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Study on Laboratory Performance Evaluation of Anti-gas Invasion and Solid-free Killing Fluid for Carbon Dioxide Flooding

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ABSTRACT

Gas prodution in the CO_2 flooded production wells of low permeability reservoirs in Daqing Oilfield is increasing year by year, which makes conventional pump inspection operation impossible, and leads to the high cost of the operation with pressure. A new type of solid-free killing fluid is developed to balance formation pressure and ensure the safe field operation. The killing fluid is mainly composed of weighting agent, corrosion inhibitor, anti-gas invasion synergist and filtrate reducer. Laboratory performance evaluation results show that the density of the kill fluid can be adjusted in the range of 1.0~2.0g/cm^3, the corrosion rate is less than 0.070mm/a, the anti-swelling rate can reach 95.9%, the API water filtration loss is less than 10mL/30min, and the water loss at high temperature and high pressure (4.1MPa, 85℃) is less than 10mL/30min after CO_2 gas invasion. It has the characteristics of solid-free, low corrosion, low filtration loss, strong anti-swelling, and anti-gas invasion, etc., which can meet the requirement of well killing for CO_2 flooding in peripheral low permeability reservoir.

Keywords: CO_2 flooding; Anti-gas invasion; Density; Solid-free; Well killing fluid; Performance evaluation; Low filtration

1. INTRODUCTION

With the continuous expansion of the scale of carbon dioxide flooding test in peripheral low permeability reservoirs of Daqing oilfield, the number of operating Wells is increasing year by year, and the proportion of gas channeling high-pressure Wells is also increasing. At present, the number of high-pressure oil well pump inspection Wells accounts for about 15% of the total number of annual pump inspection Wells, among which the number of Wells with gas-oil ratio greater than 300m^3/t in the Ⅰ test area accounts for 16.3%. And the carbon dioxide content in the casing gas is more than 50%, the highest casing pressure of some gas channel Wells in the Ⅱ test area is 12.0MPa, resulting in the conventional pump inspection operation can not be built, and the operation with pressure will inevitably cause the pump inspection cost to increase significantly. In order to prevent blowout during high-pressure well operation, killing fluid is usually used to balance formation pressure and ensure safe operation.

Although the density of conventional low-solid killing fluid or drilling mud can reach more than 1.9g/cm^3, the solution contains a large number of suspended matter and solid particles, causing great damage to the low-permeability reservoir and making it difficult to apply [1]. Solid-free well killing fluid mainly includes calcium chloride inorganic salt killing fluid, nitrate type killing fluid and formate organic salt killing fluid, etc. With appropriate selection of salt, the density required to meet most formation conditions can be obtained. Chemical treatment agent can also be added to increase viscosity and reduce water loss. However, there are various problems in common solid-free well killing fluid applied in the CO_2 flooding test area. For example, the highest density of low-cost inorganic chloride killing fluid is 1.35g/cm^3, which cannot meet the requirements of high-pressure well operation and seriously corrods the string. Calcium-containing inorganic salt killing fluid is easy to cause scale formation. Although the nitrate type killing fluid has low corrosion and low cost, it does great harm to the environment and human health, and has certain side effects on the formation with high carbon dioxide flooding content. High cost of organic kill fluid; Salt crystallization temperature is high, crystallization precipitation will form blockage, brine density decreases, solid phase may make brine lose pumpability, especially affecting winter construction; The performance of some kill fluid is obviously affected by carbon dioxide flooding [2-4].

According to the characteristics of CO2 flooding reservoir in Daqing, a new type of high density anti-gas invasion solid-free well killing fluid was developed, which is mainly composed of complex bivalent metal chelate salt

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aggravating agent, salt-resistant thiurea methylimidazoline corrosion inhibitor, propylene glycol alginate anti-gas invasion synergic agent, FP-3 anti-swelling agent and LS-2 fluid loss reducer[5-9]. In addition, indoor evaluation was carried out on important parameters such as density, corrosion, swelling resistance, filtration reduction, gas invasion effect and core permeability damage rate[10-11]. The results confirmed that the well kill fluid has the characteristics of solid free, low corrosion, little filtration loss, good swelling resistance and gas invasion resistance. It can meet the well killing requirements of reservoir depth of 1600 ~ 2100m and reservoir pressure below 38MPa, and provide technical support for the smooth construction of CCUS demonstration zone in Daqing Oilfield.

2. EXPERIMENTAL PART

2.1 Materials and instruments

Experimental material: N80 steel sheet: 50mm×10mm×3mm; Artificial core: ϕ25 mm×25 mm, $50\times10^{-3}\mu m^2$; Nitrogen bottle for industrial use: purity 99.99%; Carbon dioxide gas cylinder for industrial use: purity 99.99%; Hydrochloric acid: analytically pure; Hexamethyltetramine: analytically pure; Anhydrous ethanol: analytically pure; Acetone or petroleum ether: analytically pure.

Instrument equipment: portable densitometer (0.0g $/cm^3$ ~ 3.0g $/cm^3$; Accuracy is 0.0001 g/cm^3); Corrosion reactor: carbon dioxide corrosion resistant material, volume 300 mL; Shale dilatometer: accuracy 0.01mm; High temperature medium pressure water loss instrument or similar products; High pressure water loss instrument or similar products; Gas invasion simulation device: Independently developed (patent No. ZL201520963292.9), withstand temperature 90 ℃, pressure ≥5 MPa; Artificial core gas permeability tester; Electronic balance: 0 g ~ 4100 g, accuracy 0.01g; Electronic balance: 0 g ~ 410 g, accuracy 0.001 g; Electronic balance: 0 g ~ 210 g, accuracy 0.0001 g; Constant temperature oven: room temperature ~ 300 ℃, temperature control accuracy is ±1 ℃; ISCO pumps or similar products.

2.2 Experimental methods

2.2.1 Sample preparation

According to SY/T 5834 "Low Solid Phase Well Killing Fluid Performance Indicators and Evaluation Methods" indoor sample preparation method to prepare the well killing fluid.

2.2.2 Evaluation method

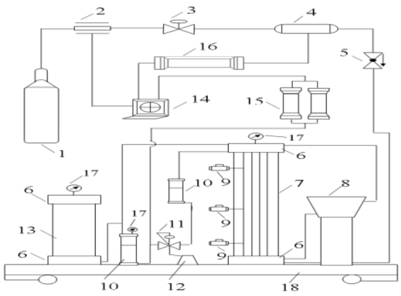
(1) Density test. A portable densitometer is used to measure the density of the prepared well killing fluid at a certain temperature. The number of measurement times is not less than 3, and the average value is determined as the density value.

(2) Anti-corrosion performance evaluation. The corrosion rate evaluation experiment was carried out in the high-temperature and high-pressure corrosion reactor with reference to the static exposure method in SY/T 0026. The experimental temperature and carbon dioxide pressure were set according to the CO_2 flooding reservoir conditions in Daqing.

(3) Evaluation of anti-swelling performance. According to SY/T 5971 medium shale dilatometer method, the swelling rate of killing fluid was measured. The core powder used in the experiment was reservoir core powder.

(4) Filtration loss performance evaluation. Evaluate the fluid loss performance of the kill fluid system by the water loss of the kill fluid. API water loss measurements were performed in accordance with "7.2 Low Temperature and Low Pressure (API) filtration Test" in GB/T16783.1, Field Testing of Drilling Fluids for the Oil and Gas Industry -- Part 1: Water-Based Drilling Fluids. High temperature and high pressure water loss evaluation: According to the solid phase free characteristics of kill fluid and the low permeability reservoir characteristics of carbon dioxide flooding, the developed high temperature and high pressure low permeability core filtration instrument was used for testing. Its main components were designed according to the GB/T16783.1 medium high temperature and high pressure filtration instrument. On this basis, the core mesh cup cover was added, and the filtration medium was changed to ϕ25mm×25mm low permeability core. The fluid loss can be visually evaluated and the permeability damage of the core can be measured. The test method refers to "7.3 High Temperature and High pressure (HTHP) water loss test" in this standard, and the temperature simulates the reservoir temperature.

(5) Evaluation of gas penetration resistance. The experimental device is a carbon dioxide gas invasion simulation device (as shown in Figure 1), which is composed of simulated wellbore, charging cylinder, circulating water bath, etc., which can simulate working conditions (spatial structure, temperature, pressure environment, etc.), intuitively present the gas invasion phenomenon, establish an evaluation method using gas invasion pressure to characterize the anti-gas invasion performance of well killing fluid, and evaluate the influence degree of carbon dioxide gas invasion on the performance of well killing fluid.



1. Carbon dioxide storage tank; 2.Pressure sensor;3. Pressure regulating valve; 4. Core holder; 5. Check valve; 6. Sealing joints; 7. Simulated wellbore; 8. Water bath;

9. Sampler; 10. Back pressure valve; 11. Intermediate container; 12. Liquid feeding device; 13. Liquid collector; 14. Pressure control system software; 15.ISCO pump; 16. Hydraulic booster pump; 17. Mechanical pressure gauge; 18. Movable base.

Fig. 1 Flow chart of gas invasion simulator

The ϕ25 mm×25 mm artificial core is placed into the core gripper, and the outlet of the core gripper is connected with the air inlet of the wellbore simulation device, and the air inlet valve is closed. The sample of kill fluid was added to the sample port at the top of the wellbore simulator, and the top cover was sealed after filling. ISCO pump was used to press the kill fluid in the piston container according to the designed wellbore pressure at constant pressure displacement to stabilize the top of the wellbore assembly, and the pressure of the back pressure valve at the liquid overflow outlet was increased to the designed wellbore pressure. When the reservoir temperature is reached, the adjustable pressure source is connected to the air inlet of the core holder to adjust the gas injection pressure. Observe the bottom of the simulated wellbore until a small number of discontinuous small bubbles appear, and it is considered that carbon dioxide gas invasion occurs. Adjust the gas injection pressure slightly lower than the gas invasion pressure until there is no obvious gas invasion. Monitor the amount of kill fluid spillover at the wellbore fluid overflow outlet for the next 24 hours. After the experiment, kill fluid samples were taken to measure its density and water loss. The influence of gas invasion on the performance of kill fluid was evaluated by the change of density and water loss before and after gas invasion.

Low damage performance evaluation. The permeability damage rate of core was measured by high temperature, high pressure and low permeability core filtration apparatus and artificial core, and the influence of kill fluid on reservoir permeability was further evaluated. Firstly, the artificial core gas permeability was measured, and then the artificial core was put into the high temperature and high pressure low permeability core filtration instrument. The operation was conducted according to the high temperature and high pressure water loss measurement method, and the filtration time was 24h. After the filtration test, the core was taken out and the gas was measured again to measure the permeability. Core permeability damage rate calculation:

$$R_d = (1 - \frac{k_2}{k_1}) \times 100\%$$

Where:

-- core permeability damage rate, %;

-- Permeability measured by gas of core before experiment, $\times 10^{-3}\mu m^2$;

-- Permeability measured by gas of core after experiment, $\times 10^{-3}\mu m^2$.

3. RESULTS AND DISCUSSION

3.1 Density

Weighting agent is a key component that determines the density of kill fluid. After laboratory study, a compound bivalent metal chelate salt was synthesized. Figure 2 shows the general schematic diagram of the structure of the compound chelate salt (R^{2+} represents metal ions). Compared with traditional inorganic salt or organic salt, this chelate salt is more soluble in water.

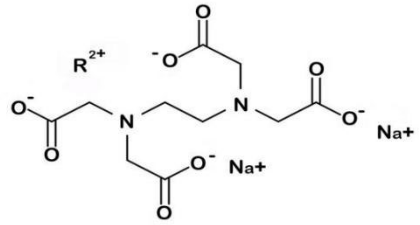


Fig. 2 Structure diagram of complex chelated salt

At room temperature (20℃), the density of killing fluid under different concentration of chelate salt weighting agent was measured, as shown in Figure 3. It can be seen that the density gradually increased with the increase of dosage of weighting agent, and the highest density of prepared killing fluid was 2.0g/cm^3, but the relationship was not completely linear. The solubility of the aggravating agent gradually increases with the increase of temperature, as shown in Figure 4.

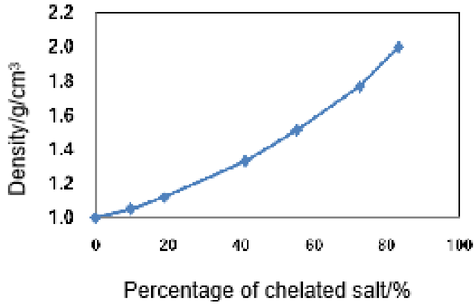


Fig. 3 The relationship between the weight percentage of weighting agent and the density of killing fluid

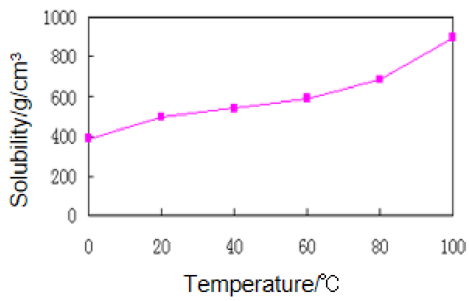


Fig. 4 Solubility curve of aggravating agent at different temperatures

The structure of the chelate salt and synergistic agent propylene glycol alginate can form a more stable spatial structure, so that carbon dioxide flooding gas is difficult to invade, and thus improve the anti-gas invasion performance of the system. In addition, after the bivalent metal ions accrete, the prepared aqueous solution is not easy to produce free metal ions, which weakens the inorganic properties of the metal salt itself, and its physical and chemical properties are more inclined to inertia, not easy to react with the well fluid to precipitate or scale, good compatibility, safety and non-toxic, and a wide range of sources, easy preparation.

3.2 Corrosion Resistance

Due to the high salinity of kill fluid, there are corrosion problems on downhole pipe string, and the conventional corrosion inhibitors appear incompatibility, stratification and other phenomena, and it is difficult to play the role of corrosion inhibition. A new salt-resistant thiourea methylimidazoline corrosion inhibitor was synthesized in the laboratory (structural formula is shown in Figure 5). Compared with conventional corrosion inhibitors, the imidazoline corrosion inhibitor modified by thiourea group (CH_3N_2S) greatly improves its hydrophilic properties and has good solubility in the well killing liquid system, which can guarantee the effective content of corrosion inhibitor. Meanwhile, it strengthens the adsorption of N-Fe coordination bond and π bond in C=N. The stability of the adsorption film formed on the surface of the pipe is improved, and the corrosion inhibition performance is obviously improved. The experimental results are shown in Table 4. Thiourea-methylimidazoline corrosion inhibitor can ensure that the corrosion rate of kill fluid with different densities is less than 0.076mm/a (see Table 1), which is in line with the standard requirements of the petroleum industry.

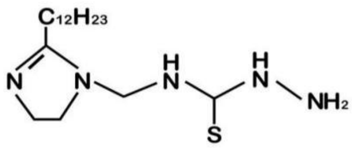


FIG. 5 Thiourea methyl imidazoline

Tab 1 Performance evaluation results of corrosion inhibitor for kill fluid

Type of corrosion inhibitor	Kill fluid density (g/cm^3)	Corrosion (ratemm/ a)	Experimental conditions
Thiourea methyl imidazoline	1.3	0.065	The experimental temperature was 80℃, the partial pressure of carbon dioxide drive was 5MPa, and the experiment time was 72h
	1.6	0.069	
	2.0	0.070	

3.3 Anti-swelling performance

By screening and formulation optimization of various bulking agents, FP-3 was determined to have excellent bulking performance, and the bulking rate was up to 95.9%. See Table 2.

Tab 2 Swelling resistance of kill fluid

Anti-swelling agent	density（g/cm^3）	Anti-swelling rate（%）
FP-3	1.3	95.9
	1.6	95.9
	2.0	95.7

3.4 Filtration loss performance

According to GB/T16783.1 standard, the evaluation and screening experiments of filtration reduction agents such as polymer and cellulose were carried out. The well killing fluid with a density of 1.3g/cm^3, 1.6g/cm^3 and 2.0g/cm^3, respectively, was added proportionally with additives such as anti-swelling agent and filtration reducer. API filtration loss (0.7MPa, 25℃) and high temperature and high pressure water loss ($50\times10^{-3}\mu m^2$ core was used as filtration medium) were measured. It can be seen from the experimental results (see Table 3) that the API and high temperature and high pressure water loss of fluid loss agent LS-2 are less than 10mL/30min, in line with industry standards. LS-2 is a kind of fluid loss reducer, which is formed by the copolymer, hydrolysis and sulfonation of modified cellulose and acrylonitrile under certain conditions. It has the advantages of good thermal stability, little influence on adhesion and strong anti-electrolyte ability, and can be used as an ideal additive in well killing liquid system [5-6].

Tab 3 Kill fluid loss reduction performance

Fluid loss reducer	density（g/cm^3）	API（25℃，mL/30min）	High temperature and high pressure water loss（4.1MPa、85℃，mL/30min）
LS-2	1.3	7.7	2.5
	1.6	8.0	2.9
	2.0	6.9	2.6

3.5 Gas penetration resistance

Propylene glycol alginate is the preferred anti-gas invasion synergist for the formulation of kill fluid (see Fig.6 for structural formula), which has certain anti-acid and anti-salt-out capabilities

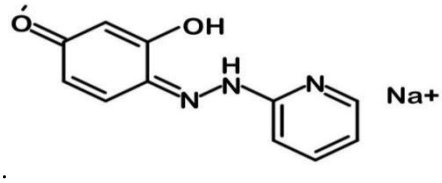


Fig. 6 Structure diagram of propanediol alginate ester

In the high-density and acidic solution, the synergist can still maintain the stretch and extension of the molecular chain, and associate with the chelating salt aggravating agent to form a six-membered ring network stable structure, which can effectively resist carbon dioxide gas flooding, as shown in Figure 7.

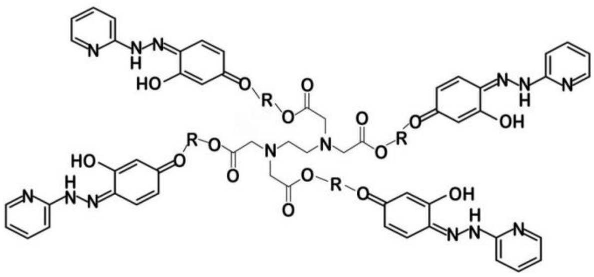


Fig. 7 Gas invasion resistant structure

The indoor evaluation of anti-gas invasion effect of synergist under different concentrations was carried out. The simulated pressure of well killing fluid liquid column was 3, 5 and 8MPa respectively, and the corresponding carbon dioxide drive gas invasion pressure was measured, so as to calculate ΔP (additional pressure) =Pk(liquid column pressure) -Pc (gas invasion pressure).

As can be seen from Figure 8, with the increase of synergist concentration, the additional pressure of killing fluid against gas invasion gradually decreases. When the concentration of synergist was between 0.2% and 0.5%, the additional pressure decreased greatly. Under the same conditions, the higher the density of kill fluid, the lower the additional pressure.

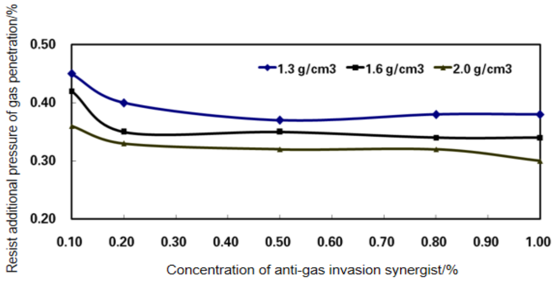


Fig. 8 The relationship between the concentration of different anti-gas invasion synergists and the additional pressure of anti-gas invasion

As can be seen from Table 4, gas invasion has little impact on the performance of kill fluid, density retention rate is about 99%, and water loss at high temperature and high pressure increases slightly, but it is still far below the requirements of industry standards.

Tab 4 Effect of gas invasion on performance of kill fluid

Kill fluid density			High temperature and high pressure water loss（4.1MPa、85℃，mL/30min）		
Pregas invasion（g/cm³）	Post-gas invasion（g/cm³）	Retention rate（%）	Pregas invasion（mL/30min）	Post-gas invasion（mL/30min）	Increase rate（%）
1.30	1.29	99.2	2.5	2.6	4.0
1.60	1.58	98.8	2.9	3.0	3.4
2.00	1.98	99.0	2.6	2.7	3.8

Tab 5 Kill fluid core damage

density（g/cm³）	Core diameter（cm）	Core length（cm）	permeability K1（$\times10^{-3}\mu m^2$）	permeability K2（$\times10^{-3}\mu m^2$）	Core damage rate（%）
1.3	2.495	2.497	50.36	45.68	9.3
	2.496	2.498	51.82	47.01	9.28
1.6	2.494	2.499	53.69	48.59	9.49
	2.497	2.498	52.84	47.81	9.51
2	2.491	2.499	52.04	46.9	9.86
	2.493	2.496	51.87	46.75	9.88

3.6 Low damage performance

For the killing liquid system, the core permeability damage rate experiment was carried out. The low-permeability core with the permeability measured by gas of $50\times10^{-3}\mu m^2$ was taken as the evaluation medium. Under the condition of 110℃, the low-permeability core was immersed in the killing liquid system for 24h. This is lower than the standard requirements of the oil industry, which indicates that the damage to the reservoir is low and meets the requirements of field operations.

To sum up, the fluid system with adjustable density of 1.0 ~ 2.0g/cm³ has the characteristics of low damage and gas invasion resistance, and can meet the killing requirements within 2100m reservoir depth and below 38MPa reservoir pressure, as shown in Table 6.

Tab 6 Different density of kill fluid to meet the reservoir conditions

density（g/cm³）	Reservoir depth/reservoir pressure（m/MPa）		
	1600	1800	2100
1.30	18.03	20.29	23.67
1.60	22.74	25.58	29.84

2.00	29.01	32.64	38.07

4. CONCLUSION

The high density solid-free well killing fluid is mainly composed of compound bivalent metal chelate aggravating agent, which has a wide range of adjustable density, good compatibility, safety and non-toxic, and has excellent synergism with synergist propylene glycol alginate to resist gas invasion. By combining with the optimized additives such as corrosion inhibitor, anti-swelling agent and fluid loss agent, a new well killing fluid formulation system has been formed. It has good stability, API and high temperature and high pressure water loss are less than 10mL/30min, and core damage rate is less than 10%. It can be used in the well killing operation of low permeability reservoir carbon dioxide flooding high temperature and high pressure injection-production well in Daqing oilfield. In the next step, we will continue to develop low cost and low damage solid-free well killing fluid system for complex reservoir conditions and study on performance evaluation methods.

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