasing polymer concentration.
- 2) The viscosity of gelled acid, as a function of shear rate, can be expressed by power-law model indicating a non-Newtonian shear thinning fluid.
- 3) From the reaction kinetics measurements, the reaction kinetics equations, activation energy, and effective diffusion coefficients were determined.
- 4) For low polymer concentration, the reaction rate increased proportionally with the rotational speed, which indicated that the reaction of gelled acid with calcite, at 50°C , is mass transfer limited reaction.
- 5) At higher gelled concentrations, the reaction of gelled acid and calcite tend to move toward the region where the reaction becomes surface reaction limited.
- 6) As the polymer concentration increased, the diffusion rate decreased. But this effect was not significant.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Notations

- J : Reaction rate, mol/(cm²·s)
- C_s : Acid concentration at the surface, mol/cm³
- C_b : Acid concentration in the bulk solution, mol/cm³
- K : Specific reaction rate, mol/(cm²·s)(mol/cm³)^{-m}
- m : Reaction order, dimensionless
- K_ϕ : Pre-exponential factor, mol/(cm²·s)(mol/cm³)^{-m}
- E_a : Activation energy, kJ/mol
- R : Gas constant, 8.314J/(°C·mol)
- T : Temperature, °C
- μ : Apparent viscosity, cp
- k : Power law constant, g/(cm·s²⁻ⁿ)
- γ : Shear rate, s⁻¹
- n : Power law index, dimensionless
- $\varphi(n)$: Function depends on n
- ω : Disk rotating speed, s⁻¹
- ρ : Density, g/cm³
- D : Effective diffusion coefficient, cm²/s

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