A study of new low-cost anti-scaling compound salt high-density solid-free killing fluid

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Abstract. A new low-cost anti-scaling compound salt high-density solid-free killing fluid system is developed by adopting the high-efficiency scale inhibition technology, using a newly-developed weighting agent, and taking cheap inorganic salts as the base fluid, to solve the problems that the common killing fluids for high temperature and high pressure oil and gas reservoirs include bromine, zinc, heavy calcium, etc. are poorly compatible with the formation water, pollutional to soil and highly corrosive to human body, and that the formate high density killing fluid has a high cost. The system contains neither solid-phase components nor divalent ions that are prone to scaling, such as calcium and magnesium ions. The salts used are all monovalent salts with a density of up to 1.70 g/cm³. Compared to the same grade of formate system, the cost is reduced by more than 50% while all the advantages of the formate system are remained. In addition, it is also consistent with the future development trend and the requirements of the national new safety and environmental protection for the low damage, low cost, high density, solid-free and non-toxic environment-friendly killing fluid system.

1. Introduction

The high-density workover fluid is mainly used for the workover of medium and high pressure oil and gas wells to balance the formation pressure and protect the oil and gas formations. At present, the medium and high-density workover fluids applied at home and abroad are mainly divided into three systems, high density mud system, with the density up to 2.6g/cm³; solid-free brine system, with the density up to 2.30g/cm³; and high density water-in-oil workover fluid, with the density of 1.40-2.0 g/cm³.

The high-density mud system functions mainly relying on the suspension capacity of the clay, and the calcium carbonate powder, the iron ore powder, the barite powder etc. are added therein to increase the density, and the rheological properties are maintained by adding other treating agents. It has the characteristics of relatively-low price and high density, but there are problems such as precipitation of the weighting agent and excessive solid content.

The solid-free brine system forms a solid-free brine workover fluid with the maximum density of 2.3 g/cm³ through weighing by adding calcium bromide, zinc bromide, zinc chloride and formate. It is featured as expensive, large loss of leakage, severe corrosion, and scaling. The formate system of which can overcome the corrosion and scaling problems and stands for the main development...
direction of high-density workover fluid.

The high-density water-in-oil workover fluid is formed by using high-density brine as a base fluid, and adding an emulsifier and related oils. If necessary, the solid weighting agent is also added. It is applied to high temperature and severe water-sensitive formations, but has the disadvantages of poor environmental protection performance and system stability.

Dagang Oilfield encountered many problems in the past workover process. For example, the formation is damaged due to the common use of brine killing fluid, and the operation is difficult due to the high pressure of slab bridge injection wells, etc.. The high temperature and high pressure in the deep layer of Qikou require high-density workover fluids to solve the problem of on-site operation. At present, the medium and high pressure wells are mostly 1.4 g/cm³ liquid calcium medium-density workover hydraulic wells. Such fluid is not only prone to crystallization and instability, but also incompatible with the formation water, causing scaling and damage to the formation and reducing the production.

2. Development of the New Weighting Agent

The new solid-free weighting agent is a compound salt. The solubility of a single salt alone cannot reach the required density of the solid-free killing liquid, so it is necessary to compound two or more kinds of salts with relatively high solubility to form a compound salt. The weighting agent is composed of an inorganic salt and an organic salt, but it is impossible to achieve the density of the prepared fluid by the natural solubility of the two salts.

Indoors, we widely choose cheap inorganic salts and organic salts and modify the two substances by substitution reaction, and adopt the solubilization technology to increase the solubility of cheap inorganic salts and organic salts to form soluble intermolecular complexes, associations or double salts to increase their solubility, for example: The double salt is an isomorphous compound composed of two or more simple salts. Since the lattice energy is large, the double salt crystal is more stable than the simple salt constituting it. The ions ionized by the simple salt constituting the double salt are the same as the ions ionized by dissolving in water. The double salt may be obtained by crystallization of a mixture of two simple salts in a saturated state. For example, the copper ammonium sulfate [(NH₄)₂SO₄·CuSO₄·6H₂O] may be prepared by mixing and crystallizing the solutions of CuSO₄ and (NH₄)₂SO₄. With this method, we have developed a new solid-free weighting agent with a maximum density of 1.70 g/cm³ (see Table 1), which reduces the use of expensive formate and the cost is reduced by more than 50%, compared to the same grade of formate. According to the market price of formate high-density killing fluid, nearly a million yuan is saved for an individual well.

Table 1 Variation law in the density of the new weighting agent solution with its concentration

| No. | System density g/cm³ | Total added dosage g | System volume mL | Mass concentration of weighting agent g/100 mL |
|-----|----------------------|----------------------|------------------|------------------------------------------|
| 1   | 1.0                  | 0                    | 100              | 0                                        |
| 2   | 1.036                | 2                    | 106              | 1.88                                     |
| 3   | 1.085                | 6                    | 109              | 5.5                                      |
| 4   | 1.14                 | 15                   | 116              | 12.93                                    |
| 5   | 1.172                | 18                   | 120              | 15                                       |
| 6   | 1.205                | 20                   | 125              | 16                                       |
| 7   | 1.3                  | 50                   | 135              | 37.04                                    |
| 8   | 1.4                  | 100                  | 155              | 64.52                                    |
| 9   | 1.5                  | 160                  | 175              | 91.43                                    |
| 10  | 1.6                  | 260                  | 225              | 115.56                                   |
| 11  | 1.7                  | 400                  | 295              | 135.59                                   |
3. Development of the new low-cost anti-scaling solid-free killing fluid system

Indoors, we widely choose cheap industrial salts as the base fluid to reduce the comprehensive cost of the killing fluid system. At the same time, a small amount of surfactant is added for solubilizing, so that the solubilizing agent enters the micelle environment, and the position and state in which the solubilizing agent enters the micelle depend on the the type of surfactant and the nature of the solubilizing agent. On this basis, we add the newly-developed weighting agent. After the compounding of the two, the dosage of the weighting agent to be added is decreased from 400g to 380g, which can further reduce the cost. Refer to the table below.

**Table 2 Optimization and Compounding of Two Salts**

| No. | System density g/cm³ | Added dosage of Salt A g | Added dosage of Salt B g | System volume mL |
|-----|----------------------|--------------------------|--------------------------|------------------|
| 1   | 1.0                  | 0                        | 0                        | 100              |
| 2   | 1.7                  | 40                       | 380                      | 300              |

At the same time, we have developed a new scale inhibition technology to make the system have a certain ability to resist the contamination from calcium and magnesium ions; and a compound agent with dispersed scale inhibition effect to form a high-efficiency anti-scaling killing fluid. See the table below.

**Table 3 Anti-scaling Test Results of High-density Killing Fluid**

| Concentration of scale inhibitor | Solid-free killing fluid | Simulated mixed formation fluid | Temperature | Is there turbidity / scaling? | Sample No. |
|----------------------------------|--------------------------|---------------------------------|-------------|-------------------------------|------------|
| 0                                | New killing fluid        | 500mg/l CaCl₂                  | Normal temperature | Yes                          | 29        |
| 0.65% Fe                         | New killing fluid        | 500mg/l NaHCO₃                 | Normal temperature | No                           | 28        |
| 0.65% Fe                         | New killing fluid        | 1000mg/l NaHCO₃                | Normal temperature | No                           | 27        |
| 0.65% Fe                         | New killing fluid        | 1500mg/l NaHCO₃                | Normal temperature | No                           | 46        |
| 0.6% Fe                          | New killing fluid        | 2000mg/l NaHCO₃                | Normal temperature | No                           | 44        |

The weighting agent is completely from cheap materials, so the cost is greatly reduced compared to the use of single formate system. The maximum density of the conventional potassium formate killing fluid is only 1.57g/cm³, and the price is 16,000 yuan. The formate system with the required density of more than 1.57g/cm³ needs to be prepared using cesium formate, which is super expensive. The bromine and zinc salts are toxic and harmful, severely corrosive, costly, easy to scale and have poor oil layer protection effect, which are not consistent with the new national safety and environmental protection law, so their application are limited. Refer to the table below for details.
Table 4 Comparison table of high-density killing fluids commonly used at home and abroad

| Type Property | Drilling fluid | Brine | Formate | Low cost killing fluid |
|---------------|----------------|-------|---------|-----------------------|
| Density (g/cm³) | High | ≤1.4 | <1.58 | ≤2.3 | ≤2.3 | ≤1.7 |
| Solid phase content | High | High | Not available | Not available | Low | Not available |
| Heat resistance | Medium | High | High | High | High | High |
| Viscosity | High | Low | Low | Low | Low | Low |
| Corrosion | Low | High | Low | Low | High | Low |
| Reservoir protection | Poor | Poor | Good | Good | Poor | Good |
| Process | Complex | Simple | Simple | Simple | Complex | Simple |
| Price | High | Low | High | Extremely high | Extremely high | Medium |

It can be seen from the above table that the new low-cost compound enhancing killing fluid has great advantages in various indicators, and the appearance is clear and transparent, with a wide prospecting application space. Refer to the figure below for details.

Figure 1 Appearance of the Killing Fluid

4. Comprehensive Performance Evaluation of New Low-cost Anti-scaling and Solid-free Killing Fluid

(1) Good stability
The new killing fluid under this technology has a density of up to 1.70 g/cm³, exceeding the upper limit of 1.40 g/cm³, and has a good stability, stable and free of crystallization or precipitation at high temperature of 140 °C and low temperature -1°C. See Table 5. The technology does not involve solid phase components, nor divalent ions such as calcium and magnesium ions, and adopts monovalent salt materials completely, as shown in Table 6.

Table 5 Solution Stability Test of this Technology

| Density g/cm³ | Standing duration | Phenomenon |
|---------------|-------------------|------------|
| 1.7           | 2 (Normal temperature) | Relatively stable, free of crystallization or precipitation |
| 1.7           | 4 (Normal temperature) | Relatively stable, free of crystallization or precipitation |
| 1.7           | 3 (140 °C)        | Relatively stable, free of crystallization or precipitation |
| 1.7           | 1(-1°C)           | Relatively stable, free of crystallization or precipitation |
Table 6: Impurity Tests of New High Density Killing Fluid with Different Densities

| Density g/cm³ | Salt      | Impurity content % | Temperature °C |
|--------------|-----------|--------------------|----------------|
| 1.45         | This technology | 0.12               | 20             |
| 1.5          | This technology | 0.20               | 20             |
| 1.6          | This technology | 0.26               | 25             |
| 1.7          | This technology | 0.28               | 25             |

(2) Good temperature resistance
The technology has a temperature resistance of 180 °C, and the density of the system does not change after hot rolling at high temperature. See Table 7.

Table 7: Evaluation of temperature resistance of new solid-free high-density killing fluid

| formula       | Pre-rolling density g/cm³ | Density after hot rolling at 180 °C g/cm³ |
|---------------|---------------------------|------------------------------------------|
| This technology | 1.70                      | 1.70                                      |

(3) Good oil layer protection performance
This technology has a strong property of inhibiting shale expansion, better oil layer protection performance, and its core permeability recovery rate is greater than 85%, as shown in Table 8.

Table 8: Core Damage Evaluation Test

| System       | Core No. | Liquid phase permeability before pollution ×10⁻³μm² | Liquid phase permeability after pollution ×10⁻³μm² | Permeability Recovery value% |
|--------------|----------|------------------------------------------------------|---------------------------------------------------|------------------------------|
| This technology | 6#       | 20.5666                                              | 18.9886                                           | 92.32                        |
| This technology | 9-2#     | 18.5689                                              | 16.3689                                           | 88.15                        |

(4) Good compatibility and non-toxic properties
In this technology, all the components are monovalent salt ions, providing a good compatibility. No precipitation and scaling occurred when mixed with different proportions of sodium bicarbonate formation water, as shown in the figure below.

Figure 2: Compatibility test between the killing fluid and formation water
The solid-free compound enhancing high-density killing fluid was tested for the toxicity of the treated agent, and the results prove that: The treating agent used is non-toxic and meets environmental
protection requirements, as shown in Table 9.

### Table 9 Bio-toxicity determination table of the killing fluid

| Sample designation | Concentration adopted | EC<sub>50</sub> Mg/L | Toxicity analysis |
|--------------------|-----------------------|----------------------|------------------|
| This technology    | 1.0                   | >1000000             | Non-toxic        |

(5) Good rheology

The viscosity of the killing fluid decreases and becomes suitable with the increase of temperature, which can improve the rheology of the killing fluid without increasing the pumping difficulty on site.

![Figure 3 Viscosity curve of the killing fluid](image)

(6) Low corrosion

Although the killing liquid has a high degree of salinity but its corrosion is low and the corrosion rate is within 0.1mN/m, which can meet the on-site technical requirements shown in Table 10.

### Table 10 Corrosion evaluation of the killing fluid

| Material No. | Pre-test quality | Post-experiment quality | low quality | Corrosion rate | Sample            |
|--------------|-----------------|-------------------------|-------------|----------------|--------------------|
| N80 266      | 11.0102         | 11.0138                 | 0.0036      | 0.0560         | 1.70 killing fluid |
|              |                 |                         |             |                | 1.70 kill fluid    |
| 268          | 10.9126         | 10.9096                 | 0.003       | 0.0520         | 1.70 kill fluid    |
| 289          | 10.9928         | 10.9909                 | 0.0019      | 0.0306         | 1.70 kill fluid    |

5. Conclusion

This paper presents a new low-cost anti-scaling and solid-free killing fluid technology through new method and new mechanism, to overcome the technology and cost problems of high-pressure oil and gas reservoirs. This new technology has the following advantages:

① The new low-cost anti-scaling and solid-free killing fluid has a high stability and the
heat-resistance reaches 180 °C.

② The new low-cost anti-fouling and solid-phase killing fluid has a high density of up to 1.70g/cm³, exceeding the upper limit of conventional solid-free system of 1.4 g/cm³. Compared to the formate-free solid-free high-density system with the same density, it reduces the cost by 50%.

③ The new low-cost anti-fouling and solid-phase killing fluid also has a low corrosion, meeting the standard requirements. It overcomes the problem of the corrosion of high salinity to the tools, achieving the high-density, low-cost, low-corrosion win-win goal and realizing the technical breakthrough.

④ The new low-cost anti-fouling and solid-phase killing fluid contains neither solid phase components, nor calcium and magnesium divalent ions that are prone to scaling. All the components are monovalent salts, and there is no risk of pore throat of the reservoir or downhole tools being blocked by precipitation. In addition, it also has a high resistance to divalent ion scaling, a good ability to inhibit shale expansion, and a compatibility with formation water and reservoir rocks and minerals. It will not pollute the reservoir and cause the production reduction. The core permeability recovery rate is greater than 85%.

⑤ The new low-cost anti-fouling and solid-phase killing fluid has been tested against all the toxicities of the treated agent, and the results prove that: The treating agent used is non-toxic and meets environmental protection requirements.

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