

# The Research of JA Composite Acidizing Plugging Removal System: Formulation Optimization and Performance Evaluation

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According to the abnormal pressure and poor water absorption of the JA reservoir, JA complex acidizing plugging removal system was proposed to improve oil production. The main acid of JA composite acid system was screened by acid sensitivity evaluation experiments. According to the corrosion evaluation experiment, the optimal concentration of HCL, HF and organic mixed acid (mixed by organic acid A and B in 1:1) in JA composite acid system is 15%, 3 % and 10%, respectively. In order to ensure the compatibility of JA composite acid, both preflush and overflush acid were used the mixed solution of 15% HCL and 3% HF. The evaluation of corrosion resistance indicated that the corrosion rate of JA composite acid could be reduced from 11.92 to 1.92 g/(m<sup>2</sup>·h) when the corrosion inhibitor H was loaded at the concentration of 1%. While 1% ferric ion stabilizer (JYS-1) was added, the stabilization efficiency of JA composite acid could reach 97.20%. The optimal formulation of JA composite acid is 15%HCL + 3%HF + 10% organic mixed acid + 1% corrosion inhibitor H + 1% JYS-1.

## 1. Introduction

JA oil field is a large ultra-low permeability oilfield. The average permeability of Chang 6 reservoir is  $1.81 \times 10^{-3} \mu\text{m}^2$ . The reservoir pressure and single well production is low. Especially after water occurrence, the oil production index dropped sharply. Therefore, effective measures need to be adopted to keep the well's productivity. Due to the abnormally low pressure of Chang 6 reservoir, the driving pressure gradient is difficult to improve. However, the cost for repeating fracturing is expensive. The acidification plugging removal technique is a cheap and effective method to improve the production (Li et al., 2007; Chen et al., 2007). In this paper, the compound acidification system which is suitable to Chang 6 reservoir was investigated. In addition, the suitable additives were also screened to inhibition the corrosion rate and improve the effective distance of compound acid. It could be provided an effective technology to remove plugging and improve the water-flooding effect of Chang 6 reservoir.

## 2. Analysis of formation blockage in Chang 6 reservoir

The factors that cause reservoir blockage are various. The major potential factors of Chang 6 reservoir can be summarized as follows: (1) Acid sensitivity, A large amount of chlorite in Chang 6 reservoir which has acid sensitivity will be a potential damage factor to the reservoir. (2) Jamin and water-blocking effect caused by external fluids may be another factor which results in formation damage. (3) Formation scaling. Due to the incompatibility of formation water and injection water, the scaling will be produced by the mixing of two fluids, and consequently the formation blockage occurs; (4) The organic deposits which caused by the incompatibility of Injection water with rocks and crude oil and the pressure drop during reservoir development will also result in formation damage.

### 3. The experimental method

#### 3.1 The experimental materials

Hydrochloric acid (HCL), Hydrofluoric acid (HF), Phosphoric acid, Organic acid A, Organic acid B, Organic acid C, Formaldehyde, Urotropine, Iodide, Toluene, Light petroleum, Ethanol, analytical reagent; Corrosion inhibitor H, Corrosion inhibitor X, Industrial grade; ferric ion stabilizer JYS-1, JYS-2, Laboratory self-made; JPU-1, Industrial grade.

The core samples used in this paper are all from Chang 6 reservoir. Simulate formation water is prepared for the experiments, and the ionic components are showed in Table 1.

Table 1: the ion concentration in formation water

Total salinity (mg/L)	pH	Ion concentration (mg/L)						Water type
		K <sup>+</sup> /Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	
78430	6	20684	7977	909	48130	184	544	CaCl <sub>2</sub>

#### 3.2 Experimental Methods

##### (1) Physical simulation experiment

The core flow experiments are conducted to evaluate the acid sensitivity and acidification effect. The variation of permeability is used as the evaluation index, and the specific steps are as follows:

(a) After saturating with formation water, the initial permeability of core ( $K_i$ ) is determined by injecting simulation formation water. The head face injected the formation water is defined as the front of core.

(b) 1.0 PV of acid solution is injected into the core from the reverse side. After that, the core holding unit is sealed and set 4 hours.

(c) The formation water is injected into the core from the front for removing the residual acid, and the permeability of core ( $K_{ia}$ ) is measured by continuous injecting the formation water.

Acid-sensitivity index is used to evaluate acid sensitivity damage, which is calculated as follows (National energy administration of the People's Republic of China; National energy administration of the People's Republic of China):  $I_a = \frac{K_i - K_{ia}}{K_i} \times 100\%$ .

Where  $K_i$  is the initial permeability of core in mD, and  $K_{ia}$  is the permeability after acidification in mD.  $I_a$  is the acid-sensitivity index. Acid sensitivity evaluation index are shown in Table 2.

Note that the experiment are conducted at 61°C. 5.0PV of pre-flush acid solution should be injected into the core after measuring the initial permeability. Other experimental procedures are the same as above.

Table 2: Acid sensitivity evaluation index

Acid sensitivity	Acid sensitivity index	Acid sensitivity	Acid sensitivity index
None	≤0.05	Medium	0.31 ~ 0.70
Weak	0.06 ~ 0.30	Strong	> 0.70

##### (2) Corrosion rate test

The dry core powder ( $m_0=5.0g$ ) was added into the acid solution (50ml) and placed in 61°C. After reacting a certain period of time, the mixture was get out and filtered. The residual solid was flushed by distilled water until the pH value of filtrate was 7. After that, the residual powder was dried at 105°C to constant weight. And its weight was measured and recorded as  $m_1$ . The corrosion rate of acid solution can be calculated as follow (National energy administration of the People's Republic of China):  $C = (m_0 - m_1)/m_0 \times 100\%$ .

##### (3) Corrosion inhibition test

The length, width, thickness and hole diameter of the N-80 stainless steel hanger was measured and calculated the surface area. The hanger was flushed by petroleum ether and then steeped 1min in ethyl alcohol. After blowing dry in cold air, the hanger was placed in drying oven for 20 min and weighted. The hanger which had been weighted was bathed into 250ml acid solution for 4h. The reaction temperature kept constant at 61°C. After that, the hanger was cleaned, dried and weighted like step two. The average corrosion rate and corrosion inhibition rate are calculated as follow (National energy administration of the People's Republic of China):  $V_i = 10^6 \times \Delta m_i / (A_i \times \Delta t_i)$ ,  $\eta = (V_0 - V_i) / V_0 \times 100\%$ . Where  $V_i$  is corrosion rate, g/(m<sup>2</sup>·h);  $\Delta m_i$  is mass loss, g;  $A_i$  is specimen surface area, mm<sup>2</sup>;  $\Delta t_i$  is reaction time interval, h;  $\eta$  is corrosion inhibition

rate, %;  $V_0$  is the average corrosion rate without corrosion inhibitor in acid,  $g/(m^2 \cdot h)$ ;  $V_i$  is the average corrosion rate which added corrosion inhibitor in acid,  $g/(m^2 \cdot h)$ .

#### 2.2.4 Ferric ion stability efficiency test

The core powder was dissolved in 15% HCL solution. The residual mixture was filtered and prepared as blank sample. Four blank samples were prepared, and three of them were added into 1% of JYS-1, JYS-2 and JPU-1 solution. All four samples were set them at 61°C for 4 hour. Excess calcium carbonate was added into the mixture and reacted fully. The residual mixture was centrifuged 5 min and extracted the supernatant. The ferric iron concentration in the supernatant was measured by atomic absorption spectrometer. The ferric ion stability efficiency was calculated as follow (National energy administration of the People's Republic of China):  $A = (C_0 - C_1)/C_0 \times 100\%$ .

Where A is ferric iron stability efficiency;  $C_0$  is ferric iron concentration in blank sample;  $C_1$  is ferric iron concentration in the samples which were added three kinds of ferric ion stabilizers respectively.

## 4. Results and discussion

### 4.1 Formula Optimization of JA composite acid

#### (1) Screening of JA complex acid

The sensitivity experiments of many kinds of acid were conducted, and the results are shown in Table 3. It can be seen that the Chang 6 oil reservoir in JA oilfield has strong acid sensitivity to some inorganic acids (such as  $H_3PO_4$ ) and organic acids (such as organic acid C). However, Organic mixed acid (organic A+B) and mud acid was observed no acid sensitivity. Therefore, the acid solution for the acidification of Chang-6 oil reservoir in JA oilfield needs strong pertinence, and the mixed acid of mud acid and organic acid A and B could be selected.

Table 3: Experimental data of acid sensitivity

Acid type	Permeability, mD		$I_a$	acid sensitivity
	Behind acidification	After acidification		
15%HCL	0.66	0.58	0.12	weak
15%HCL+3%HF	0.06	0.059	0.02	none
15% $H_3PO_4$	0.011	0.0011	0.9	strong
organic acid A:B=10%:20%	0.29	0.29	0	none
15% organic acid C	0.044	0.0065	0.85	strong

#### (2) Hydrochloric acid concentration in JA composite acid

The corrosion rate in different concentrations of hydrochloric acid were investigated at 61°C. The experimental results were shown in Table 4. When HCL concentration is relatively small (<8%), the corrosion substantially unchanged with increasing HCL concentration. The corrosion rate increased gradually with the increase of HCL concentration at the range of 10 to 14%. When the concentration of HCL exceeded 15%, the corrosion rate decreased with the increasing HCL concentration. Therefore, the preferred concentration of HCL was 15% in consideration of the losses generated in field application.

Table 4: Solution ratio and erosion rate of hydrochloric acid in different time

X% HCL	6	8	10	12	14	16	20
corrosion rate, %	7.68	7.7	7.78	7.82	7.84	7.72	7.68

#### (3) Hydrofluoric acid concentration in JA composite acid

When HCL concentration was fixed at 15%, the corrosion rate was studied for different concentrations of HF. As shown in Table 5, the concentration of HF had great influence on the corrosion rate of mud acid. The corrosion rate increased with the increase of HF concentration. When HF was loaded at the concentration of 3%, the corrosion rate decreased in growth and reach to 32.6%. According to the result, the optimal concentration was 3%.

Table 5: Corrosion rate and corrosion speed of HF in different concentration

15%HCL+X%HF	0.5	1.0	1.5	2.0	2.5	3.0
corrosion rate, %	12.08	17.34	22.7	26.34	30.78	32.60

#### (4) Organic mixed acid concentration in JA composite acid

When HCL concentration was loaded at 15%, the corrosion rate was investigated for different concentrations of organic mixed acid (organic acid A: B=1: 1). As shown in Table 6, the corrosion rate first increased and then decreased with increasing the concentration of organic mixed acid. Compared with the corrosion of 15% HCL (Table 5), the corrosion rate decreased when added different concentrations of organic mixed acid. This observation is because the speed of acid-rock reaction is retarded by the low consumption of organic mixed acid, and consequently the effective distance of acid solution increases (Sridhar, 2016; Ye et al., 2002). In addition, the multivalent metal ions produced by acid-rock reaction such as  $Fe^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Al^{3+}$  can be complexed with organic acid ions, which will prevent the second precipitation of multivalent medallions (Boussa and Bencherif, 2003; Wen et al., 2015). The optimum concentration of organic mixed acid was 10%. As shown in Table 7, when 10% organic mixed acid was added in mud acid, the corrosion rate also decreased. This is similar with the result in Table 5.

Table 6: Corrosion rate and corrosion speed of in organic acid in different time

15%HCL+X%(organic acid A+B)	1	3	5	10
corrosion rate, %	7.36	7.62	7.54	7.10

Table 7: Corrosion rate and corrosion speed of two acid solutions in different times

Time, h		2	6	10
15%HCL+3%HF	corrosion rate, %	25.93	25.93	29.42
15%HCL+3%HF+10%organic mixed acid	corrosion rate, %	22.38	22.38	25.23

#### (5) Corrosion inhibitor

The corrosion inhibition rate of different types of corrosion inhibitors for JA complex acid system was investigated, and the experimental results were shown in Table 8. It can be seen that the acid-rock reaction speed is very rapidly when corrosion inhibitor is free. The average corrosion speed can reach 122.26  $g/(m^2 \cdot h)$ . Comparison of the corrosion inhibition rate of five inhibitors, the corrosion inhibitor-H and corrosion inhibitor-X has good inhibition effect. The corrosion inhibition rate is more than 98%. However, the corrosion inhibitor-X was observed to generate precipitate. Therefore, the inhibitor-H is chosen as inhibitor for JA composite acid and its concentration is 1%.

Table 8: The corrosion speed and corrosion inhibition Rate with different corrosion inhibitors

Corrosion inhibitor	Average corrosion speed, $10^{-3}g/(m^2 \cdot h)$	Corrosion inhibition Rate, %
JA Complex acid system	122.26	—
2% Formaldehyde	17.64	85.57
2% Urotropine	12.59	89.70
2%Formaldehyde+0.5%Iodide	5.92	95.16
1% Corrosion Inhibitor-H	1.92	98.43
1% Corrosion Inhibitor-X	1.16	99.05

Table 9: ferric ion stabilizer evaluation

Ferric Ion Stabilizer	JYS-1	JYS-2	JPU-1
Ferric Ion Stability Efficiency, %	97.20	95.33	87.24

#### (6) Ferric Ion Stabilizer

The Stability Efficiency of three types of ferric ion stabilizers (JYS-1, JYS-2 and JPU-1) were investigated at 61°C. As shown in Table 9, JSY-1 has the best effect on the ferric ion stability compared with other two stabilizers, and its efficiency is approximately 97% while 1% JSY-1 is loaded. It can meet for the acidizing reconstruction requirement of Chang 6 reservoir in JA oilfield.

## 4.2 Performance evaluation

### (1) Compatibility

According to the study above, the formulation of JA complex acid is 15%HCL+3%HF+10% Organic mixed acid+1% Inhibitor-H+1%JYS-1. Due to the high corrosion rate and considering the compatibility of the JA composite acid, the formula of pre-flush acid and over-flush acid is 15%HCL+3%HF+1% inhibitor-H+1% JYS-

1. According to the formula, three kinds of acid solutions were prepared, all of which had no precipitate or floccule formed after mixing with the crude oil.

(2) Acidizing effect

The effect of acid plugging removal was studied by physical simulation experiment. In these experiments, the long core is composed of three cores in series. The acidizing curves of mud acid (15%HCL+3%HF) and JA composite acid system were shown in Figures 1 and 2 respectively. As shown in Figure 2, After acidizing by JA composite acid, the permeability of the first section is 10.2 times higher than that before acidification. The permeability in the second and third sections is 1.77 and 1.28 times compared to that before acidification. The acidification of mud acid mainly acts on the first core. After acidification, the permeability of the first core is 1.75 times as high as that before acidification. This indicates that JA compound acid has a good acidification effect on Chang 6 reservoir, and the effective distance is long.

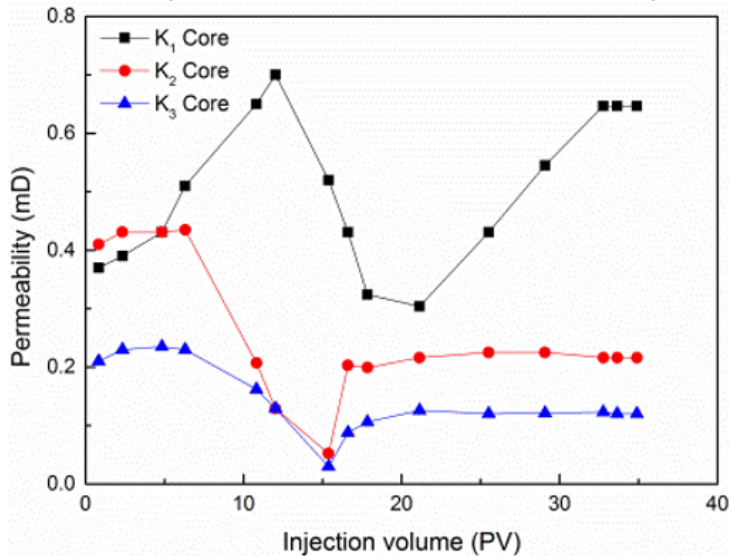


Figure 1: Acidification effect of mud acid

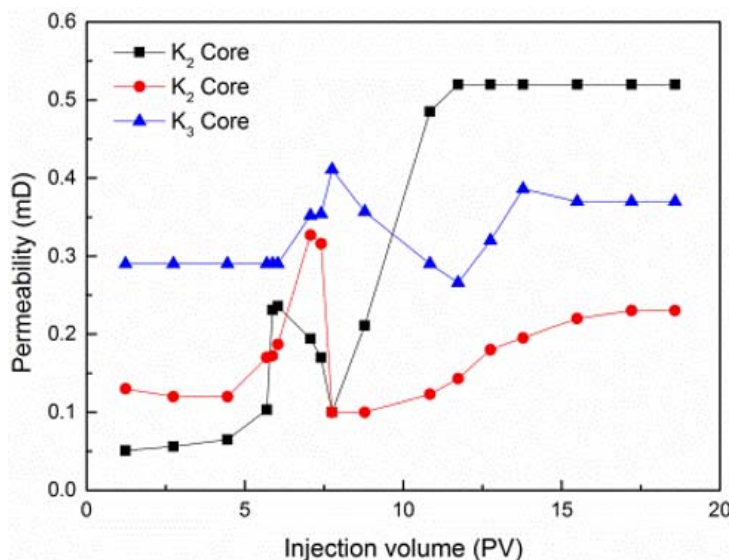


Figure 2: Acidification effect of JA composite acid

## 5. Conclusion

The preliminary optimal formula of JA compound acid is: 15%HCL+3%HF+10%organic mixed acid. Considering the compatibility, the formula of pre-flush acid is: 15%HCL+3%HF as same as over-flush acid. The corrosion rate of the acid solution was reduced from 11.19 to 1.92 g/ (m<sup>2</sup>·h) with the introduction of 1%

inhibitor -H, and the corrosion inhibition rate was 98.43%. When the ferric ion stabilizer JYS-1 is added to 1%, the stability efficiency is above 95%. The optimum formula of JA compound acidification is as follows: 15%HCL+3%HF+10%organic mixed acid+1%corrosion inhibitor-H+1%JYS-1. JA compound acid, pre-acid and post-acid have good compatibility with crude oil. The acid system has good plugging removal effect and penetrability, and the permeability of three cores in the long core experiment increases by 10.77, 1.77 and 1.28 times, respectively.

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