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Study on Oilfield Chemical Formulations of CCUS-EOR

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ABSTRACT

Oil recovery is increased by about 15% by CO_2 flooding in Daqing Oilfield. However, problems such as corrosion,gas channeling, and freezing blocking occur frequently in the process of production. Since ordinary carbon steel is generally adopted for well completion, CO_2 corrosion affects the well life and the overall development of the test area. CO_2 flooding low-cost chemical corrosion prevention technology is formed, and the corrosion rate is only 0.065mm/a under the CO_2 partial pressure of 5MPa and the temperature of 80 ℃. Due to the low gas viscosity and the heterogeneity of the oil layer, viscous fingering and channeling are easy to occur. Therefore, acid-resistant and oil-resistant CO_2 foam channeling sealing agent was developed. Under the condition of pH=3 and oil saturation of 60%, the foaming volume was 430mL and the half-life was 83h. In the process of delaying gas channeling by water alternating gas injection, CO_2 hydrate is easy to be generated, which leads to freezing and blocking of wellbore and surface pipelines, resulting in low production rate. Therefore, a low-temperature and efficient plugging removal technology was developed, which realizes 100% dissolution of freezing and blocking at -20℃ for the first time. The improvement of a series of low cost oilfield chemical technologies of CO_2 flooding has improved the well running rate, reduces the operation cost, and provides technical support for the sustainable and effective development of CO_2 flooding.

Keywords: carbon dioxide flooding; corrosion inhibitor; channeling sealing agent; freezing blocking removal agent.

1. INTRODUCTION

Since 1965, Daqing Oilfield has carried out the research and test of CO_2 flooding after water flooding in Changyuan. Compared with continuous water flooding, the ultimate oil recovery is expected to increase by 7.8 and 6.0 percentage points respectively. In 1985, two field tests of WAG (water alternating gas) injection were conducted in the SD transitional zone, resulting in a 2.07 percentage point improvement in the central well and a 4.67 percentage point improvement in the whole area. Changyuan immiscible CO_2 flooding achieved a smaller increase in oil recovery compared with polymer or multiple composite flooding. Due to the low gas viscosity and the heterogeneity of the reservoir, it is easy to appear viscous fingering and channeling, resulting in unfavorable mobility ratio. Serious gas channeling wells show obvious oil increase, but serious liquid production drop. Due to the existence of these adverse factors, CO2 flooding has not been applied in Daqing Changyuan industrially. Since 2003, aiming at the problem that ultra-low permeability reservoirs of peripheral oilfield and water-sensitive reservoirs of HLE are difficult to establish an effective driving system for water flooding, research and experiments on CO_2 flooding technology has been carried out, and two industrial applications of YSL and HLE CO_2 flooding are implemented. The production scale has maintained at an annual output of more than 90,000 tons of crude oil, with enhanced recovery of about 15%. However, CO_2 corrosion also affects the well life and the overall development of the test area because the test area is mainly completed with ordinary carbon steel during operation. In order to delay gas

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channeling, water and gas are injected alternately, but it is easy to generate CO_2 hydrate in the alternating process, resulting in freezing blockage of wellbore and surface pipeline, and low production rate. These factors lead to the decrease of production and low development efficiency in the CO_2 test area, so it is necessary to develop corrosion inhibitors, channeling sealing agents and hydrate plugging removal agents and other oilfield chemical formulators to improve the well running rate, reduce operating costs, and ensure the production of the test area.

2. CORROSION INHIBITOR FOR INJECTION AND PRODUCTION WELLS

Corrosion protection measures such as corrosion resistant pipe, coated pipe, glass fiber reinforced plastic lining pipe and cathodic protection are usually adopted in injection and production wells. However, due to the limited high temperature resistance of glass fiber reinforced plastic lined tubing, too much reduction in inner diameter, and easy crushing of filling between lining and tubing body, the application is limited. The cathodic protection is widely used, but because of the complex technical operation process, and high requirement for the basic parameters used in the scheme design, which are easy to be affected by the site environment, it is difficult to achieve the best anti-corrosion effect, especially for deep wells, in addition, the operation cost is high. Therefore, corrosion inhibitor is mainly used to prevent corrosion. Corrosion inhibitor prevents the occurrence of metal corrosion by adsorption with metal.

2.1 Principle of corrosion inhibitor

At present, the commonly used corrosion inhibitors mainly include proparyl alcohols, organic amines, imidazolines and quaternary ammonium salts. Proparyl alcohols and aromatic amines have greater toxicity, imidazoline corrosion inhibitor has no special irritating odor, good thermal stability, low toxicity, so this kind of corrosion inhibitor is adopted.

Imidazoline corrosion inhibitors belong to adsorption film corrosion inhibitors. The molecule contains two N atoms with lone pair electrons, which are easy to form coordination bonds with Fe atoms and adsorb on metal surfaces, changing the interface properties and charge states of metal surfaces. In addition to adsorption, the shielding effect of non-polar groups is indispensable. When the corrosion inhibitor molecules adsorbs on the metal matrix, the non-polar groups, namely alkyl groups, are oriented on the metal surface. A dense hydrophobic film is formed throughout the anode and cathode regions, thereby preventing and slowing down the corresponding electrochemical reactions and decelerating the corrosive dissolution of the metal.

2.2 Formulation of corrosion inhibitor

2.2.1 Optimization of main agent of corrosion inhibitor formulation

According to the conditions of CO2 flooding reservoir in Daqing, the corrosion inhibition performance was evaluated, and the experimental results were shown in Tab.1.

As can be seen from Tab.1, there are 5 main ingredients of corrosion inhibitor formulations whose corrosion inhibition rate can reach more than 80%, and their main components and effective content are shown in Tab. 2.

Tab.1 Main ingredient optimization of corrosion inhibitor

Corrosion inhibitor	Concentration（mg/L）	Corrosion rate（mm/a）	Weight loss（g）	Corrosion inhibition rate（%）
Blank	/	3.4529	0.1036	/
ZY-273	1000	0.3111	0.0094	91.0
MHHG-2	1000	1.7845	0.0541	47.8
DYJY-3	1000	0.6360	0.0193	81.4
YQHS	1000	0.9707	0.0294	71.6
MD	1000	1.1895	0.0356	65.6
MD-9	1000	0.3849	0.0116	88.7
TM200	1000	0.9101	0.0276	73.3
BZYC-2	1000	0.5626	0.0169	83.6
BUCT-Y	1000	0.9992	0.0304	70.6

DZF-QHJ	1000	0.5473	0.0166	83.9
HL-X	1000	1.5624	0.1406	10.1
LS	1000	1.5441	0.1343	16.4

Tab.2 Main ingredient and price of corrosion inhibitor

Corrosion inhibitor	Corrosion inhibition rate（%）	main ingredient	Effect content （%）
ZY-273	91.0	imidazolines	50
DYJY-3	81.4	imidazolines	40
MD-9	88.7	imidazoline derivative	50
BZYC-2	83.6	imidazoline derivative	55
DZF-QHJ	83.9	modified imidazoline	10-15

As can be seen from the above, there are 5 corrosion inhibitors with corrosion inhibition rate of more than 80% at concentration of 1000mg/L, among which ZY-273 has the best CO2 corrosion resistance capability with corrosion inhibition rate more than 90%. Therefore, corrosion inhibitor ZY-273 is preferred for The formulation.

2.2.2 Optimization of additives of corrosion inhibitor formulation

The additives of main agent ZY-273 are optimized, and the results are shown in Tab. 3. It can be seen from Tab. 3 that the corrosion inhibition rate of ZY-273 increases the most after additive A is added, so the additive is determined as agent A.

Tab.3 Optimization of additives of corrosion inhibitor formulation

Corrosion inhibitor (1000 mg/L)	Additive (500 mg/L)	Corrosion rate (mm/a)	Weight loss (g)	Corrosion inhibition rate (%)	Corrosion inhibition rate increment (%)
Blank	/	3.4529	0.1036	/	
ZY-273	/	0.3111	0.0094	91.0	
	A	0.2636	0.0079	92.4	1.4
	B	0.5243	0.0159	84.7	-6.3
	C	0.3045	0.0091	91.2	0.2
	D	0.3056	0.0092	91.1	0.1

2.2.3 Determination of corrosion inhibitor formulation

The concentration of ZY-273 and additive A was optimized, and the experimental results are shown in Tab.4. The optimal cost performance is achieved by adding 100mg/L agent A and 600mg/L ZY-273, and the corrosion rate was the lowest at 0.065mm/a.

Tab.4 Concentration optimization of corrosion inhibitor formulation

Corrosion inhibitor		Additive		Corrosion rate(mm/a)	Weight loss（g）	Corrosion inhibition rate(%)
Type	Concentration (mg/L)	Type	Concentration (mg/L)			
Blank	/	/	/	3.4529	0.1036	/
ZY-273	400	A	300	0.1013	0.0088	83.8
	500		200	0.0985	0.0070	85.5
	600		100	0.0650	0.0061	91.2
	800		0	0.0744	0.0064	91.0

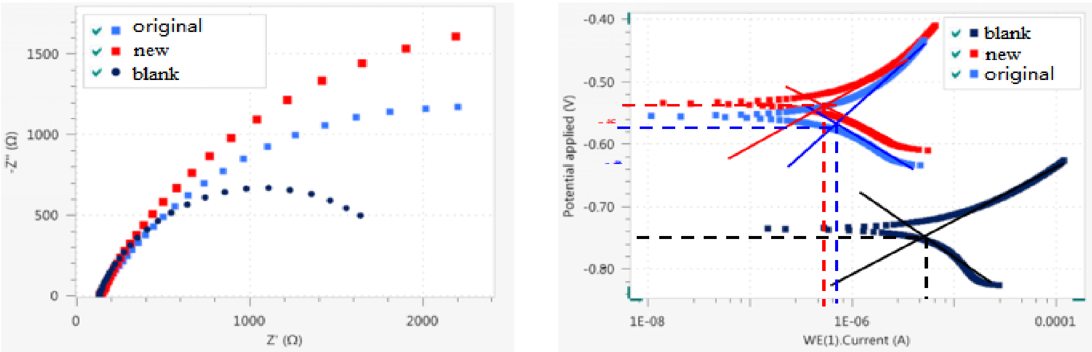
2.3 Performance of corrosion inhibitor

2.3.1 Corrosion inhibition performance

When different proportions of crude oil are introduced into the experimental system, the corrosion rate is greatly reduced, because crude oil is easy to form a relatively uniform and stable adsorption film on the surface of sucker rod and tubing, which reduces the active point of corrosion reaction on the metal surface and protects the metal corrosion to a certain extent. The corrosion rate is less than 0.076mm/a, and the corrosion inhibition rate is more than 85%.

Tab.5 Evaluation of corrosion inhibition properties of corrosion inhibitors under different oil content

Oil content （%）	Corrosion rate without corrosion inhibitor （mm/a）	Corrosion rate with corrosion inhibitor （mm/a）	Corrosion inhibition rate （%）
40	0.1032	0.0167	84
30	0.1763	0.0129	93
20	0.2317	0.0170	92
10	0.3964	0.0333	91
0	1.3899	0.0650	86



a.impedance spectroscopy b.polarization curve

Fig.1 Results of electrochemical comparative analysis of corrosion inhibitor formulations

2.3.2 Electrochemical performance

Electrochemical analysis (Fig. 1) further verified the corrosion protection effect of the new corrosion inhibitor. The impedance spectroscopy shows a capacitive reactance arc, indicating that it is only caused by adsorption. After adding inhibitor, the arc of the curve in impedance spectroscopy is larger than that of the old formula and blank sample, and the impedance is larger. From the polarization curve, E_c is the corrosion potential (the potential measured when the metal reaches a stable corrosion state without external current), I_c is the corrosion current density (corresponding to the current density of the corrosion potential), E_c of new formulation and the old one is larger than E_c, indicating that the corrosion inhibitor is the anode typed corrosion inhibitor, while I_c of new formulation and the old one is smaller than I_c, indicating that new corrosion inhibitor has smaller polarization current and better corrosion inhibition effect.

2.3.3 Solubility

The corrosion inhibitor has good water solubility, forming a uniform, more transparent solution, insoluble in oil, water soluble corrosion inhibitor.

2.3.4 Film formation

Compared with the blank sample without corrosion inhibitor, the corrosion inhibitor has better film forming performance, which can ensure its uniform distribution on the surface of the pipe and reduce corrosion.

2.3.5 Emulsification tendency

The demulsification rate of the inhibitor at different time was determined. Compared with the blank sample, it could demulsify quickly and completely without emulsification tendency.

Tab. 6 Demulsification rate at different times

Corrosion inhibitor（mg/L） Time	10min	60min
0	25	100
1000	17	100

2.4 Field Application

The field test of corrosion inhibitor injection was carried out for 51 wells, and the hanging ring corrosion monitoring was carried out on the wells before and after dosing. The results showed a sound corrosion protection effect with corrosion rate less than 0.076mm/a after dosing.

3. ACID AND OIL RESISTANT CO_2 FOAM CHANNELING SEALING AGENT

Due to the permeability difference between reservoirs, crack development, and the low viscosity and good mobility of CO_2, CO_2 flooding is more prone to the problem of gas fingering. Once gas channeling occurs, gas swept volume will be significantly reduced, oil displacement efficiency is greatly reduced, seriously influence the result of gas injection development. Therefore, in order to prevent CO_2 moves along the gas channeling inteval, expand the swept volume, and take maximum advantage of CO_2 flooding, acid and oil resistant CO_2 foam channeling sealing agent is developed.

3.1 The plugging principle of acid and oil resistant CO_2 foam channeling sealing agent

By introducing hydrophilic combination groups such as hydroxyl, carboxyl, sulfonic acid, etc., the foam surfactant can be hydrolyzed under acidic conditions and neutralize excess hydrogen protons, thus improving the hydrophilic activity of hydrophobic chains at the interface. Moreover, the introduction of hydrophilic groups can also increase the polarity difference between hydrophobic groups and the oil phase, hinder the oil phase aggregation, and enhance the thickness of the interface film. Through cyclization reaction, hydrophobic straight chain alkyl is transformed into hydrophobic epoxy group, which increases steric hindrance and viscoelasticity of interfacial film, so as to improve the stability of foam in acid and oil environment.

3.2 Performance of acid and oil resistant CO_2 foam channeling sealing agent

3.2.1 Performance of foam channeling sealing system at room temperature and pressure

The stability of SD-4 and SD-5 foam sealing system has been greatly improved with the addition of foam stabilizing agent. The foaming volume of SD-5 foam sealing system is 430mL and the half-life is 83h under the condition of pH=3 and oil saturation of 60%. The specific performance is shown in Tab.7.

Tab.7 Comprehensive performance of foam sealing system

Type	Foam channeling sealing agent			Prepared with water (pH=3)		Oil saturability 60％ (pH=3)		Surface tension (mN/m)
	Foaming agent (%)	Foam stabilizing agent (%)	Corrosion inhibitor (%)	Foaming volume (mL)	Half-life (h)	Foaming volume (mL)	Half-life (h)	
SD-4	0.5	0.2	0.01	480	192	465	52	25.7
SD-5	0.9	0.6	0.01	460	352	430	83	28.3

3.2.2 Stability performance of foam channeling sealing system at high temperature and high pressure

The foam stability of the developed SD-4 foam channeling sealing system is tested under high temperature and high pressure. The foam stability is tested under different pressures at 45℃, 108℃, 10 MPa and 20 MPa, respectively. The experimental results are shown in Fig.2 and Fig.3.

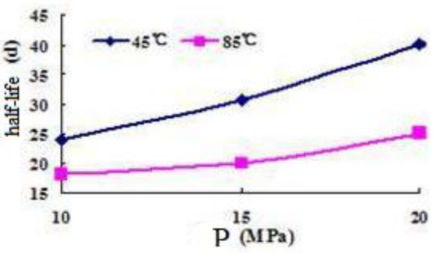


Fig. 2 Curve of foam half-life with pressure

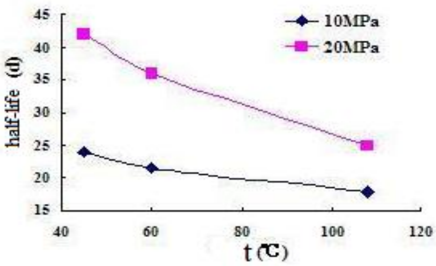


Fig. 3 Curve of foam half-life with temperature

As shown in the figures, with the increase of temperature, the stability of the foam sealing system becomes worse, with the increase of pressure, the stability of the foam sealing system increases. Low temperature, high pressure is conducive to the stability of the foam. Under the conditions of 45℃, 10MPa, the half-life of the foam is 24 days, under the conditions of 108℃, 20MPa, the half-life of the foam is 25 days.

3.3 Field Application

This techonlogy was applied for 9 wells, gas entry profile was improved obviously with effect of reducing gas production and increasing oil production. The average gas-oil ratio decreased from 379.8m^3/t to 134.8m^3/t, and the average oil increase of connected wells was 579.7t, and the average validity period was more than 12 months.

4. CO_2 HYDRATE PLUGGING REMOVING SYSTEM

By changing the thermodynamic balance of water molecules in wellbore fluid and reducing the steam pressure of water molecules, conventional low carbon alcohol achieves the purpose of hydrate plugging removal. But the plugging agent needs a certain temperature coordination, and constantly exchange heat with the surrounding environment, in order to achieve the purpose of plugging removal. The dissolution rate is relatively slow, and the complete plugging period (about 45d) is long.

4.1 Mechanism of CO_2 hydrate plugging removing agent

Modified non-ionic surfactant with hydrophilic structure, has strong polar groups which can destroy hydrogen bond in the ice phase and reduce the interfacial tension, and then lead to the collapse of the cage structure of CO_2 hydrate, increasing system entropy and local temperature, thus accelerate the dissolution of hydrate (see Fig.4). After CO_2 releases, it combines with modified non-ionic surfactant, which increases the molecular geometric radius of CO_2 and prevents CO_2 hydrate from regenerating.

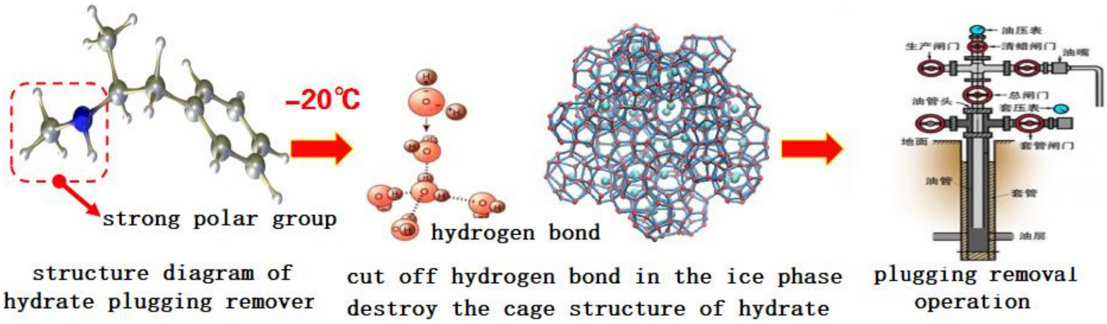


Fig.4 Plugging removal mechanismof low temperature hydrate plugging removing agent

4.2 Performance of CO_2 hydrate plugging removal agent

Evaluation experiment of low-temperature (-20℃) resistant plugging removal agent was carried out in the laboratory. Hydrate plugging can be removed by equivalent remover in 5d completely(see Fig.5). The corrosion rate of the formula was 0.053mm/a, and the technical indicators (see Tab.8) met the site requirements of low-temperature plugging removal and safe and environmental construction.

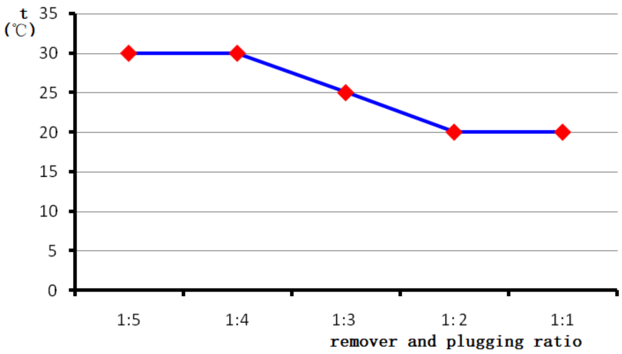


Fig.5 Plugging contrast curves of different proportions of plugging agents

Tab.8 Main performance indexes of low-temperature plugging remover

Freezing point	Dissolution rate	Boiling point	Ignition point	Corrosion rate
no freezing at -40℃	-20℃\5d\ 100%	>170℃	Non-flammable in open fire	0.053<0.076 mm/a

4.3 Field application

The CO_2 hydrate plugging removing test was conducted for 26 wells, and the plugging success rate was 100%. The average operation period was 15 days.

5. CONCLUSIONS

1) Chemical anticorrosion technology has been developed to solve the problem of undesirable adsorption of conventional corrosion inhibitors which are easy to fall off from the metal surface caused by liquid rinsing. The developed bicyclic imidazoline corrosion inhibitor has a "C=N" π-bond polycyclic

structure and electronegative groups, which can strengthen the coordination ability of "N-Fe", and the non-polar hydrophobic groups can form bimolecular protective film. The corrosion rate is only 0.065mm/a at CO2 partial pressure of 5MPa and 80℃. this technology was applied for 51 wells, with corrosion rates lower than 0.076mm/a.

2) The development of acid and oil resistant CO_2 foam channeling sealing agent realizes the blocking of gas channeling passage, and ensures the effect of CO_2 flooding. Through the introduction of hydroxyl, carboxyl, sulfonic acid group and other hydrophilic combination, improve the stability of the foam in acid and oil environment, under the condition of pH=3, oil saturation of 60%, foaming volume reaches 430mL, and half-life is 83h.

3) The low-temperature plugging removal technology is developed to realize the efficient and green plugging removal of hydrate freezing and heavy component plugging. Electronegative groups are used to destroy hydrogen bonds, reduce interfacial tension, resulting in the collapse of hydrate cage structures, increase entropy of the system, and accelerate dissolution. For the first time, the frozen plugging is dissolved completly at -20℃ .

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