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Effect of Free Ammonium on Performance Destabilization of Drilling Fluid and Chemical Remedial Measures

Zhou Jian[1], Wu Weilin[2], Liu Haobing[3], Liu Xin[4], Luo Xiao[1*], Lu Fuwei[1], Hu Sanqing[1]

1. College of Chemistry and Environmental Engineering, Yangtze University, Jingzhou, Hubei 434023, China;

2. Petroleum Engineering Technology Research Institute, Jiangsu Oilfield Company, Sinopec Group, Yangzhou, Jiangsu 225009, China;

3. No. 1 Drilling Company, Sinopec Oilfield Service Jianghan Corporation, Qianjiang, Hubei, 433121, China;

4. Drilling Fluids Technology Service Company of CNPC Bohai Drilling Engineering Company Limit., Tianjin 300457, China

ABSTRACT

While long-term storage of amine-based inhibitors was injected into the drilling fluid, many problemswould come out such as increased fluid loss and wellbore instability.Ammonia was added to the inhibitor to simulate the free ammonium in the amine-based inhibitor, and the effect of free ammonium on destabilization performance of drilling fluid was investigated.The results showed that the inhibitor had no damage to the performance of the drilling fluid when the ammonium ion concentration was not more than 0.185 mmol/L. When the ammonium ion was higher than 0.301 mmol/L, the filter cake became thicker and the water loss increased greatly.The free ammonium component of the displacement inhibitor is neutralized with acetic acid and its potassium salt.The results show that the same molar concentration of potassium acetate as the free ammonium can produce an ion exchange effect with free ammonium.The addition of the corresponding concentration of potassium acetate to the amine-based inhibitor containing free ammonium restores the fluid loss and can be used to urgently treat amine-based inhibitors with unstable field properties.

Keywords : amine-based inhibitor; free ammonium; well wall instability; potassium acetate; ion exchange

INTRODUCTION

In the process of oil and gas drilling, hydration expansion and dispersion of mud shale can lead to problems such as instability of the borehole wall, difficulty in purifying the mud bit and purification of the wellbore[1-3].In order to solve these problems, the shale hydration expansionwas mainly suppressed by adding an amine inhibitor to the drilling fluid[4].Tian Yuexi et al.[5] used electrostatic adsorption between the primary amine and the clay layer at the end of the amine polymer to weaken the hydration of the clay. The hydrophobic group of HGI covered the surface of the clay layer to form a hydrophobic barrier, which improved the inhibition performance of the drilling fluid in the field.Chuzheng[6] used a small cationic inhibitorto inhibit clay hydration.When small cation encounters shale formation during drilling, it can effectively solve a series of problems such as hydration expansion of shale, wellbore instability caused by dispersion, bit mud pack and wellbore purification[7-9] .

However, a series of complicated situation are caused when using an expired amine-based inhibitor with a long storage time.On-site sampling indoor test results show that when the amount of amine-based inhibitors stored for too long is about 1%, the pressure loss in the drilling fluid is out of control, and the mud cake is thick.Field engineers are struggling to come up with specific solutions when the performance of drilling fluids due to the addition of unqualified amine-based inhibitors deteriorates.In view of the relationship between the specific problems at the site and the structure of the amine-based inhibitor, ammonia was added to the high-quality amine-based inhibitor to simulate the free ammonium in the amine-based inhibitor, and the relationship between the free ammonium concentration and the performance of the drilling fluid was investigated, and the solution was found. A solution to the deterioration of drilling fluid performance caused by free ammonium in amine based inhibitors.

MATERIALS AND METHOD

Experimental materials and instruments

Experimental materials: bentonite (Jianghan Drilling Mud Company), anhydrous sodium carbonate (Chemical Reagent Co., Ltd.), MMCA (Jiangsu Drilling Mud Company), Coater (Jiangsu Drilling Mud Company), K-1 (Jianghan Drilling Mud Company), YFT (PetroChina Bohai Drilling Mud Company), QS-2 (Jiangsu Drilling Mud Company), NH-1 Organic Amine Inhibitor (Taizhou Fine Chemical Plant), Concentrated Ammonia Water (25%), Acetic Acid, Potassium Acetate (Sinopharm Group Chemical Reagent Co.,Ltd.).

Experimental equipment: frequency conversion high-speed mixer (Qingdao Haitongda special instrument factory), JJ-1 precision booster electric mixer (Changzhou Hao Instrument Co., Ltd.), rotational viscometer (Qingdao Chuangmeng Instrument Co., Ltd.), medium pressure water loss meter (Qingdao Chuangmeng Instrument Co., Ltd.), XGRL-4A high temperature roller heating furnace (China Qingdao Haitongda Special Instrument Factory), LG10-24 Centrifuge (Shanghai Zhizheng Centrifuge Co., Ltd.), constant temperature drying oven, X'PertPRO MPD Type X-ray diffractometer.

Drilling fluid preparation and performance test

Drilling fluid formula: 5% bentonite + 0.15% anhydrous sodium carbonate + 0.3% MMCA + 0.2% Coater + 0.6% drilling fluid with anti-collapse fluid loss agent K-1 + 1.5% YFT + QS-2.

The amine-based inhibitors simulating different free ammonium contents were added to the drilling fluid, and the performance of the drilling fluid was tested after aging at 120 °C for 16 h.

Clay layer spacing measurement experiment

Organic amine inhibitors and organic amine inhibitors with different ammonium ion concentrations were added to 2% bentonite slurry and stirred at high speed for 30 min.The cells were allowed to stand for 24 h under closed conditions, stirred for 5 min before the experiment, and then centrifuged at a speed of 3000 r/min for 30 min.The supernatant was decanted and a portion of the precipitate was taken for wet X-ray diffraction analysis.

RESULTS AND DISCUSSION

Analysis of the causes of deterioration of drilling fluid performance caused by expired amine-based inhibitors

In view of the problem of deterioration of drilling fluid performance caused by on-site NH-1, the comparison of NH-1 amine-based inhibitor samples and indoor recent synthetic samples in the field for more than one year was carried out, as shown in Figure 1.

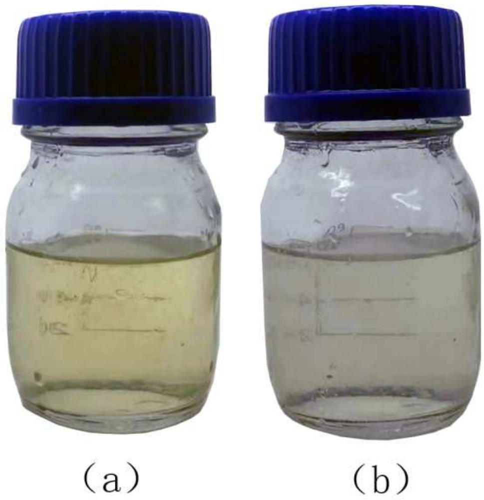

Figure 1 Different batches of nh-1 samples
(a) on-site samples; (b) indoor samples

It can be seen from the figure that the indoor synthetic sample is a colorless transparent liquid, and the NH-1 amine-based inhibitor with on-site extraction time of more than one year is yellowish, This may be due to the long-term natural decomposition of the NH-1 amine-based inhibitor.

NH-1 is a commonly used amine-based inhibitor in the drilling market, and its molecular structure in water is shown in formula (1).

$$H_2N-R_1\left(O-R_2\right)_m\left(O-R_3\right)_n NH_2 + 2\,H_2O \longrightarrow H_3\overset{\oplus}{N}-R_1\left(O-R_2\right)_m\left(O-R_3\right)_n \overset{\oplus}{N}H_3 + 2\,OH^- \quad (1)$$

Yuan Junxiu et al[11] believe that NH-1 can react with water to form $–NH^{3+}$ in water, which has weak dissociation effect.The NH-1 molecular state is relatively stable without contact with water.However, if it is exposed to moisture during the inventory, the $-NH_2$ of the NH-1 end group reacts with water to form NH^{4+}, which may generate free ammonium and small molecular alcohol after long-term oxidation.Because small molecular alcohols don't have a significant impact on the performance of the drilling fluid system, the free ammonium produced after the decomposition of nh-1 may have a destructive effect on the performance of the drilling fluid.In order to confirm the speculated result, ammonia was added to the qualified NH-1 to simulate the free ammonium produced by the decomposition of NH-1, and the effect of free ammonium on the performance of the drilling fluid was investigated.

Effect of free ammonium on drilling fluid performance

Preparation of simulated free ammonium inhibitors

Assuming no free ammonium in NH-1, different concentrations of ammonia were added to nh-1 to simulate the free ammonium in the amine-based inhibitor. The ammonium ion concentration in the sample is shown in Table 1.

Table 1 simulated free ammonium concentration in NH-1

Nh-1 sample number	Free ammonium concentration (mmol/L)
a	0
b	0.092
c	0.185
d	0.301
e	0.463
f	0.533

The above-mentioned NH-1 added with free ammonium was added to the clay base slurry and drilling fluid system, and the effect of free ammonium on the performance of the drilling fluid was investigated systematically.

Effect on Bentonite Hydration

1% of NH-1 sample was added to clay. After standing for 24 hours, the effect of free ammonium on the hydration performance of bentonite was investigated by wide angle XRD. The results are shown in Fig. 2.

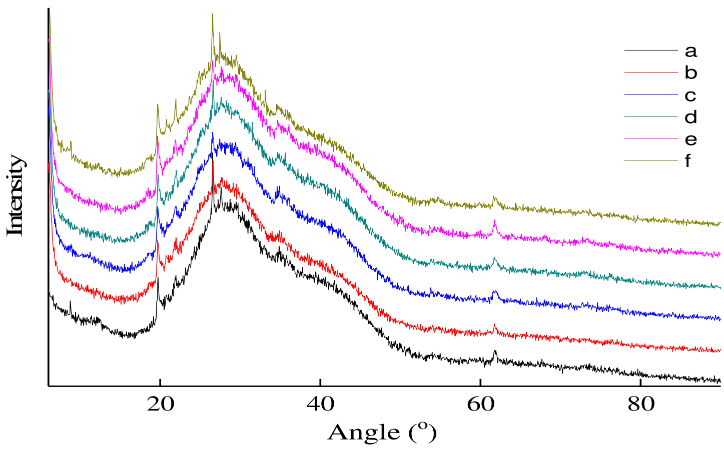

Figure 2 Effect of inhibitors on the crystal structure of clay

It can be seen from Fig. 2 that the crystal structure of clay immersed in different concentrations of free ammonium has not changed significantly, which is consistent with the interaction between nitrogen-containing compounds and bentonite.

Table 2 Inhibitors for clay crystal layer spacing

Sample	2θ(°)	d(nm)
a	26.65	0.109
b	26.76	0.103
c	26.76	0.103
d	26.71	0.106
e	26.81	0.101
f	26.76	0.103

It can be seen from Table 2 that different concentrations of free ammonium have little effect on the 2θ angle of clay, and there is no change in the overall configuration of the crystal.When blank a was added to the sodium bentonite slurry, the pitch d of the bentonite layer was 0.109 nm.After adding different concentrations of free ammonium to NH-1, the spacing of the bentonite layer was reduced.When the free ammonium concentration is greater than 0.301 mmol/L, the spacing of the bentonite layer is reduced to 0.101 nm, and the hydration of bentonite is weakened.This is due to the adsorption of free ammonium between the surface of the bentonite and the interlayer, and the water adsorbed between the layers is replaced by free ammonium and extruded.

Effect on the rheology of drilling fluid

The rheological samples of drilling fluids were tested by adding NH-1 samples containing different concentrations of free ammonium in the drilling fluid system. The results are shown in Table 3.

Table 3 Effect of free ammonium on rheology of drilling fluid system

Nh-1 number	AV(mPa.s)	PV(mPa.s)	YP(Pa)	YP/PV	G_{10s}/G_{10min}(Pa)	Aging condition
a	34	23	11	0.48	4.5/4.5	
	60	38	22	0.58	2.5/2.5	120□×24h
b	32.5	22	10.5	0.48	4/4	
	54	35	19	0.54	2.5/2.5	120□×24h
c	34.5	23	11.5	0.50	4.5/4.5	
	60	38	22	0.58	2.5/2.5	120□×24h
d	46	24	22	0.91	8.5/9	
	45	25	20	0.80	2.5/2.5	120□×24h
e	66	12	54	4.5	19/19	
	75	36	39	1.08	7.5/7.5	120□×24h
f	66	7	59	8.43	15/15	
	62.5	25	37.5	1.5	7/7	120□×24h

It can be seen from Table 3 that when the free ammonium concentration in NH-1 is below 0.301 mmol/L, the rheological index of the drilling fluid after aging does not change much, and there is no significant effect on the performance of the drilling fluid system.When the free ammonium concentration is above 0.301 mmol/L, the viscosity of the drilling fluid increases sharply, the dynamic plastic ratio exceeds the normal value, and the performance of the drilling fluid system deteriorates.This may be due to the fact that the free ammonium concentration exceeds the limit of the drilling fluid system, the negative point of the surface of the bentonite is adsorbed by the free ammonium, and the high molecular polymer MMCA cannot cooperate with the bentonite to form a weak gel structure.

Effect on mud cake quality and fluid loss

The effects of different concentrations of free ammonium on the pressure loss and mud cake quality in the drilling fluid system after 120 °C aging are shown in Figure 2 and Table 3.

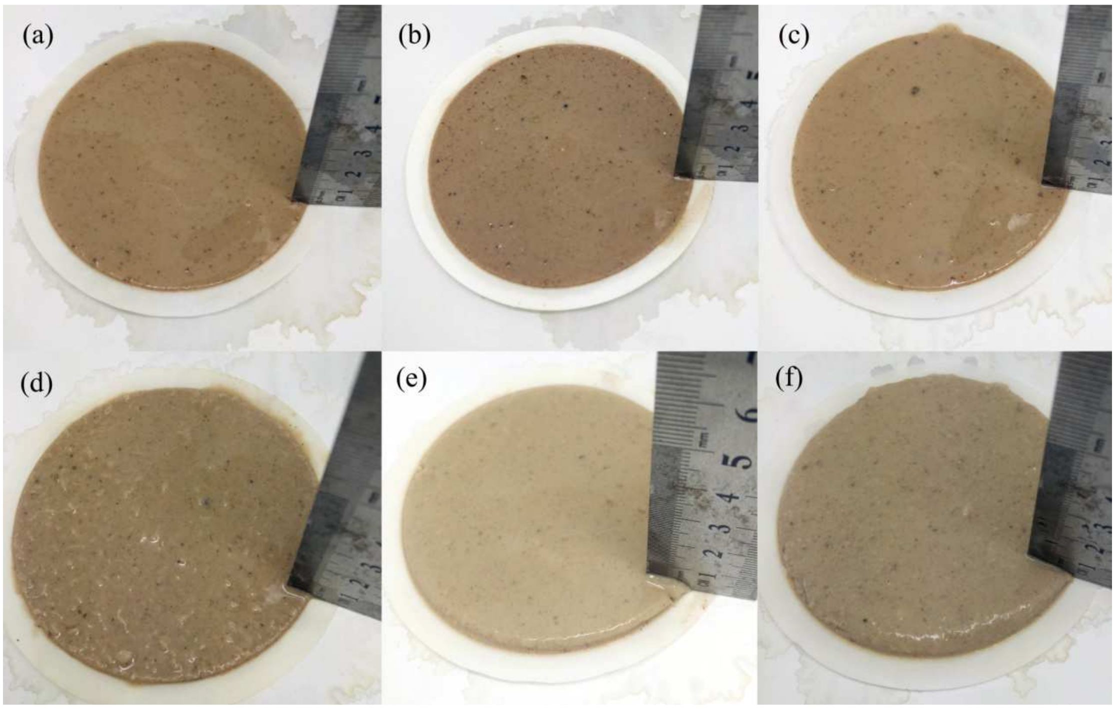

Figure 3 Effect of free ammonium concentration on filter cake

Table 4 Effect of free ammonium concentration on medium pressure filtration

Nh-1 sample	$FL_{API/ml}$	Mud cake thickness /mm
a	6.2	1.5
b	7	1.5
c	6.8	1.5
d	8	2.5
e	10	4
f	10.2	5

It can be seen from Fig. 2 and Table 2 that when the free ammonium concentration in NH-1 does not exceed 0.185 mmol/L, the thickness of the filter cake and the blank sample are both 1.5 mm, and the medium pressure filtration loss increases slightly, but the increase does not exceed 1 ml. Within the filter loss reading error range.When the free ammonium concentration is above 0.301 mmol/L, the filter cake thickness and fluid loss are greatly increased.

The above-mentioned laboratory experiments reproduce thecomplexities of the muddy cake caused by free ammonium and the deterioration of the rheological properties of the drilling fluid. The results of the natural degradation of NH-1 to produce the effect of free ammonium on the deterioration of drilling fluid performance were verified.

Chemical remedies

Equivalent molar amounts of acetic acid and potassium acetate were added to NH-1 with simulated free ammonium to investigate the effect of chemical additives on the performance of drilling fluids.The NH-1 containing different concentrations of free amine treated with an equimolar amount of acetic acid and potassium acetate was added to the drilling fluid system at 1%, and the effect on the performance of the drilling fluid was tested after aging at 120°C for 16 hours.Among them, the mass and fluid loss of the press cake in the api are shown in Figure 3 and Figure 4.

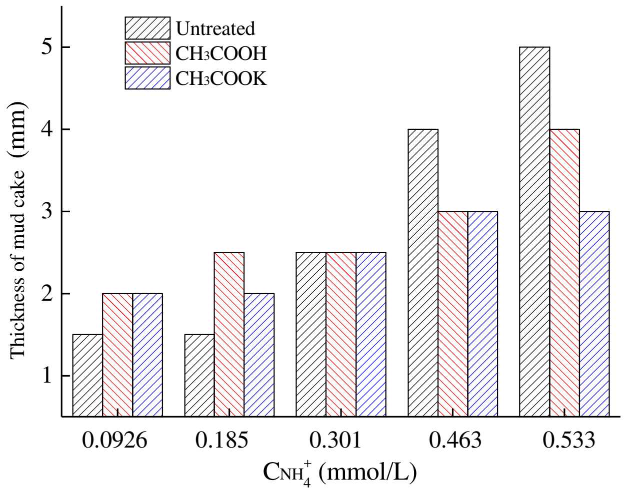

Figure 3 api mud cake thickness

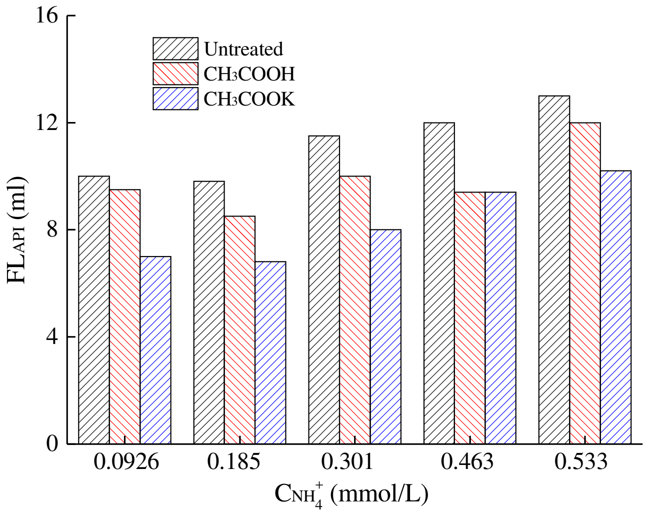

Figure 4: Pressure loss in api

It can be seen from Figures 3 and 4 that when the free amine in NH-1 is less than 0.185 mmol/L, the thickness of the mud cake is only 1.5 mm, and the fluid loss is about 10 ml, and the performance of the drilling fluid system itself does not deteriorate.However, after the treatment of NH-1 with acetic acid and potassium acetate, the mud thickness increased and the performance decreased. Therefore, when the free ammonium concentration in NH-1 is lower than 0.185 mmol/L, NH-1 is not required to be treated.When the free amine in NH-1 is higher than 0.301mmol/L, the recovery of NH-1 mud cake thickness and fluid loss after treatment with potassium acetate is better than that of acetic acid treated NH-1.

The effects of acetic acid and potassium acetate treatment on the rheology of the drilling fluid after aging are shown in Table 4.

Table 5 Effect of chemical treatment of organic amine inhibitors on drilling fluid performance

CNH_4^+ (mmol/L)	Treatment	AV(mPa.s)	PV(mPa.s)	YP(Pa)	YP/PV	G_{10s}/G_{10min}(Pa)
0		60	38	22	0.58	2.5/2.5
	Untreated	54	35	19	0.54	2.5/2.5
0.092	CH_3COOH	64.5	37	27.5	0.74	3.5/3.5
	CH_3COOK	56.5	43	13.5	0.31	2.5/2.5
	Untreated	60	38	22	0.58	2.5/2.5
0.185	CH_3COOH	59	30	29	0.97	5/5
	CH_3COOK	58	46	12	0.26	3/3
	Untreated	60	38	22	0.58	2.5/2.5
0.301	CH_3COOH	72.5	52	20.5	0.39	3.5/3.5
	CH_3COOK	52.5	37	15.5	0.42	3.5/3.5
	Untreated	75	36	39	1.08	7.5/7.5
0.463	CH_3COOH	62.5	39	23.5	0.60	3.5/3.5
	CH_3COOK	56.5	38	18.5	0.49	4.5/4.5
	Untreated	62.5	25	37.5	1.5	7/7
0.533	CH_3COOH	57	32	25	0.78	5/5
	CH_3COOK	57	41	16	0.39	4/4

It can be seen from Table 5 that the addition of free ammonium NH-1 after treatment with acetic acid and potassium acetate in the drilling fluid can restore the viscosity of the drilling fluid.The effect of potassium acetate treatment on rheological recovery of drilling fluid is more obvious. In addition to the viscosity index, the py/pv value can be restored to between 0.3 and 0.6, which is better than the drilling fluid system without free ammonium pollution.

It can be seen from the above treatment results that after the drilling fluid system is subjected to free ammonium pollution, the free ammonium treated by acetic acid is re-released into the system under the alkaline condition of the drilling fluid system, and the effect is limited.Treatment with potassium acetate in equimolar concentration with free ammonium can restore the rheological properties of the drilling fluid and the quality of the mud cake. This may be due to the ion exchange effect of potassium ions and free ammonium in potassium acetate, the free ammonium is constrained by acetate.

Even if potassium acetate is added, the free ammonium contaminated drilling fluid system can be better treated. When the drilling fluid in the drilling fluid contains excessive free ammonium, the performance of the drilling fluid is deteriorated. It is necessary to stop the corresponding treatment agent in time and make appropriate the drilling fluid system in the circulation. Treatment to reduce the effect of free ammonium on the performance of drilling fluids.

CONCLUSION

The addition of an amine-based inhibitor that has been stored for too long in the on-site drilling fluid results in deterioration of drilling fluid performance caused by free ammonium released from the inhibitor.When the free ammonium concentration in the inhibitor is less than 0.185 mmol/L, the free ammonium has little effect on the performance of the drilling fluid system, and no special treatment of the inhibitor is required.When the free ammonium concentration in the inhibitor is greater than 0.301 mmol/L, the performance of the drilling fluid can be restored by using an equimolar amount of potassium acetate.Potassium acetate can be used to treat amine-based inhibitors that are unstable in the field, but only for emergency treatment.The use of amine-based inhibitors in the field requires strict control of the concentration of free ammonium in the product prior to entry into the well.

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