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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

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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 $C_9H_{19}ClN_2O$, The molecular formula for γ-propyl three methoxy silane is $C_9H_{21}NO_3Si$, molecular formula for PEG is $HO(CH_2CH_2O)_nH$.

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 antiswelling 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 V_1 of bentonite power is read. The antiswelling agent solution is replaced by deionized water of 10ml and then the expanding volume V_2 in water of bentonite power is measure. The antiswelling agent solution is replaced by kerosene of 10ml and then the expanding volume V_0 in kerosene of bentonite power is measure.

The equation of swelling prevention percentage is $B=(V_2-V_1)/(V_2-V_0)\times100\%$

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 V_3 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 V_4 is read after swelling shrinkage.

The equation of swelling shrinkage ratio is $P=(V_3-V_4)/V_3\times100\%$

Table 1 The filtering results of main materials for clay inhibitor

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

Table 3 The filtering results of functional agents

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, %	44.8.2	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:

N-propyl-N,N,N-three methyl ammonium chloride($C_9H_{19}ClN_2O$), the dosage is from 3 to 5 percent, the best dosage is 4 percent.

γ-propyl three methoxy silane($C_9H_{21}NO_3Si$), the dosage is from 1.5 to 2 percent, the best dosage is 2 percent.

PEG ($HO(CH_2CH_2O)_nH$), 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	Interplanar spacing *d* (in different concentration)						
	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
NH_4CL	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, NH_4Cl, 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 is 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 inhibitors	Dosage %	The spacing of dry sample $\times 10^{-1}$um	The spacing of sample after washing $\times 10^{-1}$um	The spacing of sample before water immersion $\times 10^{-1}$um	The spacing of sample after water immersion $\times 10^{-1}$um
KCL	3	13.7639	19.7754	16.0854	16.6234
NH_4CL	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 NH_4C1 is poor, other clay inhibitors are better. Among them the propery 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: $F=(H_0-H_1)/H_0\times100\%$.

Table 9 The results of expansion rate for bentonite powder and core power

	Antiswelling agent dosage	Original height	Stopping height	The growth	Swelling prevention percentage	Swelling shrinkage ratio
Bentonite	/	8.197	16.749	8.552	104.33	/
	1.5% CYY-2	8.144	9.104	0.87	10.7	89.74
The well Tong 47X	/	14.256	14.422	0.166	1.3	/
	1.5% CYY-2	14.261	14.288	0.027	0.19	83.6
The well Ba 38-2	/	14.278	14.448	0.17	1.19	/
	1.5% CYY-2	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.

Table 10 The weight loss ratio of core particles in different chemicals

Chemical name and dosage	Deionized water	CYY-2			XK-2		
		1.0	1.5	2.0	2.0	2.5	3.0
weight loss ratio, %	81.6	14.7	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.

Table 11 Test results of clay inhibitor by core evaluation

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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