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The Research and Application of New Low Density Nitrogen Micro Bubble Workover Fluid

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Abstract

Aiming at the need of coiled tubing sand washing operation for the low-pressure and leaking gas pool in Qinghai gas reservoir, we developed a kind of low density nitrogen micro bubble workover fluid technology, which is composed of a new type of composite foaming agent, temporary plugging agent, composite stabilizing foam agent and the nitrogen. Observing by a microscope, we can find that the micro bubble structure is composed of a core of gas, two membranes, three layers, which has high stability (higher stability than ordinary foam stability). The performance evaluation results show that, the temperature resistance of nitrogen micro bubble workover fluid is up to 120 ℃. Compression resistance can reach 20 Mpa. API filter loss is only 11.3 ml. The high temperature and high pressure filtration is only 16.6 ml. Anti-salt can reach 10%. Anti-calcium can reach 3% and the resistance to oil pollution is more than 15%. The recovery rate of core permeability is up to 89%. The system can not only reduce the fluid column pressure and reduce the pressure difference, but the formation of micro bubble in the leakage areas on the surface of formation is widespread, and has a certain strength and toughness, and also has a certain deformability matching leakage channel of formation, which can achieve the purpose of anti-leaking. This technology was applied in Qinghai gas field for 2 wells, with an efficiency of 100%. The sand washing operation was successfully completed, with no leakage.

Key words: Low density nitrogen micro bubble workover fluid; Micro bubble; Qinghai gas field

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INTRODUCTION

At present, the major oil fields in China have entered into the middle and later periods of development, and reservoir energy loss is severe in most wells, in addition to that, leakage well, leakage layer increased rapidly, and the pressure coefficient declined rapidly. The produced large volumes of liquid leakage during the course of well completion and workover operation not only polluted reservoir, but brought significant economic losses.

The technology which was applied in low pressure and leaking wells includes the anti-leaking workover fluid which is based on the shielding temporary plugging technology and low density foam fluid, but both of which are flawed. The former is very difficult to match anisotropy of formation. The latter has poor stability and the compression resistance of common foam is so poor that the foam disappeared underground.

This paper presented a kind of new low density nitrogen micro bubble anti-leaking workover fluid which has high stability (higher stability than ordinary foam stability), which has a certain strength and toughness, and also has certain deformability matching leakage channel of formation to achieve the purpose of anti-leaking. The author is willing to share this knowledge of this technology.

1. DEVELOPMENT OF LOW DENSITY NITROGEN MICRO BUBBLE WORKOVER FLUID

1.1 Development of High Performance Foaming Agent

Firstly, according to the molecular structure of surfactants and apparent form of bubble generated by surfactants and stability, we optimized all kinds of foaming agents. The experiment was operated at room temperature, measuring water 100 ml and placing it in the stirring cup in which added anionic foaming agent SAS, SABS, hexadecylsulfonic acid sodium salt; cationic foaming agent octylamine, lauryl amine, cetylamine, both sexes type foaming agent octyl phosphonate, dodecyl dihydrogen phosphate, nonionic foaming agent octanol, dodecanol separatly , each 2 grams, 10000 r/min stirring for 5 minutes, reading volume after volume expansion by graduated cylinder separatly, at the same time, timing separatly, when the volume of liquid in the graduated cylinder reached 50 ml, stop timing and those time is the half-life period of all kinds of foaming agents. The greater half-life period can reach, the better the performance of foaming agents is. The results were showed in Table 1.

Table 1
The Performance of All Kinds of Foaming Agents

Foaming agents and quantity	Foam volume /ml	Half-life period/s	Apparent form of bubble
2% SAS	650	450	Tiny, uniform
2% SABS	510	379	Tiny, uniform
2% Hexadecylsulfonic acid sodium	500	400	Tiny, uniform
2% Octylamine	450	149	Tiny, uniform
2% Lauryl amine	400	188	Tiny, uniform
2% Cetylamine	410	261	Tiny, uniform
2% Octyl phosphonate	450	246	Tiny, uniform
2% Dodecyl dihydrogen phosphate	460	282	Tiny, uniform
2% Octanol	430	70	Tiny, uniform
2% Dodecanol	445	88	Tiny, uniform

Table 2
The Performance of Composite Foaming Agent in Fresh Water

Foaming agents and quantity	Foam volume /ml	Half-life period/s	Apparent form of bubble
2%SAS	650	450	Tiny, uniform
2%SABS	510	379	Tiny, uniform
1%SAS+1%SABS	710	486	Tiny, uniform

Table 3
The Salt Resistance of Composite Foaming Agent in Salt Water

Foaming agents and quantity	Foam volume /ml	Half-life period/s	Apparent form of bubble
2% SAS	130	60	Poor quality
2% SABS	150	66	Poor quality
1% SAS + 1% SABS	495	406	Tiny, uniform

Table 1 shows that the foam volume of anionic foaming agents SAS, SABS is max, and the half-life period of which is the best, and nucleating ability is strong so that the micro bubble is most stable.

According to the synergetic theory, there is a synergetic effect between the anionic foaming agents so that the foam volume of anionic foaming agents SAS, SABS with more strong surface activity is greater by the synergetic effect. The results were showed in Table 2 and Table 3.

From Table 1, we can find that the performance of composite foaming agent is better than each separate foaming agent.

Table 3 indicates that in 2% KCl salt water the performance of composite foaming agent is better than each separate foaming agent, which has a good Salt Resistance.

In addition, this composite foaming agent is a kind of surfactant, which can reduce oil-water interfacial tension so that it can reduce water block effect in formation, and the Interfacial tension is only 0.5075 mN/m compared to 24.8995 mN/m. The results were showed in Table 4.

Table 4
The Interfacial Tension Test of Composite Foaming Agent

NO.	Formula	Interfacial tension mN/m
1	Fresh water/Kerosene	24.8995
2	Fresh water +0.2%SAS/ Kerosene	3.5078
3	Fresh water +0.2%SABS+0.2%SAS/ Kerosene	0.5075
Remark:the used instrument: JYM-200A automatic interface tensiometer.		

1.2 Development of High Performance Composite Stabilizing Foam Agent

The efficient stabilizing foam agent was developed by synergetic effect between the anionic foaming agents for increasing the adsorption strength between active molecules, and by the hydration effect of macromolecular substances for enhancing suspension stability of system, and by mobility control technology for enhancing film strength and thickness of micro bubble. The result of all kinds of stabilizing foam agents were showed in Table 5.

Table 5
The Performance of Different Stabilizing Foam Agents

Stabilizing foam agents and quantity	Foam volume /ml	Half-life period /h	Apparent form of bubble
0.3% C	290	3.1	Tiny, uniform
0.4% C	260	3.5	Tiny, uniform
0.5% C	230	4	Tiny, uniform
0.3% M	170	2.8	Tiny, uniform
0.4% M	130	3	Tiny, uniform
0.3% P	500	0.5	Tiny, uniform
0.4% P	450	0.6	Tiny, uniform
0.5% P	380	0.65	Tiny, uniform
0.3% X	400	3.3	Tiny, uniform
0.4% X	350	3.8	Tiny, uniform
0.5% X	300	4.5	Tiny, uniform

Table 6
Assessment of Stability of Micro Bubble System in Room Temperature

Formula	Storage period, h	Density, g/cm^3	Apparent form of bubble
1#	0	0.85	Tiny, uniform
1#	6	0.85	Tiny, uniform
1#	12	0.85	Tiny, uniform
1#	24	0.86	Tiny, uniform
1#	48	0.89	Slight tratification

Table 7
Assessment of Stability of Micro Bubble System in High Temperature

Type	Density g/cm^3	Φ600 /Φ300	Φ200 /Φ100	Φ6 /Φ3	AV mPa·s	PV mPa·s	API FL /ml
Room temperature	0.85	53/38	30/25	11/8	22	9	16
120 ℃/12h Hot rolling	0.89	32/26	21/16	9/6	16	6	30
120 ℃/12h Hot rolling*	0.86	46/39	35/31	17/14	11	5	36

Note: * represents that The system was stirred for 5 minutes at a low speed after hot rolling.

Table 5 indicated that the performance of stabilizing foam agent X which the half-life period is up to 4.5h is better than other stabilizing foam agents.

Adding stabilizing foam agent H with large molecular weight with stabilizing foam agent X and at the same time add a little viscosity retention agent, we can form this micro bubble fluid by velocity mixing. The stability was assessed. After 48 hours, the density of micro bubble system is still 0.89 g/cm^3, which has a good stability. The result was showed in Table 6.

The formula is as follow:

1# 1-1.5% stabilizing foam agent H + 0.6% stabilizing foam agent X + 0.4% composite foaming agent + 0.6% thiourea

Stability of micro bubble system in High Temperature 120 ℃ is also assessed and the density of micro bubble system is still 0.89 g/cm^3. After pulp mixing, the density of micro bubble system is 0.86 g/cm^3, and can keep a good rheology, which has a good stability. The result was showed in Table 7.

2. FORMULATING

1.0%-1.5% stabilizing foam agent H, 0.6% stabilizing foam agent X, 0.2% SAS, 0.2% SABS, and 0.6% thiourea were added in 100 ml fresh water in sequence and at the same time filled small amounts of nitrogen, stirring them at a high speed for 30 minutes, which can form the low density nitrogen micro bubble workover fluid showed in Figure 1.

Figure 1
Sample of Laboratory

3. THE RESEARCH OF MICROSTRUCTURE OF MICRO BUBBLE SYSTEM

In the 400 times electron microscope a lot of hairy air pockets which dispersed in the liquid phase by single or double-joint style were found in this system showed Figure 2 and Figure 3.

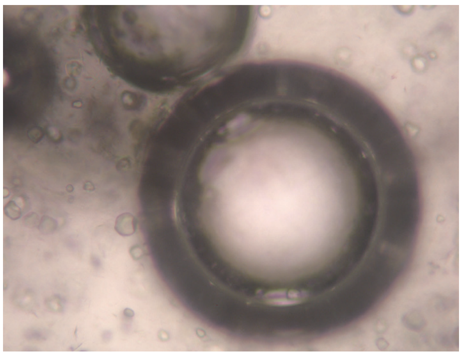

Figure 2
Microstructure of Single

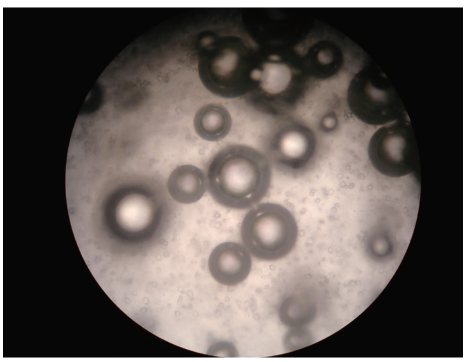

Figure 3
Distribution of the Multiple

Figure 2 and Figure 3 showed that the gas was wrapped by micro bubble, and the outside of gas was wrapped by dense layer, which looked like a hairy air pockets, so that the structure of micro bubble is composed of a core of gas, two membranes, three layers. The detail showed in Figure 4.

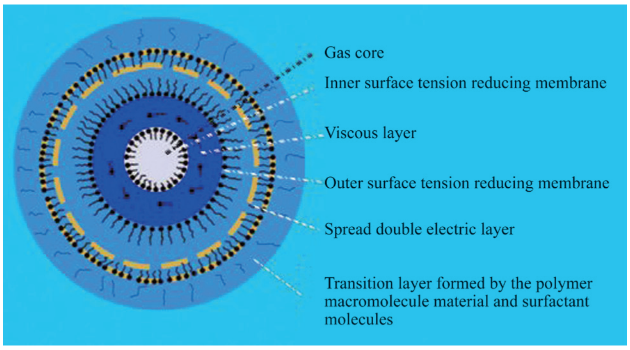

Figure 4
Schematic Diagram of Micro Structure of Micro Bubble

As shown in Figure 4, the wrapped gas located in the center of the micro bubble, so we call it "gas core". The dark blue area of the gas core is the solid layer which wrapped gas, and it is formed by the hydrophilic hydration of the hydrophilic end of the surfactant on either side of the inside and outside and the association between the hydrophilic end and the macromolecule polymer, and its viscosity is much higher than that of the liquid viscosity, so it is called "viscous layer". The lipophilic group of the surfactant which is inside of the viscous layer was closely arranged inward into membrane, so it is called the "inner surface tension reducing membrane" which was mainly used for reducing the surface tension between gas and liquid. The lipophilic group of the surfactant which is outside of the viscous layer was closely arranged outward into membrane, mainly used for maintaining the high viscosity of the viscous layer , so it is called "outer surface tension reducing membrane". What beside outer surface tension reducing membrane is was the so called "spread double electric layer". What beside spread double electric layer is was formed by the polymer macromolecule material and surfactant molecules, because this layer has no fixed thickness, so we call it a "transition layer".

4. COMPREHENSIVE PERFORMANCE EVALUATION OF LOW DENSITY NITROGEN MICRO BUBBLE RESERVOIR PROTECTION FLUID

4.1 Rheology Evaluation

Basic properties of workover fluid including density, filtration, viscosity, rheological property, etc were estimated in lab, and the results were showed in Table 8.

Table 8
Assessment of Rheological Property of Micro Bubble System

Formula	2%KCl+0.6% stabilizing foam agent X+1.5% stabilizing foam agent H + 0.4% composite foaming agent + 0.05%sterilizing agent + 0.5%deoxidant			
Density, g/cm³	0.8	reheological parameter	AV, mPa.s	15
API FLml/30min	11.3		PV, mPa.s	11
HPFLml/30min	16.6		K(mPa.sⁿ), n	532.1, 0.585
Viscosity, mPa.s	430		YP, Pa	9.6

From Table 7, we can find that API filter loss is only 11.3 ml/30min. The high temperature and high pressure filtration is only 16.6 ml/30min. Rheological parameters showed that the fluid is pseudoplastic fluid, and has a very good shear thinning, a strong thixotropy, so it is advantageous to suspend solid particles. This fluid has a moderate viscosity, which can satisfy the requirement of site construction.

4.2 Thermal Stability Evaluation and PVT Test

The thermal stability evaluation result was showed in Figure 5.

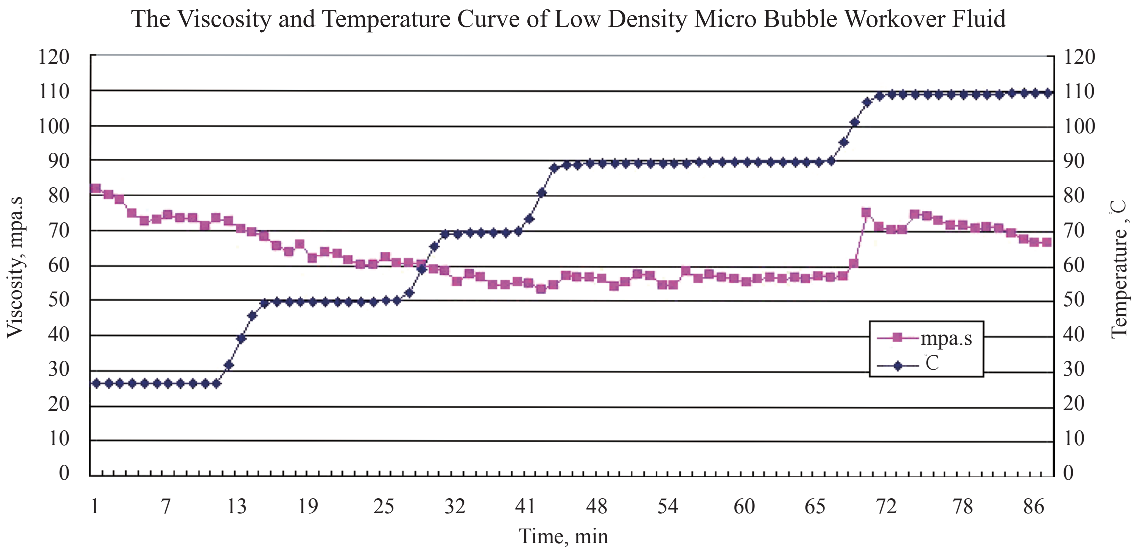

Figure5
Viscosity-Temperature Curve of Micro Bubble System

Figure 5 indicated that in 110 ℃, the viscosity of this system didn't decline but rise, so this micro bubble system can keep a good condition under 110 ℃, which showed a good thermal stability.

The PVT test result was showed in Figure 6.

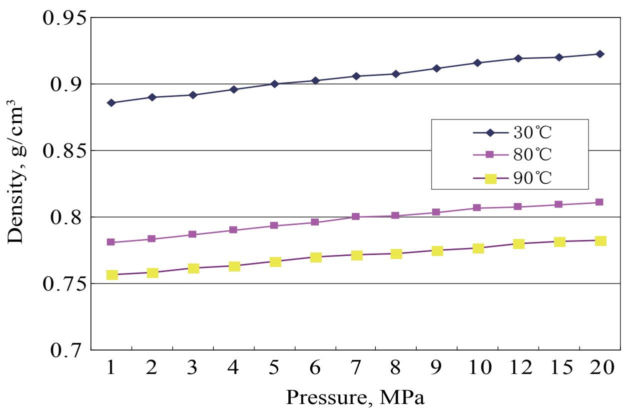

Figure 6
PVT Curve of Micro Bubble System

Figure 6 indicated that this micro bubble workover fluid appeared a good property of anti-temperature and anti-pressure, and the micro bubble didn't disappear in the 2000 meters underground (20 MPa).

4.3 Anti-Leaking Evaluation

Figure 7
The Test of Plugging Sand

In the lab the micro bubble workover fluid whose density is 0.85 g/cm^3 was applied to plug the sand which its particle size is 40-60 mesh, displacement pressure 2 MPa, return pressure 0.5 MPa. After 20 minutes, there is no leakage during the whole process and measure the length of wetting section showed in Figure 7.

The test indicated that this micro bubble system can plug sand effectively compared to KCL salt water which is all the leakage. The invasion depth of micro bubble system is only 3.1 cm, which has a good effect of plugging.

4.4 Evaluation of Anti-Pollution

When the micro bubbles system we developed was applied to formation, it will contact with formation water, crude oil, brine, etc., so it should have a certain degree of anti-pollution ability. We conducted anti-salt, anti-calcium and anti-oil test in the lab.

4.5 Evaluation of Anti-Salt

The anti-salt pollution evaluation test of micro bubble system was performed in the lab, using NaCl as salt, and the test results were as follows:

Table 9
Anti-Salt Evaluation of Micro Bubble Fluid

Add salt, %	Density, g/cm^3	Micro bubbles quality
0	0.8400	Tiny uniform
1% NaCl	0.8456	Tiny uniform
2% NaCl	0.8476	Tiny uniform
3% NaCl	0.8499	Tiny uniform
4% NaCl	0.8580	Tiny uniform
5% NaCl	0.8525	Tiny uniform
6% NaCl	0.8588	Tiny uniform
7% NaCl	0.8625	Tiny uniform
8% NaCl	0.8766	Tiny uniform
9% NaCl	0.8890	Tiny uniform
10% NaCl	0.8998	Slightly larger

The test results showed that the system density remain at 0.9 g/cm^3, micro bubble size slightly increased when the amount of NaCl reached 10%. This showed the micro bubble system has a good salt resistance, and salt resistance can reach more than 10%.

4.6 Evaluation of Anti-Calcium

The anti-calcium pollution evaluation test of micro bubble system was performed in the lab, using $CaCl_2$ as materials, and the test results were as follows:

Table 10
Anti-Calcium Evaluation of Micro Bubble Fluid

Add quantity, %	Density, g/cm^3	Micro bubbles quality
0	0.8356	Tiny uniform
1%$Cacl_2$	0.8716	Tiny uniform
2%$Cacl_2$	0.8926	Tiny uniform
3%$Cacl_2$	0.8950	Tiny uniform
4%$Cacl_2$	0.95	Slightly larger
5%$Cacl_2$	0.95	Slightly larger

The test results showed that system density decreased largely and micro bubble volume increased significantly when the amount of $CaCl_2$ more than 3%, so the anti-calcium of micro bubble system can reach 3%.

4.7 Evaluation of Anti-Oil

The anti-oil pollution evaluation test of micro bubble system was performed in the lab, using neutral kerosene as materials, and the test results were as follows:

Table 11
Anti-Oil Evaluation of Micro Bubble Fluid

Add quantity, %	Density, g/cm^3	Micro bubbles quality
0	0.8292	Tiny uniform
3% Kerosine	0.8292	Tiny uniform
6% Kerosine	0.8281	Tiny uniform
9% Kerosine	0.8168	Tiny uniform
12% Kerosine	0.8199	Tiny uniform
15% Kerosine	0.8188	Tiny uniform

The test results showed that system micro bubble volume decreased largely when neutral kerosene was added. The micro bubble was tiny and uniform and the appearance does not change after 24 hours when the amount of kerosene reach 15%, so the anti-oil of micro bubble system can reach 15%.

4.8 Evaluation of Core Damage

The system uses KCl solution as a base fluid, which has a good compatibility with formation water, and has a low filtration volume, which can prevent the base fluid into the formation. Micro bubble also has a strong cleaning ability, which can remove the impurities and oil dirty in wellhole, so it has a good reservoir protection characteristic.

Table12
Micro Bubble System Core Damage Evaluation Test

System	Core number	Block	Displacing medium	Liquid penetration before pollution×10^{-3} μm^2	Liquid penetration after pollution×10^{-3} μm^2	Return Permeability %
Micro bubble	1#	Wang guantun	Standard saline	125.6986	112.3676	89.39
Micro bubble	2#	Wang guantun	Standard saline	283.7868	266.7858	94
Micro bubble	3#	Zao yuan	Standard saline	383.8969	378.8679	98.69

Through the core damage evaluation test of this fluid, it can be seen that the core permeability recovery rate is between 89% - 98%. It indicated that formula has a good reservoir protection effect.

5. FIELD APPLICATION

So far, the micro bubble technology was successfully applied in Se 4-18 well and Se 1-21 well in Qinghai gas field which were low pressure sand washing Wells. The result of field application indicated that the low density micro bubble workover fluid has characteristics of strong carrying sand, less leakage, small injured to formation. During the sand washing process, there is no leakage, creating favorable conditions for the smooth implementation of the subsequent process, with good prospects.

Take the example for Se 4-18 well which is a coiled tubing sand washing leaking well.

The well is located in the Qaidam Basin No.1 constructor from the southeast flank in Se bei of Qinghai, artificial well bottom 1317.8 m, pressure coefficient of 0.67, belonging to low pressure and leaking wells. The soft ground sand surface of this well is 1230 m. Due to the low coefficient of this well, the site used low-density micro bubble workover fluid to conduct sand washing operation, reducing the pressure to reduce leakage.

The predicting formation pressure coefficient of this well is only 0.67, and is gas well. The density of nitrogen micro bubble workover fluid was designed as 0.70 g/cm^3 for reducing pressure difference and controlling the leakage. Micro bubble sand washing fluid formulation and performance was determined.

Properties of sand washing fluid are as follows

Table 13
Properties of Sand Washing Fluid

Performance	Φ600	Φ300	Φ6	Φ3	Density g/cm³	AV mPa•s	PV mPa•s	pH
Design parameters	30-40	20-30	/	/	0.6-0.8	15-25	10-15	7-8
Actual parameters	38	27	9	8	0.7	19	11	7

The process of field operation were showed in Table 14:

Table 14
The Field Operation

Date	Time		Operation
2013.5.30	8:30	11:00	Preparation of low density micro bubble nitrogen workover fluid for 40 m^3, Parameter: AV:19mPa·S, PV:11mPa·S, API filter loss:13.5 ml.
	11:00	12:00	Wellsite tools installation, connecting pipes, wellhead installation.
	12.00	12:15	Normal circulation workover fluid and pressure testing 10 Mpa for 10min .
	12:15	15:00	Start to trip in the coiled tubing, and normal circulation injection nitrogen micro bubble workover fluid, output volume: 9 m^3/h, pressure: 19 MPa. The operation was last for 3 hours and the whole process is ok.
	15:00	16:00	Tripping out the tube.
	16:00	17:00	Examining tools.

The field application figure is as follow:

Figure 8
The Field Application

SUMMARY

a. Aiming at the need of workover for the low-pressure and leaking gas pool in Qinghai gas reservoir, we developed a kind of low density nitrogen micro bubble workover fluid technology, which has a certain strength and toughness, and also has a certain deformability matching leakage channel of formation, which can achieve the purpose of anti-leaking.

b. The temperature resistance of nitrogen micro bubble workover fluid is up to 120 ℃. Compression resistance can reach 20 Mpa. Density is a range of 0.5-0.98 g/cm^3. API filter loss is only 11.3 ml. The high temperature and high pressure filtration is only 16.6 ml. Anti-salt can reach 10% and anti-calcium can reach 3% and the resistance to oil pollution is more than 15%. The recovery rate of core permeability is up to 89%.

c. This technology was applied in Qinghai gas field for 2 wells, with an efficiency of 100%. The sand washing operation was successfully completed, with no leakage.

d. The low density nitrogen micro bubble workover fluid fills up the blank of the research of Da gang oilfield in low-density field, which provides a new path for sand flushing operation and pump inspection operation of low pressure sandstone, low pressure fractured oil and gas reservoir and low pressure heavy oil reservoir.

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