The development and application of bi-functional clay inhibitor of CYY-2

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Abstract. With the constant discovery and gradual development of low-permeability and water-sensitivity formation, reservoir protection is especially important for improving water-injection development efficiency and enhancing working level of low-permeability reservoir, which will be a critical sector in enhancing development quality of low-permeability and water-sensitivity reservoir. Combined with the understanding of clay mineral expansion theory, starting from hydratability, polarity and oxidability of adopted materials, one type of bi-functional clay inhibitor, CYY-2, is developed which has the function of swelling prevention and swelling shrinkage, and property evaluation is carried out by adopting different methods and measures. Test results indicated that: by using this bi-functional clay inhibitor, the swelling prevention rate of magcogel and natural core powder could reach to 91.7% and 89.8%, swelling shrinkage of which could reach to 61.3% and 81.5%; in the natural flowing experiment, core damage ratio was declined from 86.3% to 12.8%, and the core permeability could be raised by 3 times averagely; in the field experiment of 5 wells, effective rate of 80%, the well effect, is reached. With the extension of injection time of injecting wells, injection pressure rose constantly, injection allocation request was not finished, which influenced the overall reservoir development effect. So reservoir protection is important to deal with the above problems.

1. Introduction

Reservoir protection research is one of important technologies in the oilfield development as well as an important element to improve exploration and development quality. As the extension of develop time, some injection wells in the seriously water-sensitive reserves had many conditions such as rising injection pressure, decreasing injection volume and being difficult to accomplish injection allocation, which had bad influence on the reservoir development effect. The reservoir clay content is high and easy to be water-sensitive. In the water injection development, the salinity of injection water is lower than that of formation water, so clay mineral will be hydrate and swell, break and migrate which make oil layer damaged, injection pressure raised, injection allocation decreased. Thus, aiming at the conditions that clay content is high and clay is easy to hydrate and swell with fresh water and to migrate in the water-sensitive reserves of Huabei oilfield, on the base of taking example by domestic and overseas experiences of swelling prevention measures, bi-functional clay inhibitor of CYY-2 is developed. The CYY-2 has the functions of preventing clay from hydrating and swelling and dredging.
formation hole of low-permeable and water-sensitive reserves, realizing decompression and stimulation. The CYY-2 can achieve well effects through the field pilot tests.

2. The development of clay inhibitor formula

2.1. Main materials molecular formula
The molecular formula for N-propyl-N,N,N-three methyl ammonium chloride is C₉H₁₉ClN₂O. The molecular formula for γ-propyl three methoxy silane is C₉H₂₃NO₃Si, molecular formula for PEG is HO(CH₂CH₂O)ₙH.

2.2. Main materials filtering
Through literature researches, four chemical raw materials are chose of which main materials are easy to get and price is reasonable. By using centrifugation evaluation methods, swelling prevention effect is confirmed.

Swelling prevention percentage and swelling shrinkage percentage is measured by centrifugation methods, experiment methods are as follows:

Swelling prevention percentage: The mass of bentonite power is 0.50g (montmorillonite content is higher than 80 percent), accurate to 0.01g. The power is put into centrifuge tube of 10ml, added antisywlling agent solution of 10ml to the tube and shaking enough. The mixture is placed for 2 hours in the indoor temperature and then put into centrifugal machine. After being centrifugalized for 15minutes in the rotate speed of 1500r/min, the expanding volume V₁ of bentonite power is read. The antisywlling agent solution is replaced by deionized water of 10ml and then the expanding volume V₂ in water of bentonite power is measure. The antiswelling agent solution is replaced by kerosene of 10ml and then the expanding volume V₀ in kerosene of bentonite power is measure.

The equation of swelling prevention percentage is B= (V₂-V₁) / (V₂-V₀) ×100%

Swelling shrinkage ratio: According to the above method, deionized water and injecting water of 10ml are added to the centrifuge tube and then the volume V₃ is read. Clay inhibitor solution of different concentrations are added into the above centrifuge tubes, placed for 4 hours in the indoor temperature and then put into centrifugal machine. After being centrifugalized for 15minutes in the rotate speed of 1500r/min, bentonite power volume V₄ is read after swelling shrinkage.

The equation of swelling shrinkage ratio is P= (V₃-V₄) / V₃×100%

| Material name          | Swelling prevention percentage, % | Swelling shrinkage ratio, % |
|------------------------|-----------------------------------|-----------------------------|
| alkylolamides          | 83.9                              | 46.8                        |
| N-propyl-N,N,N-three methyl ammonium chloride | 88.2 | 51.4 |
| Potassium polyacrylate | 80.4                              | 49.3                        |
| Aluminium polychlorid | 79.7                              | 47.9                        |

From the experiment results, all the filtered main materials have higher swelling shrinkage percentage and swelling shrinkage ratio. By contrast, the swelling prevention and swelling shrinkage effect of N-propyl-N,N,N-three methyl ammonium chloride is excellent, so N-propyl-N,N,N-three methyl ammonium chloride is chose as main material of clay inhibitor.
Table 2 the influence of N-propyl-N,N,N-three methyl ammonium chloride dosage on the swelling prevention and swelling shrinkage effect

| N-propyl-N,N,N-three methyl ammonium chloride dosage, % | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|-------------------------------------------------------|---|---|---|---|---|---|---|---|---|----|
| Swelling prevention percentage, %                     | 66.5 | 80.9 | 84.1 | 90.7 | 92.1 | 92.3 | 92.2 | 92.0 | 92.4 | 92.8 |
| Swelling shrinkage ratio, %                           | 35.6 | 45.4 | 48.2 | 50.1 | 50.6 | 50.4 | 50.6 | 50.2 | 50.7 | 50.6 |

From Table 2, the influence of N-propyl-N,N,N-three methyl ammonium chloride dosage on the swelling prevention and swelling shrinkage effect is: when dosage is lower than 3 percent, swelling prevention percentage and swelling shrinkage ratio rise obviously, but when dosage is higher than 3 percent, the property is stable. So, the range of N-propyl-N,N,N-three methyl ammonium chloride dosage is from 3 to 5 percent.

2.3. Functional agents filtering

By using centrifugation evaluation methods, the swelling prevention effect of 3 functional agents is evaluated.

| Material name | 0 | DMC | γ-propyl three methoxy silane | cetyl trimethyl ammonium bromide |
|---------------|---|-----|--------------------------------|---------------------------------|
| Swelling prevention percentage, % | 54.2 | 87.9 | 91.6 | 84.6 |
| Swelling shrinkage ratio, % | 9.6 | 43.8 | 52.3 | 45.9 |

From Table 3, the addition of functional agents could improve swelling prevention effect of clay inhibitor. Among them, the addition of functional agent γ-propyl three methoxy silane improves swelling prevention percentage obviously, so it is chose as functional agent.

Table 4 the influence of γ-propyl three methoxy silane dosage change on the swelling prevention and swelling shrinkage effect

| γ-propyl three methoxy silane dosage, % | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 5.0 |
|----------------------------------------|---|-----|-----|-----|-----|-----|-----|-----|-----|----|
| Swelling prevention percentage, %      | 44.8 | 73.3 | 86.2 | 90.5 | 92.3 | 92.4 | 92.6 | 92.1 | 92.4 | 92.3 |
| Swelling shrinkage ratio, %            | 9.4 | 38.3 | 42.7 | 50.8 | 54.1 | 54.8 | 54.2 | 54.6 | 54.5 | 54.4 |

From the experiment results, along with the addition of γ-propyl three methoxy silane and the increase of dosage, the swelling prevention percentage of core sample improves obviously. When dosage is lower than 2 percent, swelling prevention percentage improves from 44.8 to 92.5 percent and swelling shrinkage ratio improves from 9.4 to 54.1 percent, but when dosage is higher than 2 percent, the property is stable. So, the range of γ-propyl three methoxy silane dosage is from 1.5 to 2 percent.

2.4. Additives filtering

In order to improve swelling prevention effect of clay inhibitor, additive is needed. Table 5 is filtering experiment of different additives.
Table 5 The filtering results of additives

| Material name                  | 0              | 2,3-propylene oxide three methyl ammonium chloride | PEG | secaline |
|-------------------------------|----------------|--------------------------------------------------|-----|---------|
| Swelling prevention percentage, % | 52.2           | 88.4                                             | 91.5 | 90.7    |
| Swelling shrinkage ratio, %    | 18.6           | 44.4                                             | 51.9 | 47.9    |

From Table 5, all the additives are polymeric substances in strong-polarity which owns bigger molecular clew, diffusion ability and proper molecular shape. Additives are absorbed to several clay particles to form the bridge through hydrogen bond force and electrostatic force, in order to prevent clay particles from dispersing. Thus, PEG is chose as additive.

Table 6 the influence of PEG dosage change on the swelling prevention and swelling shrinkage effect

| PEG dosage, % | 0       | 0.1     | 0.2      | 0.3       | 0.4 | 0.5       | 0.6       | 0.7     | 0.8       | 0.9     |
|---------------|---------|---------|----------|-----------|-----|-----------|-----------|---------|-----------|---------|
| Swelling prevention percentage, % | 56.4 | 69.2 | 72.6 | 80.1 | 90.3 | 92.8 | 92.2 | 92.4 | 92.7 | 92.5 |
| Swelling shrinkage ratio, %       | 18.4 | 29.8 | 37.6 | 46.7 | 53.6 | 54.4 | 54.1 | 53.9 | 54.5 | 54.1 |

From the experiment results, long with the addition of PEG and the increase of dosage, the swelling prevention percentage of core sample improves obviously. When dosage is lower than 0.5 percent, swelling prevention percentage improves from 56.4 to 92.8 percent and swelling shrinkage ratio improves from 18.4 to 54.4 percent, but when dosage is higher than 0.5 percent, the property is stable. So, the range of PEG dosage is from 0.4 to 0.5 percent.

2.5. Confirm the basic formula

On the basis of optimizing every component, the basic formula of clay inhibitor CYY-2 is confirmed. The main components are:

1. N-propyl-N,N,N-three methyl ammonium chloride(C₉H₁₉ClN₂O), the dosage is from 3 to 5 percent, the best dosage is 4 percent.
2. γ-propyl three methoxy silane(C₉H₂₁NO₃Si), the dosage is from 1.5 to 2 percent, the best dosage is 2 percent.
3. PEG (HO(CH₂CH₂O)nH), the dosage is from 0.4 to 0.5 percent, the best dosage is 0.5 percent.

3. Performance evaluation of clay inhibitor

3.1. Swelling prevention effect evaluation

3.1.1. The examine on interplanar spacing change. By using X-ray diffractometer evaluation method, the spacing of calcium montmorillonite sample is determined by diffraction analysis. The interplanar spacing, d value, of calcium montmorillonite in completely hydrated state is regarded as upper limit ratio to estimate swelling prevention effects of clay inhibitor.

Eight clay inhibitors and the developed clay inhibitor are prepared to solutions of different concentration respectively, and then calcium montmorillonite of a certain quality is put into different solutions. After 24 hours, they are centrifuged and sedimentated, then prepared to samples for X-ray diffraction analysis. The spacing of calcium montmorillonite of different clay inhibitors under different concentrations is measured. The results are shown in Table 7.
Table 7 The spacing of calcium montmorillonite of different clay inhibitors under different concentrations

| Clay inhibitor | 0.5% | 1.0% | 1.5% | 2.0% | 2.5% | 3.0% | 4.0% |
|----------------|------|------|------|------|------|------|------|
| KCL            | 21.3635 | 18.6419 | 16.8321 | 16.2745 | 16.1852 | 15.8871 | 15.7982 |
| NH₄Cl          | 22.6550 | 16.1852 | 16.0968 | 16.6420 | 16.0968 | 15.7874 | 15.6541 |
| BC-61          | 19.7623 | 18.5241 | 15.8371 | 14.5761 | 14.5834 | 14.8284 | 14.7124 |
| BC-81          | 19.8571 | 18.0704 | 16.8575 | 14.6541 | 14.4984 | 14.3651 | 14.7524 |
| XK-2           | 19.6542 | 18.5436 | 16.7425 | 15.6332 | 14.7965 | 14.6547 | 14.7125 |
| HT-1           | 19.7852 | 18.5541 | 16.8124 | 15.8126 | 14.8274 | 14.7691 | 14.6873 |
| HYZ-g          | 21.3214 | 19.2456 | 18.2125 | 16.4531 | 15.6547 | 14.7723 | 14.8142 |
| JDB            | 22.1251 | 19.8823 | 18.5641 | 16.7652 | 15.6642 | 14.2387 | 14.5124 |
| CYY-2          | 17.8155 | 16.2446 | 14.5596 | 14.2728 | 14.3732 | 14.4785 | 14.5562 |

Some conclusions can be drawn from the test results. For the clay inhibitors BC-81 and BC-61, when the concentration is more than 2 percent, interplanar spacing diminishes and the swelling prevention effect is best. For the clay inhibitors XK-2, HT-1, HYZ-g and JDB, when the concentration is more than 2.5 percent, the swelling prevention effect is best. For the developed clay inhibitors CYY-2, when the concentration is more than 1.5 percent, the swelling prevention effect is best. For the inorganic salt KCl, NH₄Cl, their swelling prevention effect is poor, because the ionic adsorption of inorganic salt is reversible.

3.1.2. Stable effect evaluation. Washing experiment: The dry samples treated with clay inhibitors are rinsed with deionized water for 3 times, then the spacing d changes before and after washing are analyzed and measured.

The water immersion test: The calcium montmorillonite samples were soaked in the clay inhibitor solution of best concentration. They are placed for 24 hours after fully stirring. Then clay inhibitor solution is emptied and deionized water is added. After stirring and 24 hours of fully immersing, the samples are centrifuged and sampled to analyze. Test results are shown in Table 8.

Table 8 The spacing changes of calcium montmorillonite samples before and after washing and water immersion

| Clay inhibitor | Dosage % | The spacing of dry sample ×10⁴um | The spacing of sample after washing ×10⁴um | The spacing of sample before water immersion ×10⁴um | The spacing of sample after water immersion ×10⁴um |
|----------------|----------|--------------------------------|------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| KCL            | 3        | 13.7639                        | 19.7754                                  | 16.0854                                       | 16.6234                                       |
| NH₄Cl          | 3        | 13.5586                        | 21.0346                                  | 16.0966                                       | 16.5217                                       |
| BC-61          | 2        | 14.1412                        | 14.9532                                  | 14.5561                                       | 14.6532                                       |
| BC-81          | 2        | 14.2426                        | 14.5213                                  | 14.6231                                       | 14.7156                                       |
| XK-2           | 2.5      | 14.1953                        | 14.5741                                  | 14.8421                                       | 14.9781                                       |
| HT-1           | 2.5      | 14.8652                        | 14.6213                                  | 14.3215                                       | 14.4452                                       |
| HYZ-g          | 2.5      | 14.8032                        | 14.5214                                  | 14.2254                                       | 14.5416                                       |
| JDB            | 2.5      | 14.8621                        | 14.5126                                  | 14.6213                                       | 14.8791                                       |
| CYY-2          | 1.5      | 14.1034                        | 14.2236                                  | 14.1567                                       | 14.2213                                       |
Except that the swelling prevention effect and stable effect of inorganic salt KC1 and NH4C1 is poor, other clay inhibitors are better. Among them the property of clay inhibitor CYY-2 is excellent.

3.2. Dynamic evaluation of swelling prevention effect

3.2.1. Dilatometer test method. By using JHPZ-II intelligent dilatometer bearing high temperature and pressure, at the temperature of 60°C, pressure of 5MPa conditions, bentonite powders and natural core powders crushed to below 0.9mm in different reservoirs are added to different clay inhibitors solutions. The expansion rate of them is determined. Table 9 is the measured swelling prevention percentage and expansion rate.

The specific experimental method is: the core powder of 5.0g is put into core barrel of dilatometer. Suppress for 5 minutes under the pressure of 5MPa. The expanding height \( H_0 \) is measured by using deionized water. The expanding height after antiswelling agent solution is added is \( H_1 \). The calculation formula is: \( F = \frac{(H_0 - H_1)}{H_0} \times 100\% \).

| Antiswelling agent dosage | Original height | Stopping height | The growth | Swelling prevention percentage | Swelling shrinkage ratio |
|---------------------------|----------------|----------------|------------|-------------------------------|-------------------------|
| Bentonite                 | /              | 8.197          | 16.749     | 8.552                         | 104.33                  |
| CYY-2                     | 1.5%           | 8.144          | 9.104      | 0.87                          | 10.7                    | 89.74                  |
| The well Tong 47X         | /              | 14.256         | 14.422     | 0.166                         | 1.3                     | /                      |
| CYY-2                     | 1.5%           | 14.261         | 14.288     | 0.027                         | 0.19                    | 83.6                   |
| The well Ba 38-2          | /              | 14.278         | 14.448     | 0.017                         | 0.19                    | /                      |
| CYY-2                     | 1.5%           | 14.001         | 14.03      | 0.029                         | 0.21                    | 82.9                   |

The results show that for bentonite powder and core powder from different reservoirs, the screened clay inhibitors CYY-2 have better swelling prevention effect under the condition of 60°C and 5MPa. The swelling prevention percentage on bentonite can reach 90 percent, for different reservoir core powder it can reach 80 percent.

3.2.2. The ability tests on preventing core particles from spalling and dispersing. Take reservoir core particles of 20 to 40 meshes from well Zhou 16-41 of 3.00g. They are put into sieve of 4cm diameter and 60 meshes. Deionized water of 100ml and different concentrations of clay inhibitor CYY-2 and antiswelling agent XK-2 solution is put for 4 hours of soak. They are weighed after sieving and analyzing. The weight loss ratio is calculated. Test results are shown in Table 10.

| Chemical name and dosage | Deionized water | CYY-2 | XK-2 |
|--------------------------|-----------------|-------|------|
| weight loss ratio, %     | 81.6            | 14.7  | 10.2 |
|                          | 10.2            | 8.5   | 42.1 |
|                          | 38.7            | 35.9  |      |

Test results show that if the dosage of filtered clay inhibitor in solution is 1.0 to 2.0 percent, the weight loss ratio of core particles used in test is less than 15 percent. If the dosage of antiswelling agent XK-2 in solution is 2.0 to 3.0 percent, the weight loss ratio of core particles used in test is more than 35 percent. The weight loss ratio is 81 percent in deionized water. The above conclusions show
that clay inhibitor CYY-2 has better ability to inhibit reservoir clay minerals from hydrating, expanding and dispersing in the static condition.

3.2.3. Evaluate prevention effect of clay inhibitor by core tests. Using washing oil core from block Tong 47 with well Tong 12X, block Yan 9 with well Yan 9-5X and block Ba 38 with well Ba 38-2, adopting core evaluation test method, prevention effect of screened clay inhibitor in 1.5 percent concentration is examined. Test results are shown in Table 11.

| Well   | Core NO. | Permeability of injecting saline $\times 10^3\mu m^2$ | Permeability of injecting deionized water $\times 10^3\mu m^2$ | Damage rate of permeability % | Injection order |
|--------|----------|------------------------------------------------------|---------------------------------------------------------------|--------------------------------|----------------|
| Tong 12X | 12-1     | 6.8                                                  | 0.89                                                          | 86.9                          | Inject saline and then deionized water |
|         | 12-2     | 6.45                                                 | 5.63                                                          | 12.8                           | Inject saline and then clay inhibitor, deionized water |
| Yan 9-5X | Y5-1     | 3.29                                                 | 0.45                                                          | 86.3                           | Inject saline and then deionized water |
|         | Y5-2     | 2.93                                                 | 2.57                                                          | 12.3                           | Inject saline and then clay inhibitor, deionized water |
| Ba 38-2 | 38-1     | 3.29                                                 | 0.45                                                          | 87.3                           | Inject saline and then deionized water |
|         | 38-2     | 2.93                                                 | 2.57                                                          | 12.6                           | Inject saline and then clay inhibitor, deionized water |

Core test results show that due to prevention effect of clay inhibitor, core damage rate of each block is greatly reduced after being treated with clay inhibitor.

4. Field test and effect
As the extension of developing time, some injection wells had many problems such as rising injection pressure, decreasing injection volume and being difficult to accomplish injection allocation, which had bad influence on the reservoir development effect. Since 2006, the field tests of 5 wells were carried out and 4 wells effective which measurement success rate is 80 percent, achieving good effect. For example, well Quan 241-9 was constructed on April 30 2006, and then water flooding pressure was rising from 20.5MPa to 18.5MPa, injection water volume was increased from 13.3m$^3$ to 19.7m$^3$, the cumulative injection water increased by 3146 m$^3$ in validity period, the validity period is 165 days. The cumulative increased oil of connected well, Quan 241-12, is 2064 tons.

5. Conclusions
Antiswelling agent matching water sensitive reservoir is used for water injection well treatment. It is not only necessary for low- permeability and water- sensitive reservoir development, but also can effectively control or slow down pressure rising rate of injection wells, thus improving exploration effect.

The developed bi-functional clay inhibitor not only could achieve good performance of 90 percent swelling shrinkage percentage and 90 percent swelling shrinkage ratio, but also obtained well effect in field application. The measurement success rate was 80 percent, the average decreasing water injection pressure was 3.2MPa, the average improving injection volume was 14.43m$^3$, and cumulative oil increment of oil wells corresponding to effective wells was 2680.9 tons.
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