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Research of Temperature Resistant Clay Stabilizer

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Abstract

A new polyquarternary ammonium clay stabilizer was synthesized in aqueous solution at low temperature by chosing acrylamide (AM) and dimethyldiallylammonium chloride (DMDAAC) as starting materials and redox system as initiator. Its properties were evaluated, action mechanism was deeply studied and field tests were carried out in Chunliang oil field. Laboratory test of performance evaluation shows that it has good compatibility with acid and formation water, good swelling inhibiting ability, swelling inhibiting rate of 1% CSR is over 90% measured whether by dilatometer or centrifugalization method, it has good erosion and temperature resistant property and long effect. It has been applied for 19 wells, the results also indicate it has success ratio of 100% and period of validity is more than 200 days when CSR is applied as clay stabilizer to deal with oil and water well, it has achieved great stimulation effect.

Key words: Clay stabilizer; Swelling inhibiting ability; Performance evaluation; Long effect; Temperature resistant property

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INTRODUCTION

With the increasing development of oilfield, the reserves are decreasing rapidly and the reservoir protection technology is attracting more and more attention. The reservoirs with high clay content, fine pore and strong hydrophilic, are likely to occur clay hydration swelling, migration and plugging pores and result in serious damage to the reservoirs as long as water based filtrate invades the formation during drilling, cementing, water injection, fracturing, acidizing, workover, killing and any treatment.[1-3] Thus, it is importance of developing excellent and adaptable clay stabilizer. This paper introduces a new polyquaternary ammonium cationic clay stabilizer synthetized at low temperatures over long periods. The molecular chains of this clay stabilizer contain both cations and non-ionic groups. The cations could neutralize negative charges of clay, decrease repulsive force between the crystal layer and the particles, and result in crystal layer shrinking and difficult to hydration swelling and dispersing. The non-ionic groups could adsorb clay particles to the particles between multi-crystal layers, thereby stabilize the clay particles. This stabilizer could employ in water injection, acidification and other treatment with fine compatibility, anti-scour ability, long-term effect, high-temperature resistance, etc.

1. EXPERIMENT

1.1 Reagents and Instruments

Reagent: acrylamide (AM), analytical pure; dimethyl diallyl chloride (DMDAAC), 60% aqueous solution, polymerization level (low temperature storage); oxidant, analytical pure; reducing agent, analysis pure; ethylenediamine tetraacetic acid disodium (EDTA), analytical pure.

Instruments: NP-01 shale dilatometer; WGI-2 turbidimeter; core flow test apparatus.

1.2 Polymerization Reaction

Add AM, deionized water, DMDAAC and EDTA to a reaction flask and stir them adequately until dissolved. Put the flask in the ice water bath for cooling (below 20℃) then nitrogen is injected for sweeping away oxygen. Add initiator to the flask and seal it. Reacting under constant temperature below 20℃ for 3 hours, then warming up to 40℃ and reacting 6-8 hours. The reaction products appear elastic and transparent gels. Then the products are prilling, dried and crushed to turn into CSR clay stabilizer.

1.3 Experience Procedure

1.3.1 Centrifuging

Take 0.5 g of bentonite in a 10 mL centrifuge tube, then add 10 mL of clay stabilizer solution and shake sufficiently. Store the tube for 2 hours at room temperature, then place it in the centrifuge for separating over 15 min at 1,500 r/min. Turn off and read the swelling volumes of bentonite in the centrifugal tube for recording as V_1. Take 0.5 g of bentonite powder in a 10 mL centrifuge tube, then add 10 mL distilled water or kerosene to respectively for replacing clay stabilizer solution, and repeat aforementioned experience procedures for measuring the swelling volumes of clay in water or kerosene, recording as V_2 or V_0. Calculate the anti-swelling rate followed by Equation 1.

$$\text{The Anti-Swelling Rate } B_1 = \frac{V_2 - V_1}{V_2 - V_o} \times 100\% . \qquad (1)$$

In the equation: B_1: the anti-swelling rate, %; V_1 : The swelling volume of bentonite in clay stabilizer solution, mL; V_2: The swelling volume of bentonite in water, mL; V_0: The swelling volume of bentonite in kerosene, mL.

1.3.2 Swelling Testing

Take 10 g of clay in the test cylinder, then pressurize until 4 MPa by the core pressurization device and hold for 10 min. Take out the cylinder for ready-to-use. Install the cylinder in the swelling test instrument and set to zero. Add stabilizer solution to the cylinder for soaking the core. Start the recorder. When swelling curve is vertical, record height of core swelling as H_1. Measured the swelling height of the core in water or kerosene in the same way, and record as H_2 or H_0. Calculate the anti-swelling rate followed by Formula (2).

$$\text{The Anti-swelling rate } B_2 = \frac{H_2 - H_1}{H_2 - H_o} \times 100\% . \qquad (2)$$

2. RESULTS AND DISCUSSION

2.1 Compatibility With Acids and Additives

Take 100 ml of each acid system and 3.0% CSR for compatibility experiments in normal temperature/pressure and 150℃/high pressure respectively. The acid systems include acids (15% HCl, conventional mud acid and 20% of multivariate low-damage composite acid) and other acid additives (1.5% complexing agent, 2.0% YJN gelling agent, 1.0% YSH-1 corrosion inhibitor, 0.5% YQX-3 detergent, 1.0% YZP-1 discharge aiding agent). Place for three days under normal temperature then place for 6 hours under high temperature. Observe any appearance such as sediment, layer, turbidity and so on (see table 1). The results show that the acid solution is clear and transparent without sediment, layer and turbidity. It shows that CSR is compatibility with acid and additives.

Table 1
Compatibility of CSR With Acid and Additives

Component	Temperature (℃)	Apprearance
3.0% CSR + 15% HCl	30	Transparent, no sediment, no reaction
	150	Transparent, no sediment, no reaction
3.0% CSR + conventional mud acid	30	Transparent, no sediment, no reaction
	150	Transparent, no sediment, no reaction
3.0% CSR + 20% multivariate Low-damage composite acid	30	Transparent, no sediment, no reaction
	150	Transparent, no sediment, no reaction

2.2 Compatibility With Formation Water

Mix produced water of Chun 23-22 well in Chunliang oilfield with clay stabilizer CSR solution in different proportions, and place for 48 hours at 90℃. It shows that the water samples are clear without sediment and CSR is compatibility with formation water.

2.3 The Anti-Swelling Rate

According to chapter 6 in the petroleum and natural gas industry standard of SY/T 5971-1994 "Evaluation method of clay stabilizer for water injecting", we test the anti-swelling rate of 1.0% synthetic product solution to bentonite by centrifuging and swelling testing respectively, and the experimental results are compared with conventional clay stabilizers used in Shengli Oilfield. The experimental results are shown in Table 2.

Table 2
The Experimental Results of CSR and Anti-Swelling/Sand Control Agent Conventional Clay Stabilizers Used in Shengli Oilfield

Samples	The anti-swelling rate(%)		Sand control properties	
	Centrifuging	Swelling testing	Turbidity	Sand content(mg/L)
SW-91	91.2	88.3	68.2	36.2
FGW-1	86.6	82.2	78.3	52.7
DTE	89.3	83.4	80.1	57.5
GD-9	92.2	83.8	72.4	43.3
DQW-1	87.5	81.6	75.1	45.4
FSJ-03	90.4	82.7	70.3	38.5
CSR	93.3	90.4	62.7	32.2

Note. SW-91, FGW-1, DTE, GD-9, DQW-1, FSJ-03 and other products are produced in Shengli Oilfield or have been widely applied in the present.

2.4 Determination of Sand Control Properties and Turbidity

According to the same industry standard (SY/T 5971-1994), take 57.3 g of quartz sand and 2.7 g of kaolin and mix until blended. Then pour into the core cylinder with diameter of 25 mm and long of 100 mm, and pressurize until the core height is 86 mm. Vacuum the core cylinder till saturation. Add 1% sample solution (30 mL), and place for 10 min. Then put the cylinder into the displacement device, and displace the core with water at the flow rate of 900 mL/h for 2 hours. Collect all effluent fluids and measure the sand content and turbidity. The results also see Table 2.

From Table 2, CSR presents better properties of anti-swelling and sand control compared to conventional products used in Shengli Oilfield present. The anti-swelling rates are all over 90% measured by centrifuging and swelling testing due to the molecules of CSR possess the space grid structures, so have a strongly inhibition effects to clay particles and the non-clay particles, and can adsorp on the clay surfaces in more points and form a strongly film. Quaternary ammonium ions can neutralize the negative charges between clay crystal layers through ions exchanging, so result in less electrostatic repulsion between the clay crystal layers and are difficult to hydration swelling and migration with the properties of bridging, adsorbing, and sand encapsulating.

2.5 Long-Term Test

The long term of clay anti-swelling agent, i.e. the validity period,[4] refer to the time of preventing clay hydration swelling effectively after the formation has been treated with anti-swelling agent. The longer of anti-swelling effect, the better of the long term of clay anti-swelling agent. The properties of long term also influence effect of clay anti-swelling agent and economic benefits.

Through the core flow experiment, displace the core treated by clay stabilizer with fresh water for long time, then evaluate the long-term effect of clay stabilizer according to permeability damage value. The core is from Fan 23-724 Well, with diameter of 25 mm and length of 50-70 mm. The simulation method is as follows: inject formation water of Chunliang into the core which has been treated by extracting and washing oil with 3:1 of benzene: alcohol at flow rate of 0.25 mL/min on the constant-flux pump; measure the base permeability recorded as k_1; inject clay stabilizer solution of 10-15 PV into the core at the same flow rate, and stop the pump for 10-12 hours; displace the core with fresh water for 120 hours at higher flow rate of 5, 3, 2 mL/min, and then displace the core with formation water of Chunliang at flow rate of 0.25 mL/min for 8 h; measure core final permeability recorded as K_2, and calculate the core permeability damage rate. The results are shown in Table 3.

Table 3
Measures Long-Term Performance of Clay Stabilizer

Core samples No.	1% clay stabilizer	Initial permeability k_1 ($10^{-3}\mu m^2$)	Final permeability K_2 ($10^{-3}\mu m^2$)	Core permeability damage rate (%)
Fan 23-724-1	SW-91	9.36	8.23	12.07
Fan 23-724-2	FGW-1	9.42	7.28	22.72
Fan 23-724-3	DTE	9.38	8.21	12.47
Fan 23-724-4	GD-9	9.48	8.32	12.24
Fan 23-724-5	DQW-1	9.32	7.52	19.31
Fan 23-724-6	FSJ-03	9.36	7.31	21.90
Fan 23-724-7	CSR	9.43	8.98	4.77

From Table 3, after scour the core which has been was treated by clay stabilizer with water for long time, the permeability of core decreases a little. The core minimum damage rate of CSR is only 4.77%. It shows that CSR possess preferable resistance to scouring and longer term properties for core. This is because the molecular structure of CSR contains stable six-member ring structures, and non-ionic monomer contains functional groups in the side group, so the product could form strongly adsorption film on clay surface and improve the ability of its resistance to scouring, and then provent the invasion of water molecules and clay particle dispersion, thus clay hydration swelling is inhibited and particles dispersion/ migration is controlled effectively.

2.6 Resistance to Temperature

Prepare 10% aqueous solution of CSR anti-swelling sand inhibitor and put in the high-pressure vessel, heat slowly at 1℃/min, place for 20 days in constant 300℃. At first take the sample every two days, after 10 days taking the sample every five days. Observe any changes of the solution and perform clay anti-swelling experiment with clay stabilizer treated at high temperature. The results are shown in Table 4.

Table 4
Temperature Resistance Properties of CSR

Aging time at high-temperature(day)		0	2	4	6	8	10	15	20
Appearance		Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
The anti-swelling rate (%)	Centrifuging	93.3	91.8	91.1	90.9	90.4	90.2	90.2	90.1
	Swelling testing	90.4	88.2	87.7	87.3	87.2	87.1	87.1	86.6

From Table 4, the solution of CSR clay stabilizer presents clear, non-discoloring, 20 days, no floccules and sediments after 20 days at high temperature of 300℃. Its anti-swelling properties decrease less comparing with the properties before the heat treatment process. It shows that CSR possess excellently temperature resistant performance.

3. MECHANISM OF CSR

The molecular chains of CSR organic cationic polymer contain positively charged macromolecules and can act on clay minerals strongly. Thus CSR can prevent wellhole collapse and cuttings dispersing and reduce reservoir damages by external fluid. CSR can be widely applied in drilling fluid, completion fluid, workover fluid, water injection and acidification fracturing fluid. Its mechanism is as follows:[5~6]

(a) The positively charged atoms or groups on molecular chains of CSR may be exchanged by monovalent or bivalent cations on clay, thus numerous positively charged atoms on macromolecular chains or groups “neutralize” the negative charge between the crystal layers or on the surface of clay. So the electrostatic repulsion between crystal layers and particles is reduced, tightly bound, not easy to decompose and hydration swelling when touching water.

(b) CSR polymer molecules possess strongly electrostatic attraction, hydrogen bonding and Van der Waals force with clay, therefore the large molecules can firmly adsorb on the clay and other particles to form a layer of adsorption layer, so as to prevent the clay hydration.

(c) The long chains of CSR can adsorb on multiple crystal layers and particles at the same time, thus inhibit dispersion and migration of clay. It is because of multipoint adsorption of CSR molecular, adsorption force is very strong, and is difficult to release adsorption force under external force in the meantime. Due to the stability of the molecular structures of CSR quaternary ammonium itself, its base properties are not essentially affected by acid and alkali , so CSR can resist to wash with acid, alkali, oil and water, and is stable and long-term.

In a word, CSR cationic polymer can form permanent irreversible adsorption on the clay particles. Once adsorbing on clay, it is difficult to be desorpcia or exchanged by other monovalent or bivalent ions, and can form the strongly protective film, so as to prevent the intrusion of water molecules and particles dispersed, and to meet the requirements of inhibiting hydration swelling of the clay and controlling dispersing or migrating of the particles.

CONCLUSION

(a) The clay stabilizer CSR is developed. It possess excellent properties of compatibility, anti-swelling, sand control and temperature resistance.

(b) The core can not be damaged by CSR clay stabilizer. After injection of a large number of fresh water, CSR still has strongly anti-swelling effect on clay. The permeability damage values of all cores are less than 5%. SCR presents excellent anti-scour ability and long-term effect.

(c) CSR is an adaptable stabilizer and can be used in acidizing process for high efficiency, long-term validity, and increased production or injection.

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