Research of the Anti-Scale Technology for High Density Brine Killing Fluid

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Abstract. There are various formation damage in the exploitation of shale oil, for example water blocking, water sensitive and incompatibility, and so on, which will influence the recovery period and recovery rate of oil well. In this paper, an Anti-Scale technology for high density brine killing fluid was researched. The result show that the brine killing fluid can withstand high salinity (Ca²⁺≤180000mg/l, NaHCO₃≤10000mg/l), and has well compatibility with common formation water. The puzzle for the scaling of high density brine kill fluid has been resolved.

Keywords: Shale oil, High density, Brine, Anti-Scale technology, killing fluid

1. Introduction

Different countries, institutions and even scholars have different understandings and definitions of shale oil. Generally speaking, shale oil refers to low-mature-semi-mature oil and gas which is generated and stranded in source rocks, exists in the micro-nano reservoir space of strata in a free or adsorbed state, and basically does not migrate or migrates in a very short distance. Organic-rich shale is not only a source rock, but also a reservoir rock, which is a typical oil and gas accumulation type [1-2].

Shale oil is similar to conventional high-pressure well operation, that is, there is a certain contradiction between the price of kill fluid and reservoir protection performance. However, compared with conventional reservoirs, shale reservoirs are more vulnerable to damage due to their special porosity and permeability structure, which seriously affects the recovery of oil well production after operation.

The well killing fluids commonly used in oil fields may contain calcium ions, especially in high-pressure wells, because of the cost problem, cheap calcium brine and bittern are often used as high-density well killing fluids, and the calcium ion content in brine with a density of 1.38g/cm³ can reach up to 180,000 mg/l. However, the formation water in Dagang Oilfield is generally sodium bicarbonate or sodium sulfate. When the kill fluid containing high calcium ions enters the formation, incompatible reaction will inevitably occur, and the potential calcium carbonate and calcium sulfate will scale, either with the kill fluid entering the deep reservoir and blocking the throat, or with the produced fluid scaling in the pump barrel and pipe wall in the well, resulting in complex operation. According to the actual investigation, the scaling of Dagang Oilfield caused by high density brine, commonly known as "calcium brine", exceeds 100 wells every year, which often leads to complex well bore and shortened...
operation cycle, which not only increases operation cost and operation risk, but also causes the oil well output not to recover by more than 50%, which seriously affects the oil well productivity. Therefore, it is necessary to carry out anti-scaling technology of high density brine kill fluid.

2. Deficiency of Existing Anti-scaling Technology for High-density Brine Kill Fluid

In the field of high-density kill fluid, formate and compound salt system can not completely replace brine system because of its high cost. In view of the technical defects of easy scaling of brine, the chelating scale inhibitor and modifier technology were studied and applied in Dagang Oilfield in the early stage, which were mainly used in brine system with relatively low calcium content, but the anti-scaling effect on high density calcium brine kill fluid was not ideal. A detailed analysis is made below.

2.1. Salt modification technology of calcium halide

The modifier usually has a concentration of 0.25%-0.6% and a pH value of about 5.0, showing weak acidity. See figure 1 below for precipitation of brine-NaHCO$_3$ mixture before and after adding modifier.

The results showed that no obvious flocs or precipitates were formed in the initial stage after the samples without modifier and brine were mixed with NaHCO$_3$ solutions with different concentrations. After standing for 1 day, the brine mixture was clear and no scaling was found, but precipitates were formed in the calcium brine mixture (see Samples 16#, 17#, 18#).

After adding modifier, see sample 7#-12# in Figure 1, which is the mixed solution of calcium halide with different concentrations of modifier and NaHCO$_3$ solution with different concentrations, all of which produce flocculent suspended solids. By comparison, it is found that the precipitation amount does not change significantly, and the pH value and density do not change significantly.

The test results show that the effect of calcium halide modified anti-scaling technology is not obvious.

2.2. Conventional scale inhibition technology of kill fluid

Chelating scale inhibition technology is often used in brine or compound salt killing fluid with density lower than 1.35g/cm$^3$ in Dagang Oilfield. It is found that when the concentration of calcium ion is lower than 1500mg/l, it can effectively inhibit scale, while when the concentration of calcium ion is higher (about 3000mg/l, 1% calcium chloride), micro scale deposition occurs, and when calcium brine is used, obvious precipitation and scaling phenomenon occurs.

Therefore, the existing anti-scaling technology of calcium brine kill fluid is not ideal.

3. Experimental Study on Scale Prevention and Control Technology of High Density Brine Kill Fluid

According to the chelating solubilization mechanism, the traditional anti-scaling technology needs to consume a large amount of chemicals by forming complex or limiting effect. From the calcium ion chelating value (test condition 40$^\circ$C, pH=7), it can be seen that the highest complexing ability of aminotrimethylene phosphonic acid ATMP is 910 mg/g. Others, such as hydroxyethylidene diphosphate HEDP, 833mg/g, ethylenediamine diothophenyl sodium acetate EDDHANa, 845mg/g, etc. However, the calcium ion content in calcium brine kill fluid is as high as 100,000 (mg/l), and theoretically, the amount of chelating agent should be more than 100,000 (mg/l), which is too expensive. Therefore, it is necessary to focus on the technical optimization research from the aspects of dispersion scale inhibition and scale formation inhibition.

In this experiment, the compound agent with dispersion and scale inhibition function was selected and added into the mixed solution of high calcium solution and sodium bicarbonate (sodium sulfate). By observing the flocculation and precipitation phenomena in the solution, quantitatively measuring the change of calcium ion concentration before and after scale inhibition, calculating the scale inhibition rate, etc., the compatibility with high calcium solution, especially high density brine kill fluid
fluid, and the anti-scaling effect were explored, and the formula was further optimized to form a high-
efficiency anti-scaling kill fluid.

The important experimental instruments involved in quantitative analysis include atomic absorption
spectrophotometer, and the experimental methods include:

Ca$^{2+}$, Mg$^{2+}$: SY/T 5523-2006 oil and gas field water analysis method, atomic absorption method/
EDTA titration method.

Scale inhibition rate $E$ is calculated according to the following formula:

$$
E = \frac{M_2 - M_1}{M_0 - M_1} \times 100\
$$

In which: $M_2$—Calcium ion concentration in mixed solution after adding scale inhibitor
$M_1$—Calcium ion concentration in mixed solution without scale inhibitor
$M_0$—Half of calcium ion concentration in calcium halide or calcium chloride stock solution

After a large number of evaluation experiments, two kinds of scale inhibition technologies are
selected: hard scale softening technology of brine kill fluid and high-efficiency scale inhibition
technology, among which the latter has remarkable effect.

3.1. Evaluation of softening technology of hard scale

The scale inhibition performance of scale inhibitor was evaluated by mixing calcium halide and
calcium chloride with density of 1.38g/cm$^3$ with different concentrations of sodium bicarbonate and
sodium sulfate solutions. The results are shown in Table 1.

| Category | Calcium halide, density 1.38 g/cm$^3$ | Calcium chloride,10000mg/l |
|----------|--------------------------------------|---------------------------|
| Concentration | 0 | 0.1%A | 0.1%B | 0 | 0.1%A | 0.1%B |
| Mixture | 5000mg/L NaHCO$_3$ | 5000mg/L NaHCO$_3$ | 3000mg/L Na$_2$SO$_4$ | 3000mg/L Na$_2$SO$_4$ | 5000mg/L NaHCO$_3$ | 5000mg/L Na$_2$SO$_4$ | 3000mg/L Na$_2$SO$_4$ | 3000mg/L Na$_2$SO$_4$ |
| pH value before mixing | 5.0 | 4.0 | 2.5 | 6.5 | 7 | 2 | 6.0 | 2.0 |
| Appearance | Dense scale | Soft colloid | Dense scale | Loose colloid | Precipitation | Scale formation | Clear | Clear | Clear | Clear |

It is found that calcium carbonate scale formed by the mixed solution of calcium chloride and
NaHCO$_3$ is obviously deposited at the bottom before adding scale inhibitor a in calcium chloride
system; After adding scale inhibitor A, no precipitation was found. No calcium sulfate scale was found.
In calcium halide system, before adding scale inhibitor a, calcium carbonate scale formed by mixed
solution of calcium halide and NaHCO$_3$ is densely deposited at the bottom; After adding scale
inhibitor A, soft matter is deposited at the bottom of the mixed solution. Therefore, scale inhibitors A
and B can prevent scale from adhering to the pipe wall by softening hard scale, but still cannot
completely control the scale formation.

3.2. Evaluation of high-efficiency anti-scaling technology for calcium brine kill fluid

Evaluation of anti-scaling performance

Compound scale inhibitor Fc with different concentrations was added into calcium halide system,
and then mixed with sodium bicarbonate solution with different concentrations to observe its scale
formation and measure the change of calcium ion concentration. The results are shown in Table 2.
Table 2. The evaluation of anti-scale inhibition for scale inhibitor Fc

| Scale inhibitor concentration | Simulated kill fluid | Simulate mixed formation fluids | Temperature | Is there turbidity/scaling | Sample number |
|------------------------------|----------------------|---------------------------------|-------------|---------------------------|--------------|
| 0 Calcium halide system      | 5000mg/l NaHCO₃      | Normal temperature              | Yes         | 29                        |
| 0.65%Fc Calcium halide system | 10000mg/l NaHCO₃  | Normal temperature              | No          | 28                        |
| 0.65%Fc Calcium halide system | 5000mg/l NaHCO₃  | Normal temperature              | No          | 27                        |
| 0 Calcium halide system      | 5000mg/l NaHCO₃      | Normal temperature              | Yes         | 46                        |
| 0.6%Fc Calcium halide system | 5000mg/l NaHCO₃      | Normal temperature              | No          | 44                        |
| 0.6%Fc Calcium halide system | 10000mg/l NaHCO₃     | Normal temperature              | No          | 48                        |
| 0.4%Fc Calcium halide system | 5000mg/l NaHCO₃      | Normal temperature              | No          | 45                        |
| 0.25%Fc Calcium halide system | 5000mg/l NaHCO₃     | Normal temperature              | No          | 47                        |
| 0.25%Fc Calcium halide system | 10000mg/l NaHCO₃     | Normal temperature              | Yes         | 49                        |
| 0.15%Fc Calcium halide system | 5000mg/l NaHCO₃     | Normal temperature              | Yes         | 65                        |
| 0.6%Fc Calcium halide system | 5000mg/l NaHCO₃      | Normal temperature              | Yes         | 68                        |
| 0 Calcium halide system      | 5000mg/l Na₂SO₄      | Normal temperature              | Yes         | 31                        |
| 0.25%Fc Calcium halide system | 5000mg/l Na₂SO₄     | Normal temperature              | No          | 30                        |
| 0.25%Fc Calcium halide system | 5000mg/l Na₂SO₄     | Normal temperature              | No          | 38                        |

It can be seen from the above table that the scale inhibitor Fc can significantly improve the scale prevention effect of calcium brine system, and the dosage of scale inhibitor is directly proportional to the content of sodium bicarbonate in formation water. When the dosage of scale inhibitor Fc is 0.6%, the anti-sodium bicarbonate concentration can reach 10000 mg/l.

At the same time, the quantitative analysis and test of scale prevention and control (compound scale inhibitor with two proportions) were carried out, as shown in Table 3.

Table 3. Scale inhibition rate evaluation

| Numbering | Calcium containing solution | Sodium bicarbonate/ (mg/L) | Calcium ion concentration/ (mg/L) | M₀ | M₁ | M₂ | Scale inhibition rate % | Experimental temperature | Scale inhibitor concentration |
|-----------|-----------------------------|-----------------------------|-----------------------------------|----|----|----|-------------------------|--------------------------|-----------------------------|
| 27        | Calcium halide system       | 5000                        | 88400                              | 90000 | 84964 | 88400 | 68.2                    | 90°C                     | 0.65%Fc0                    |
| 42-44     | Calcium halide system       | 5000                        | 95040                              | 116295 | 88540 | 95040 | 76.6                    | 90°C                     | 0.6%Fc1                     |
| 45-46     | Calcium halide system       | 5000                        | 119690                             | 116295 | 88540 | 119690 | 100.0                   | 90°C                     | 0.4%Fc2                     |
| 18-1#     | 1/5Calcium halide system    | 5000                        | 46287                              | 24485 | 16992 | 23143 | 82.1                    | 90°C                     | 0.65%Fc0                    |
| 24-26     | 10000mg/l Calcium chloride  | 5000                        | 1060                               | 1010  | 340  | 1060  | 100.0                   | 90°C                     | 0.65%Fc0                    |
The experimental data in Table 3 show that the scale control rate of calcium brine system is over 68.2%, and some of the proportion samples can reach 100%, which can realize complete scale inhibition. The results show that the potential calcium carbonate scale in calcium halide system can be controlled.

4. Summary
Through comparative experimental study, the following conclusions are drawn:
1. The high-efficiency scale prevention and control technology is suitable for high-density calcium brine kill fluid with calcium ion concentration of 180000mg/l, which can be mixed with sodium bicarbonate with concentration of not less than 10000mg/l without scaling. It can realize the prevention and control of scaling trend of calcium brine killing fluid system.
2. The maximum calcium resistance of common scale inhibition technology is 1500mg/l, which is only applicable to low calcium solutions such as bittern, and the corresponding sodium bicarbonate concentration is not higher than 3000mg/l.
3. Scale softening technology can only make sediments soft and easy to flow, but can't really prevent scale formation.

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