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Study and Application of a New Complex Plug Removal System

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Abstract

Aiming at solving small effective acid reaction range and causing second damage in the acidizing in low permeability reservoirs, a new kind of deep penetration and little damage complex plug removal system was developed through laboratory research, which consists of an organic acid, a phosphoric acid, an ammonium organic acid, an ammonium fluoride and a strong oxidizer. The properties were evaluated and the results indicate that it has advantages of proper dissolving capacity to rock with dissolving ratio of 38.9%, little corrosion to the pipeline of equipment with corrosion rate of 2.9 $g/m^2 \cdot h^{-1}$, low interfacial tension, anti-acid-sludge, and ability to stabilize ferric ion. The plugging in deep formations can be removed with low damage to rock skeleton, which the damage rate is less than 20%. It has been applied in 19 wells with success ratio of 100% and long term of validity, average validity is more than 200 days. The oil production and water injection have been increased obviously.

Keywords: Acidization; Second damage; Complex plug removal system; Deep penetration; Rock skeleton

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INTRODUCTION

Acidizing plug-removal is an important measure to improve the development effect of low permeability reservoir, a lot of researches have been made on the improvement of acidification technology[1-3]. However, for special low-permeability reservoirs with small pore throat, multi-layer system, thin reservoir, serious heterogeneity in the layer, large differences in longitudinal properties, high feldspar content, co-existence of blockage by organic and inorganic matters[4], due to restrictions of their own conditions, certain problems still existed in acid injection, limited acid absorption capacity in acidification layers, fast response of acid rock, poor repeated acidification effects, difficulties in removing organic blocking, and potential secondary damage to reservoir and so on. Therefore, through a large number of laboratory experiments, a new complex plug removal system major composted of organic acids, phosphoric acid, organic ammonium, ammonium fluoride and strong oxidants is introduced.

1. EXPERIMENTAL RESEARCH

1.1 Main Experimental Instruments and Materials

Main experimental instruments: CC-10-S high-temperature and high-pressure dynamic corrosion instrument (Canada), JYW-200A automatic interfacial tensiometer (Chengde Dajia Instrument Co., Ltd.), Short core flow tester (laboratory-made), long core flow tester (USA), rock triaxial tester (Changchun Rising Sun Testing instrument Co., Ltd.).

Main materials: hydrochloric acid, hydrofluoric acid, sulfuric acid, boric acid, fluoboric acid, nitric acid, phosphoric acid, formic acid, acetic acid, ammonia triacetic acid, chloroacetic acid, citric acid, ammonium fluoride, organic acid salt, and etc. all are analytically or chemically pure reagents, YNW-1 stabilizer (laboratory-made), YSH-1 corrosion inhibitor (laboratory-made), YG-1303-1 ferric ion stabilizer (China University of Petroleum Yuguang Technology Co., Ltd.), surfactant (Guangzhou Achchem Technology Co., Ltd.), synergists (China University of Petroleum Yuguang Technology Co., Ltd.), chlorine dioxide solution (Hebei Cangzhou Zhengda Environmental Protection Technology Co., Ltd.), clay minerals and cores used in experiments are all provided by CL Oilfield.

1.2 Formula of the System

Deep-penetration and low-damage composite plug removal system should be featured by large effective radius and least damage to reservoir[5-6]. In this paper, acidizing fluids selected have been compounded with different additives, after core tests and formation compatibility tests, the formula of the new complex plug removal system is determined as follows (all proportions are mass percentage):

(1) Pretreatment solution: 3% of NH_4Cl solution; (2) pad fluid: 10% of hydrochloric acid + acid additives, (3) main solution: 25% of complex plug removal system (8% of organic acid and organic acid salt + 8% of phosphoric acid + 5% of ammonium fluoride + 4% of strong oxidizer) + acid additives, (4) Over-flush fluid: 3% of NH_4Cl solution.

2. RESULTS AND DISCUSSION

2.1 Erosion Performance

The core is crushed, sieved and dried obtained from C_1-C_2 and C_3-C_4 at 2605.77-2680.61 m of Well C83-2 in CL Oilfield, under the condition that the core/plug-removing agent is 0.05 g/mL, the plug removal agent is placed in a sealed container. After thorough reaction under 95 ℃ and 60 r/min, the residual acid liquid solid is filtered out with dried and weighed quantitative filter paper, then the core erosion rate was obtained; the result is shown in Table 1. It can be known that the erosion rate of 25% of the new complex plug removal system to natural core is 38.9%, which is less than conventional earth acid but higher than YFP low damage acid and FAC deep penetrating acid currently used in the oilfield, it is indicated that this system has a strong capacity in treating formation and improving or restoring formation permeability.

2.2 Corrosion Performance

Corrosion performance is tested with the high temperature and high pressure dynamic corrosion instrument on N80 steel piece. The surface to volume ratio between the plug-removing agent and the steel piece is 15 mL/cm^2. In the experiment, the rotation speed is 60 r/min, the temperature is 120 ℃, the pressure is 15 MPa, and the reaction time is 4 hours. The evaluation target should be in compliance with SY5405-1996《Performance Test Method and Evaluation Indicator of Acidification Inhibitor Used in Acidizing Operation》, and the experiment result is shown in Table 1. It can be known that the corrosion rate of the new complex plug removal system is the minimum under high temperature, high pressure and dynamic conditions. When the temperature is 120 ℃ and the pressure is 15 MPa, the corrosion rate is only 2.9 g/m^2·h^{-1}. Using this system to remove plug will cause least corrosion to the pipeline.

Table 1
Comparison of Basic Performance of Plug-Removing Agent

Plug-removing agent	Erosion rate (%)	Corrosion rate/ (g/m^2·h^{-1})	Surface tension/ (mN/m)	Interfacial tension/ (mN/m)	Acid residue (g)
Conventional earth acid	49.9	66.6	53.2	12.4	0.7
25% YFP (low damage acid)	21.5	33.3	36.4	5.7	0.5
25% FAC (deep penetration acid)	25.2	30.0	35.1	5.4	0.5
25% new complex plug removal system	38.9	2.9	20.9	1.7	0.1

Note: the value of “corrosion rate” is the average of values obtained from experiments on 3 N80 steel pieces.

2.3 Surface (Interfacial) Tension

In the experiments, JYW-200A automatic interfacial tensimeter is used, and the experiment temperature is 25 ℃. The experiment result is shown in Table 1. It can be seen from Table 1 that new complex plug removal system has good surface activity, and the surface tension is 20.9 mN/m while the interfacial tension is 1.7 mN/m, which can effectively reduce the surface (interfacial) tension of the acid.

2.4 Anti-Acid-Residue Performance

The conventional earth acid, YFP low-damage acid, FAC deep-penetration acid, and the new complex plug removal system is respectively mixed with dehydrated crude oil (with a paraffin content of 20% and a gel content of 20%) from Well 85-3 at 1:1 ratio (20 mL plug removing agent: 20 mL crude oil). After 2 h of reaction under 95 ℃, the solution is filtered with a sieve and cleaned with organic solvent, then the acid residue is dried and weighed, the result is shown in Table 1. Compared with conventional earth acid, YFP low-damage acid and FAC deep penetration acid, the acid residue generated from the reaction between the new complex plug removal system with crude oil from Well C85-3 is greatly reduced, which indicates that the new complex plug removal system can prevent the formation of acid residue due to the reaction between acidizing fluid and crude oil.

2.5 Performance of Stabilizing Ferrous Ion

Ferric sulfate is added in 100 mL of 25% new complex plug removal system till the Fe^{3+} concentration is 800 mg/L. Then 100g quartz sand pre-treated with 15% HCl is added, After that, the new complex plug removal system is put into 90 °C constant temperature water bath. After 24 h, no precipitation can be seen generated from the new complex plug removal system, which indicates that Fe^{3+} can remain stable in the new complex plug removal system and ferric hydroxide precipitation is not prone to occur, thus it is conducive to preventing secondary sedimentation generated from acidification.

2.6 Plug-Removing Performance

H^+ existed in the new complex plug removal system and HF gradually released described can corrode lime composition, ferrous compounds, siliceous, and argillaceous obstruction and release inorganic plug. The strong oxidant in the system is water solution containing stable chlorine dioxide, which can release strong oxidizing atomic-state free radicals ClO_2^- and ClO_2^- when the pH is below 2.5, relying on its strong oxidizing ability, heavy hydrocarbons can be oxidized, degraded and dissolved. Polymers, guar gum and other polymers can be oxidized and degraded, thus releasing the organic plug. At the same time, it has a strong bactericidal capacity and can kill the sulfate-reducing bacteria and clear the bacteria metabolites.

In plug-removing simulation experiment, the experiment temperature is determined according to the actual situation of reservoir in C83 block. According to acid injection procedure of acidification operation, the pre-pad fluid, pre-pad acid, main plug-removing fluid and over flush fluid was injected successively. Core plug-removing effect was determined according to the ratio between permeability when injecting flush fluid and pre-pad fluid (K_4/K_1). The core is taken from Well C83-2, the temperature is 90 ℃, the experiment flow speed is 5 mL/min, the core diameter is 25 mm and the core length is 50~70 mm. The experiment result is shown in Table 2.

Table 2
Short Core Plug-Removing Flow Simulation Experiment Result (90 ℃)

Core No.	Main plug-removing fluid	Core permeability/(10^{-3} μm^2) Pre-pad fluid (K_1)	Pre-pad acid (K_2)	Main fluid (K_3)	Displacing liquid (K_4)	Permeability ratio (K_4/ K_1)
1	12% HCl + 3% HF	4.24	5.35	14.78	11.72	2.76
2	25% YFP (low-damage cid)	5.31	6.42	17.14	17.89	3.37
3	25% FAC (deep penetration acid)	4.94	5.83	15.72	16.19	3.28
4	25% new complex plug removal system	3.41	4.46	13.25	14.16	4.15

It can be known from Table 2 that all of four plug-removing systems have a good plug-removing effect, mainly because that the core is short and the secondary sediment generated is taken away from the core by the fluid. However, the effect of the four plug-removing systems in improving the core permeability (K_4/K_1) varies widely, and the new complex plug removal system is significantly better than YFP low-damage acid, FAC deep penetration acid and conventional earth acid. Through analysis, it is believed that the reasons are as follows, after the acid corrodes sandstone core and thus increases the penetration substantially, secondary damage will be caused to the core, which results in the reduction of permeability. At the same time, in the new complex plug removal system, phosphoric acid/hydrofluoric acid reacts with the carbonate rock, generating fluorine calcium carbonate (phosphate of lime), and soon a layer of covering membrane forms on the surface of the carbonatite, which can prevent the carbonatite from continuing to dissolve, thus reducing the generation of CaF_2 precipitate. The organic acids and organic acid salt in the system form a buffer system, which maintains the pH at a lower value (pH < 2) and also has good complication properties and can chelate multivalent metal ions (eg. Fe^{3+}, Al^{3+}), thus it can reduce concentration of Fe^{3+} and Al^{3+} in the acid residue and avoid $Fe(OH)_3$ and $Al(OH)_3$ and other precipitations, so it can reduce the secondary damage to reservoir.

2.7 Deep-Penetration Performance

Three long cores (linked in series) are used to conduct plug-removing flow simulation experiment, and their plug-removing effects are compared with that of conventional earth acid, YFP low-damage acid, and FAC deep-penetration acid commonly used in domestic oilfields, as is shown in Table 3.

Table 3
Long Core Plug-Removing Flow Simulation Experiment Result (90 ℃)

Core No.	Main plug-removing fluid	Core permeability /(10^{-3} μm^2) Pre-pad liquid (K_1)	Pre-pad acid (K_2)	Main fluid (K_3)	Displacing liquid (K_4)	Permeability ratio (K_4/K_1)
1	12%HCl＋3%HF	11.28	13.21	12.28	10.21	0.91
2		10.56	11.24	10.14	8.78	0.83
3		10.32	10.96	9.56	6.77	0.66

To be continued

Continued

Core No.	Main plug-removing fluid	Core permeability /(10^{-3} μm^2)				Permeability ratio (K_4/K_1)
		Pre-pad liquid (K_1)	Pre-pad acid (K_2)	Main fluid (K_3)	Displacing liquid (K_4)	
4	25%YFP (low-damage acid)	12.71	16.85	28.84	29.31	2.31
5		16.82	18.83	30.14	31.22	1.86
6		23.13	26.12	30.45	32.44	1.40
7	25%FAC (deep penetration acid)	19.26	39.28	84.54	87.23	4.53
8		44.12	47.69	100.32	104.15	2.36
9		43.3	54.35	61.21	67.92	1.57
10	25% new complex plug removal system	9.48	12.16	32.96	59.62	6.29
11		4.46	4.96	14.25	15.48	3.47
12		2.72	3.02	7.08	7.76	2.85

It can be known from Table 3 that when the main plug-removing agent injected is conventional earth acid, compared with the original permeability, the permeability of the three cores after plug-removing is reduced rather than increased. At the same time, the core permeability increases after plug-removing with other three plug-removing systems, among which the new complex plug removal system achieves the best effect. The permeability of the first core increases by 5.29 times, while that of the second and the third core increases by 2.47 times and 1.85 times respectively. Through analysis, it is believed the causes are as follows, due to secondary damage after acidification of conventional earth acid, the permeability is reduced. Meanwhile, as organic acid and phosphoric acid in the new complex plug removal system are polybasic acid with a small ionization constant, according to chemical kinetics, which belongs to secondary reaction. Therefore, due to the low concentration of active acid concentration, the acid-rock reaction rate is also relatively low. Organic acids and organic acid salt, as well as phosphoric acid and its acidification product, dihydric phosphate salt, can form a buffer solution, making the acidizing fluid releasing H^+ gradually in the acid-rock reaction process, thus it is ensured that the plug-removing fluid still has a certain concentration of active HF after reaching the deep part of the formation and can continue to react with the formation, with deep penetration to the core dissolution, conducive to plug-removing in deep layers.

2.8 Low-Damage Performance

The erosion of acidizing fluid to blocking matters and minerals in the reservoir will increase the permeability of the reservoir and improve the injecting capacity, but it will also reduce the intensity of rock. The excessive erosion of the rock will destroy the formation skeleton, or even result in the later sanding and pore-collapse[7]. After the long core plug-removing experiments, compression strength of rock is measured with different hole sections, at the same time the compression strength is measured before plug-removing of cores from the same hole section, using this method to evaluate the degree of impact of the plug-removing fluid on rock skeleton and calculate the rate of damage, the result is as shown in Table 4.

Table 4
Compression Strength of Rock

Core No.	Compression strength (MPa)		Degree of damage(%)	Remarks
	Before plug-removing	After plug-removing		
C83-2-1	116.5	57.2	50.9	12%HCl＋3%HF
C83-2-2	114.3	59.4	48.0	
C83-2-3	117.2	64.8	44.7	
C83-2-4	109.2	74.1	32.1	25%YFP (low-damage acid)
C83-2-5	106.8	73.2	31.5	
C83-2-6	103.1	72.1	30.1	
C83-2-7	105.7	65.9	37.6	25%FAC (deep penetration acid)
C83-2-8	99.5	63.9	35.8	
C83-2-9	97.6	63.2	35.2	
C83-2-10	113.8	94.8	16.7	25% new complex plug removal system
C83-2-11	118.2	98.7	16.5	
C83-2-12	114.7	99.4	13.3	

Note: the confining pressure in experiments is 12 MPa.

It can be known from Table 4 that the core compression strength changes before and after plug-removing, which indicates that the core is damaged to different degrees after the plug-removing fluid acts on the core, that is mainly because the action of acidizing liquid changes the structure of core. Different plug-removing system caused different degrees of damage. Conventional earth acid causes the largest degree of damage, which is above 40%, followed by FAC deep-penetration acid and YFP low damage-acid. The new complex plug removal system causes the lowest degree of damage. After long core plug-removing, the degree of damage on compression strength of the first core is 16.7%, and that of the second and the third cord is 16.5% and 13.3% respectively. The degree of damage of the three cores is less than 20%, it is indicated that it has minimal damage to the rock skeleton, and with the injection of plug-removing fluid, the H^+ concentration is reduced, and thus the impact on the compression strength of rock is weakened.

3. FIELD APPLICATION AND EFFECT ANALYSIS

The first field test has been applied for 19 well times in wells of CL Oilfield, including in 10 water wells and 9 oil wells with full success. The cumulated injection increment is 71,000 m^3, with an average single well injection increment of 710 m^3, the average effective period over 250 days, with an average reduction of injection pressure of 5.8 MPa. In 9 oil wells, with effectiveness of 100%, the cumulative oil increment is 4587 t, with an average single well oil increment of 509.6 t, the average effective period reaches 220 d, achieving a favorable production increasing and injection augmenting effect.

4. ECONOMIC EFFECT ANALYSIS

4.1 Direct Economic Effect of Water Well Acidification

The low-damage acid has been applied for 10 well times in water injection wells, achieving a cumulated injection increment of 71,000 m^3. It maintains the formation energy and slows the decreasing of crude oil production. The oil production of the corresponding oil well reaches about 3,800 t. Assuming the price of stimulated oil increment to be RMB 3,500/t, and the well acidification cost to be RMB 300,000/well time, the direct economic effect of well acidification and augmented injection is:

The crude oil production of corresponding oil well × price of stimulated oil increment - well acidification and augmented injection cost = 3800×3500-400,000×10= 9,300,000 (RMB).

4.2 Direct Economic Effect of Oil Well Acidification

This system has been applied for 9 well times in oil wells, achieving a cumulated oil increment of 4,332 t. Assuming the price of stimulated oil increment to be RMB 3,500/t, and the well acidification cost to be RMB 400,000/well, the direct economic effect of low-damage acidification is:

Oil increment ×price of stimulated oil increment - oil well acidification cost = 4332 × 3500 - 400,000 × 9 = 11,562,000 (RMB).

CONCLUSIONS

(1) The new complex plug removal system developed has features of appropriate erosion capacity, low corrosion rate, low surface tension, strong anti-acid-residue and Fe^{3+} stabilizing capacity.

(2) This system can increase the permeability of low-permeability reservoirs greatly, which has characteristics of deep penetrating and speed-lowering performance. It has the least damage to the rock skeleton, with a degree of damage less than 20%, which can effectively avoid secondary contamination caused by conventional earth acid.

(3) Field application results show that this system is fully effective in plug-removing, and it has a long effective period, with an average greater than 200 days. It has obvious production increasing and injection augmenting effect and can bring favorable economic effect.

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