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The Determination of Acid-Rock Reaction Kinetic Equation With Deep-Penetration and Low-Damage Acid

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Abstract

Deep-penetration and low-damage host acid is composed of two kinds of organic acids, two kinds of inorganic acid and necessary organic additives, and the concentration is 16%. It is a kind of acid liquid system which has a strong versatility, less damage to the formation, strong acid rock reaction rate, high final dissolution rate, and organic inorganic scaling. In order to determine the reaction rate of the acid and the reaction kinetics equation of deep penetrating low damage acid, the acid rock reaction rate of common acid and deep-penetrating and low-damage acid is studied.

Key words: Acid rock reaction; Kinetic equation; Deep-penetration and low-damage acid; Mechanism

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INTRODUCTION

The determination of the kinetic equation of the acid rock reaction is an intuitive description of the chemical reaction rate after the contact between the acid liquid and the rock minerals[1]. According to the mass action law of the chemical reaction rate and the effective mass of the reactants, the reaction rate is proportional to the m power product of the reactants concentrations determines acid-rock reaction kinetic equation[2]. Based on the determination of deep-penetration and low-damage acid rock reaction kinetics equation, acid-rock reaction kinetic mechanism is studied.

1. DETERMINATION OF KINETIC EQUATION OF STATIC ACID ROCK REACTION

Under the conditions of acid liquid static and normal pressure, the temperature of the water bath is adjusted to 65 ℃, the core with the heat shrinkable tube heating wrapped tightly, leaving only the core of circular cross section, to ensure that the core to a constant area and acid reaction[3]. The reaction of deep-penetrating and low-damage acid liquid with 16%, 12%, 8%, 4% reacts respectively with core. The quality of the core is determined before and after the acid rock reaction, and the concentration of the acid is measured by chemical titration. The reaction time is 5 min. According to the formula, the static acid rock reaction rate is calculated, and lg$C$ of reactive acid concentration and lg$J$ of reaction rate are plotted. As shown in Figure 1.

$$\lg J_s = \lg K_s + m_s \lg C_s .$$

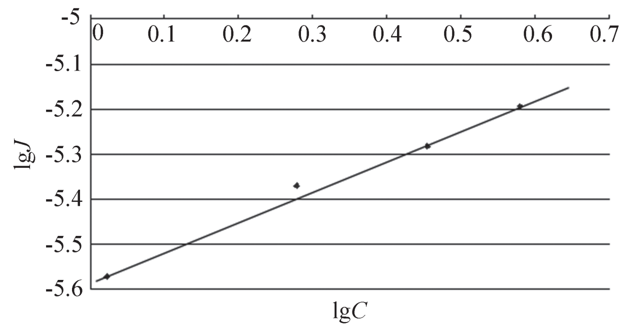

Figure 1
The Equation of Static Acid Rock Reaction Rate

The linear equation: lg$J$ = -5.5869 + 0.67851gC.

Reaction order: m = 0.6785; reaction rate constant: K = 2.5888×10^{-6}.

The dynamic equation of the reaction system is: $J = 2.5888\times10^{-6}C^{0.6785}$.

The acid rock reaction kinetics equation is the acid rock reaction experiment under static condition, and the dynamic system is different, but it can also be seen that the increase of acid concentration and the increase of acid rock reaction rate.

2. DETERMINATION OF ACID-ROCK REACTION KINETIC EQUATION WITH DEEP-PENETRATION AND LOW-DAMAGE ACID

Under the condition of 10 ℃, 800 r/min and 20 ℃, 800 r/min, and therefore, the correct kinetic equation of acid rock reaction can be obtained under this condition.

(a) Deep-penetration and low-damage acid is prepared respectively 16％, 12%, 8％, 4%. At 10 ℃, 8 MPa, the acid rock reaction was carried out in the rotating disk reactor with core, and the core quality is determined before and after reaction. The reaction rate was calculated. lg$C$ of Reactive acid concentration and lg$J$ of Reaction Rate are plotted, getting a straight line. kinetic equation of acid rock surface reaction can be obtained from the slope and intercept of line. As shown in Figure 2.

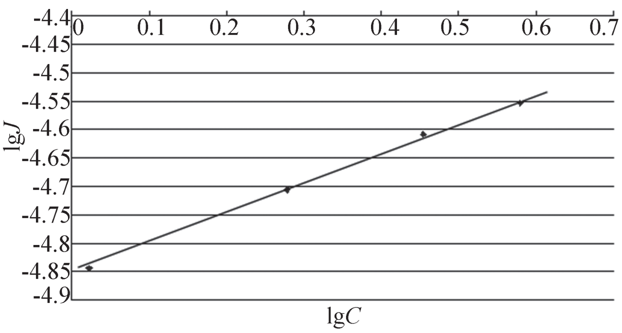

Figure 2
The Dynamic Equation of 10 ℃ Acid Rock Dynamic Reaction Rate

The linear equation: lg$J$ = -4.8470 + 0.5073lg$C$.

Reaction order: m = 0.5073; reaction rate constant: K = 1.4423×10^{-5}.

Dynamic equation of reaction system at 10 ℃: $J = 1.4423\times10^{-5}C^{0.5073}$.

(b) Deep-penetration and low-damage acid is prepared respectively 16％, 12%, 8％, 4%. At 20 ℃, 8 MPa, the acid rock reaction was carried out in the rotating disk reactor with core, and the core quality is determined before and after reaction. The reaction rate was calculated. lg$C$ of Reactive acid concentration and lg$J$ of Reaction Rate are plotted, getting a straight line. kinetic equation of acid rock surface reaction can be obtained from the slope and intercept of line. As shown in Figure 3.

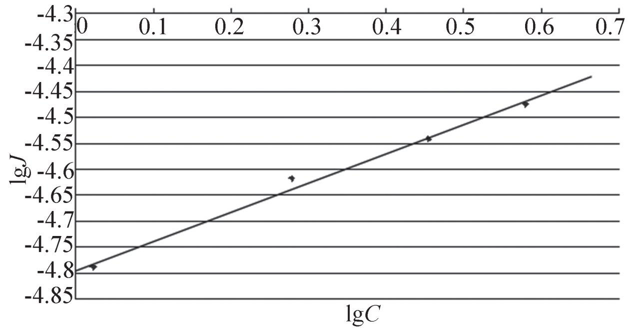

Figure 3
The Dynamic Equation of 20 ℃ Acid Rock Surface Reaction

The linear equation: lg$J$ = -4.8004+0.5684lg$C$.

Reaction order: m = 0.5684; reaction rate constant: K = 1.5845×10^{-5}.

Dynamic equation of reaction system at 20 ℃: $J = 1.5845\times10^{-5}C^{0.5684}$.

3. DETERMINATION OF THE KINETIC EQUATION OF ACID ROCK REACTION UNDER THE CONDITION OF FORMATION

Under the condition of the rotor speed of the general experimental apparatus (rotor speed is less than 1,000 r/min), acid rock reaction is in the stage of H^+ mass transfer control phrase at 65 ℃ and above[4]. Under this experimental condition of measuring rate, system of reaction system is reflected by the rate of the reaction system. Therefore, setting laccolith speed is 500 r/min, acid rock reaction speed is determined at 65 ℃ and deep-penetrating low-damage acid mass fraction of 16%, 12%, 8% and 4%. This can provide more reliable parameters for the current acidification construction. As shown in Figure 4.

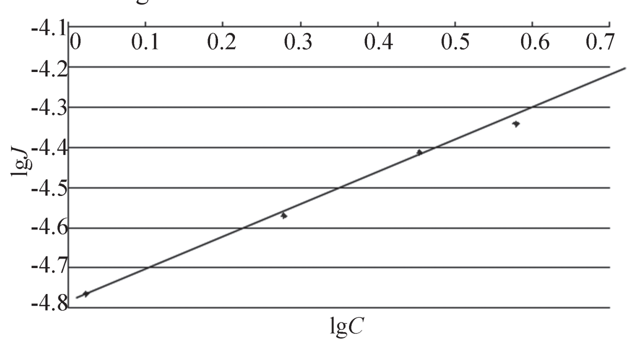

Figure 4
The Kinetic Equation of Acid Rock Reaction at 65 ℃

The linear equation : $\lg J = -4.7501 + 0.6462\lg C$.

Reaction order: $m = 0.6462$; reaction rate constant: $K = 1.7779\times10^{-5}$.

Dynamic equation of reaction system at 65 ℃: $J = 1.7779\times10^{-5}C^{0.6462}$.

The same experimental method is used to determine the rate of acid rock reaction which the temperature was 90 ℃ (The highest formation temperature is 90 ℃) and the rotation speed is 500 r/min, and deep-penetrating low-damage acid mass fractions are respectively 16%, 12%, 8%, 4%. The straight line of kinetic equation of acid rock reaction is obtained by using the kinetic parameters of acid liquid reaction. As shown in Figure 5.

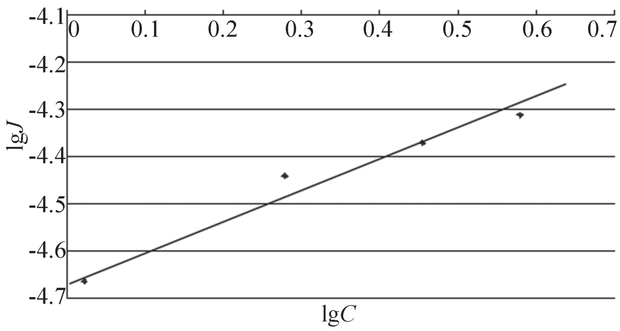

Figure 5
Acid-Rock Reaction Kinetic Equation With Deep-Penetration and Low-Damage Acid at 90 ℃

The linear equation: $\lg J = -4.6785 + 0.6776\lg C$.

Reaction order: $m = 0.6776$; reaction rate constant: $K = 2.0962\times10^{-5}$.

Dynamic equation of reaction system at 90 ℃: $J = 2.0962\times10^{-5}C^{0.6776}$.

At the reservoir temperature of 65 ℃ and 90 ℃, the reaction order of the deep penetration low acid and the reservoir rock mineral reaction are 0.6462 and 0.6776 respectively, which is less than 1, which indicates that the reaction rate is slow and the reaction is not strong. The characteristics of developed acid liquid system with slow speed and deep penetration are further confirmed by the kinetic mechanism.

4. STUDY ON MECHANISM OF DEEP PENETRATION AND LOW DAMAGE MECHANIC-SM OF DEEP-PENET-RATION AND LOW-DAMAGE ACID

The reaction kinetics equation of deep penetration low damage acid is obtained. In order to make a more systematic study of its deep penetration characteristics, the acid rock reaction rate of common acid and deep-penetration low-damage acid is compared with other conditions[5-6].

5. COMPARISON OF REACTION RATE OF COMMON ACID AND DEEP-PENETRATION LOW-DAMAGE ACID AT 65 ℃

Under the same experimental conditions (reaction temperature is 65 ℃ (reaction temperature is 65 ℃, experimental pressure is 8 Mpa, rotor speed of experimental apparatus is 500 r/min). Different concentrations of mud acid (HCl:HF = 3:1), fluoboric acid and multi hydrogen acid and deep-penetration low-damage acid liquid react cores of the same nature. The H^+ concentration is the horizontal coordinate, and the acid rock reaction rate is the vertical coordinate in the acid liquid system. The acid rock reaction rate diagram of the four kinds of acid systems is obtained at 65 ℃. As shown in Figure 6.

Table 1
The Data of Dynamic Acid Rock Reaction Rate With Mud Acid

Initial concentration (H^+) (mol/L)	Final concentration (H^+) (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm^2s)
6.336	2.050	300	0.3	4.286	2.18×10^{-4}
4.765	1.578	300	0.3	3.187	1.62×10^{-4}
3.174	1.442	300	0.3	1.732	8.83×10^{-5}
1.592	0.935	300	0.3	0.657	3.35×10^{-5}
Experimental conditions: T = 65 ℃, P = 80 atm, Core diameter: 2.5 cm					

The linear equation: $\lg J = -4.7123 + 1.3125\lg C$.

Reaction order: $m = 1.3125$; reaction rate constant: $K = 1.9394\times10^{-5}$.

Dynamic equation of reaction system at 65 ℃: $J = 1.9394\times10^{-5}C^{1.3125}$.

Table 2
The Data of Dynamic Acid Rock Reaction Rate With Fluoboric Acid

Initial concentration (H^+) (mol/L)	Final concentration (H^+) (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm^2s)
3.200	1.578	300	0.3	1.622	8.26×10^{-5}
2.400	1.247	300	0.3	1.153	5.88×10^{-5}
1.600	0.779	300	0.3	0.821	4.18×10^{-5}
0.800	0.328	300	0.3	0.472	2.41×10^{-5}
Experimental conditions: T = 65 ℃, P = 80 atm, Core diameter: 2.5 cm					

The linear equation: $\lg J = -4.7341 + 0.9827\lg C$.

Reaction order: $m = 0.9827$; reaction rate constant: $K = 1.8446\times10^{-5}$.

Dynamic equation of reaction system at 65 ℃: $J = 1.8446\times10^{-5}C^{0.9827}$.

Table 3
The Data of Dynamic Acid Rock Reaction Rate With Multi-Hydrogen Acid

Initial concentration (H^+) (mol/L)	Final concentration (H^+) (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm²s)
4.019	2.962	300	0.3	1.0582	5.39×10^{-5}
3.015	2.090	300	0.3	0.9253	4.71×10^{-5}
2.010	1.467	300	0.3	0.5432	2.77×10^{-5}
1.005	0.662	300	0.3	0.3431	1.75×10^{-5}

Experimental conditions: T = 65 ℃, P = 80 atm, Core diameter: 2.5 cm

The linear equation: $\lg J = -4.7584 + 0.6625\lg C$.

Reaction order: $m = 0.6625$; reaction rate constant: $K = 1.7442\times10^{-5}$.

Dynamic equation of reaction system at 65 ℃: $J = 1.7442\times10^{-5}C^{0.6625}$.

Table 4
The Data of Dynamic Acid Rock Reaction Rate With Deep Penetration Low Damage Acid

Order	Initial concentration (mol/L)	Final concentration (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm²s)	lgC	lgJ
1	3.7973	2.9037	300	0.3	0.8936	4.55×10^{-5}	0.5794	-4.3419
2	2.8481	2.0913	300	0.3	0.7568	3.86×10^{-5}	0.4545	-4.4134
3	1.8987	1.3701	300	0.3	0.5286	2.69×10^{-5}	0.2784	-4.5702
4	0.9494	0.6127	300	0.3	0.3367	1.72×10^{-5}	-0.0223	-4.7645

Experimental conditions: T = 65 ℃, P = 80 atm, Core diameter: 2.5 cm

The linear equation: $\lg J = -4.7501 + 0.6462\lg C$.

Reaction order: $m = 0.6462$; reaction rate constant: $K = 1.7779\times10^{-5}$.

Dynamic equation of reaction system at 65 ℃: $J = 1.7779\times10^{-5}C^{0.6462}$.

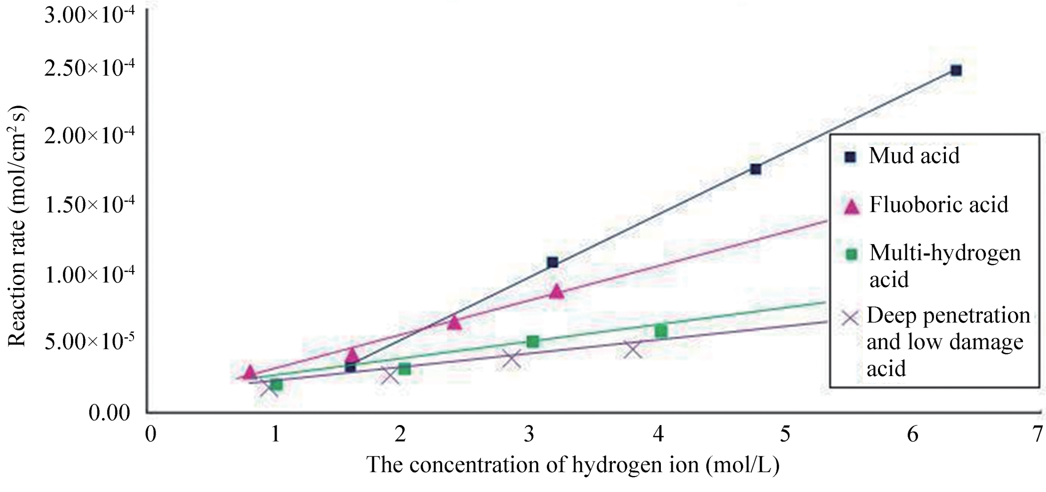

Figure 6
The Comparison of Acid Rock Reaction Rate Between Common Acid and Deep Penetration Low Damage Acid at 65 ℃

The Figure 6 shows that rock reaction order of hydrofluoric acid, fluoroboric acid, multi hydrogen acid and deep-penetration low-damage acid liquid are 1.3125, 1.1702, 0.6625 and 0.6462. The intensity of the acid rock reaction is mainly determined by the m value of the reaction order. When the difference of the reaction order is not big, reaction rate constant K is compared. The reaction order of mud acid is 1.3125, and the reaction order of deep penetrating low damage acid is 0.6462, which is only 1/2. Therefore, deep penetrating low damage acid is the characteristics of moderate reaction, long time and deep penetration.

6. COMPARISON OF REACTION RATE OF COMMON ACID AND DEEP-PENETRATION LOW-DAMAGE ACID AT 90 ℃

Different concentrations of mud acid (HCl:HF = 3:1), fluoboric acid and multi hydrogen acid and deep-penetration low-damage acid liquid react cores of the same nature. The H^+ concentration is the horizontal coordinate, and the acid rock reaction rate is the vertical coordinate in the acid liquid system. The acid rock reaction rate diagram of the four kinds of acid systems is obtained at 65 ℃. As shown in Figure 7.

Table 5
The Data of Dynamic Acid Rock Reaction Rate With Mud Acid

Initial concentration (H^+) (mol/L)	Final concentration (H^+) (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm²s)
6.336	1.475	300	0.3	4.861	2.48×10^{-4}
4.765	1.309	300	0.3	3.456	1.76×10^{-4}
3.174	1.042	300	0.3	2.132	1.09×10^{-4}
1.592	0.940	300	0.3	0.652	3.32×10^{-5}

Experimental conditions: T = 90 ℃, P = 80 atm, Core diameter: 2.5 cm

The linear equation: $\lg J = -4.7861 + 1.5214\lg C$.

Reaction order: m = 1.5214; reaction rate constant: $K = 1.6365\times10^{-5}$.

Dynamic equation of reaction system at 90 ℃: $J = 1.6365\times10^{-5}C^{1.5214}$.

Table 6
The Data of Dynamic Acid Rock Reaction Rate With Fluoboric Acid

Initial concentration (H^+) (mol/L)	Final concentration (H^+) (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm²s)
3.200	1.464	300	0.3	1.736	8.85×10^{-5}
2.400	1.113	300	0.3	1.287	6.56×10^{-5}
1.600	0.772	300	0.3	0.828	4.22×10^{-5}
0.800	0.217	300	0.3	0.583	2.97×10^{-5}

Experimental conditions: T = 90 ℃, P = 80 atm, Core diameter: 2.5 cm

The linear equation: $\lg J = -4.6651 + 1.4229\lg C$.

Reaction order: m = 1.4229; reaction rate constant: $K = 2.1621\times10^{-5}$.

Dynamic equation of reaction system at 90 ℃: $J = 2.1621\times10^{-5}C^{1.4229}$.

Table 7
The Data of Dynamic Acid Rock Reaction Rate With Multi-Hydrogen Acid

Initial concentration (H^+) (mol/L)	Final concentration (H^+) (mol/L)	Reaction time (s)	Acid volume (L)	Concentration difference (mol/L)	Reaction rate (mol/cm²s)
4.019	2.866	300	0.3	1.154	5.39×10^{-5}
3.015	2.003	300	0.3	1.012	4.71×10^{-5}
2.010	1.388	300	0.3	0.621	2.77×10^{-5}
1.005	0.604	300	0.3	0.402	1.75×10^{-5}

Experimental conditions: T = 90 ℃, P = 80 atm, Core diameter: 2.5 cm

The linear equation: $\lg J = -4.7587 + 0.8115\lg C$.

Reaction order: m = 0.8115; reaction rate constant: $K = 1.7429\times10^{-5}$.

Dynamic equation of reaction system at 90 ℃: $J = 1.7429\times10^{-5}C^{0.8115}$.

Table 8
The Data of Dynamic Acid Rock Reaction Rate With Deep Penetration Low Damage Acid

Order	Initial concentration (mol/L)	Final concentration (mol/L)	Reaction time (s)	Acid volume (L)	Concent-ration difference (mol/L)	Reaction rate (mol/cm^2s)	lg*C*	lg*J*
1	3.7973	2.8387	300	0.3	0.9586	4.88×10^{-5}	0.5794	-4.3116
2	2.8481	2.0123	300	0.3	0.8358	4.26×10^{-5}	0.4545	-4.3706
3	1.8987	1.1862	300	0.3	0.7125	3.63×10^{-5}	0.2784	-4.4401
4	0.9494	0.5236	300	0.3	0.4258	2.17×10^{-5}	0.0223	-4.6635

Experimental conditions: T = 90 ℃, P = 80 atm, Core diameter: 2.5 cm

The linear equation: $\lg J = -4.6785 + 0.6776\lg C$.

Reaction order: m = 0.6776; reaction rate constant: $K = 2.0962\times10^{-5}$.

Dynamic equation of reaction system at 90 ℃: $J = 2.0962\times10^{-5}C^{0.6776}$.

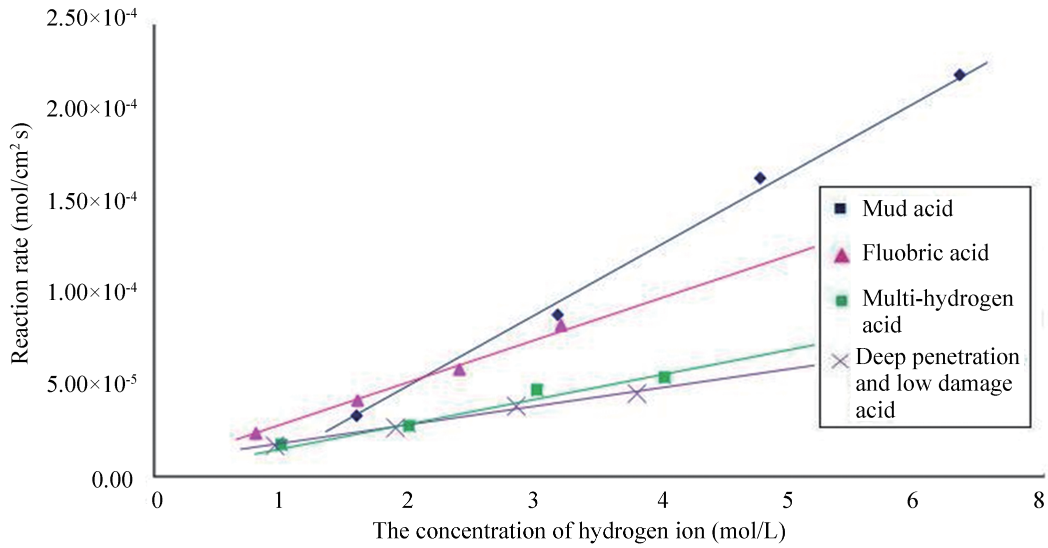

Figure 7
The Comparison of Acid Rock Reaction Rate Between Common Acid and Deep Penetration Low Damage Acid at 90 ℃

The Figure 7 shows that rock reaction order of hydrofluoric acid, fluoroboric acid, multi hydrogen acid and deep-penetration low-damage acid liquid are 1.5214, 1.4229, 0.8115 and 0.6776. The reaction order of mud acid is more 2 times than deep penetration low damage acid. The reaction of deep penetration low damage acid and rocks is mild. Even the rate of acid rock reaction is not increased with the change of total concentrationat a very high formation temperature[7]. The control of H^+ activity is outstanding which has the effect of slowing down the rate of acid rock reaction.

CONCLUSION

(a) After considering the factors such as flow rate of acid and temperature and so on, the critical point that acid rock reaction is controlled mass transfer rate of H^+ and Surface reaction rate is determined, acid-rock reaction kinetic equation with deep-penetration and low-damage acid is determined,

(b) By comparing the K values and m values in the kinetic equation of acid rock reaction, it can be seen that the reaction order of deep penetrating low damage acid is the lowest and only half of the mud acid. Even the rate of acid rock reaction is not increased with the change of total concentration at a very high formation temperature. The control of H^+ activity is outstanding which has the effect of slowing down the rate of acid rock reaction. Acid liquor can be reacted with rocks for a long time, increased and magnified acidic etching hole and improved the effect of production and injection of acidification.

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