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A New Application of Ethylenediamine to Improve CO2 Sweep Efficiency in Extremely-Low Permeability Reservoir[1]

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Abstract: Gas breakthrough is a common problem in CO2 displacement. This paper provides a new method with ethylenediamine to improve the efficiency of CO2 injection, sealing off the breakthrough channel. Experiments in porous medium model show that the ethylenediamine system can be easily injected into extremely low permeability reservoir, it can react with CO2 and the generated carbonate will reduce the permeability of the flooding region, causing the breakthrough pressure reaches 22MPa, hence, the swept efficiency is improved. Oil displacement experiment with heterogeneous core shows that the recovery factor is improved by 19.8%. Additionally, the ethylenediamine system shows high temperature resistance and CO2 erosion resistance. It also has an advantage of selective plugging, it will not injury the reservoir where CO2 does not pass by as long as we chose the suitable injection speed, prepositive and postpositive slug. So we could control CO2 breakthrough by profile control.
Key words: ethylenediamine; plugging; CO2; heterogeneity; profile control

Low permeability reservoir takes up the majority of newly discovered reserve in China, but recovering oil in low permeability reservoir is difficult, natural productivity is low, and water injection is limited because of the geological conditions, the recovery factor is low. However, gas injection has special advantages in development of low permeability reservoirs because of high mobility, reducing oil viscosity, expanding oil volume and decreasing interfacial tension (CHEN, 2000; LI, ZHANG, & RAN, 2001; Tiffin, & Kremesec, 1988; YANG, YUE, & SHEN, 1991). CO_2 miscible flooding is one of the most promising methods to enhance oil recovery (EOR). However, high microscopic sweep efficiency is not often achieved in reservoir operations, due principally to the non-uniformity of the flow patterns and unfavorable mobility ratio between injected CO_2 and oil (Li et al 2006; GUO et al, 2003). A more

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common alternative to improve the problem of poor sweep efficiency of CO_2 in oil reservoirs is by blocking the high permeability streaks, and or fractures.

Ethylenediamine（$H_2NCH_2CH_2NH_2$）is a simple diammonium, belonging to small molecular organic amines. It is colorless, transparent, a viscous liquid with ammonia odor, melting point 8.5 ℃, boiling point 116.5℃ and relative density 0.8995(20℃). It is a strong alkali, can react with acid forming amine salt. The salt forms hydrate when soluble in water.

In order to improve the sweep efficiency of CO_2 flooding, according to extremely-low permeability conditions, this paper presents a chemical reaction between injected carbon dioxide and injected ethylenediamine which improves reservoirs heterogeneity.

1. EXPERIMENT MATERIALS

Experimental materials are as follow, oil-free outcrop sands (60-100 meshes), CO_2 gas with 99.9% purity, two-dimension lengthways-heterogeneous physical core model (4.5 cm×4.5 cm×70 cm), oil mixed by white oil and jet fuel by 9:1. Ethylenediamine is provided by Beijing Chemical Works with 99.9% purity. All experiments are processed in 102℃.

Experiment equipments includes German HAKKE RS600 rheometre, constant speed and pressure pump(HXH-100B）,sand pack model with pressure detecting points, corrosion resistant and high pressure resistant vessel, automatic pressure tester, gas flow meter, automatic constant temperature control equipment.

2. EXPERIMENT METHODS

Sand pack model (φ2.5 cm×100 cm) and two-dimension lengthways-heterogeneous physical model (4.5 cm×4.5 cm×70 cm) were prepared for displacement experiment, injecting performance and plugging performance of ethylenediamine were studied, as well as the selective plugging performance and recovery improving performance.

2.1 Experiment on plugging strength in single sand pack

Sand pack was prepared with water-test permeability of $2.45\times10^{-3}\ \mu m^2$ and porosity of 40.33%. The experiment was taken in the simulating conditions of Honggangbei Block in Jilin oil field (permeability less than $10\times10^{-3}\ \mu m^2$, 102℃). First, the sand pack was put in the automatic constant temperature control equipment, and evacuated for 12hs until pressure was -0.1MPa; After that, the sand pack was saturated with water and then was displaced with CO_2 with velocity of 5ml/min until no water came out in the exit end. Then, 0.1PV of prepositive N_2 protection slug, 0.2PV of ethylene diamine slug (0.1mL/min), and 0.1 PV of postpositive N_2 protection slug were injected one by one, and after that, CO_2 was injected continuously. Pressure along the pack and gas flow rate are recorded accordingly.

2.2 Plugging stability

The sand pack used in the plugging experiment was put in constant temperature and constant pressure (102℃, 4MPa), gas flow rate at different times were recorded, and the corresponding permeability was obtained.

2.3 Experiments on selective plugging performance

2.3.1 Parallel sand packs

Two sand packs (18.3×10^{-3} μm^2, 1.2×10^{-3} μm^2) were paralleled in a constant temperature environment (102℃), pumped to vacuum, saturated with water, and experimented in the way of full injecting and separate recovery as the same steps as single sand pack experiment.

2.3.2 Two-dimension lengthways-heterogeneous physical model

This experiment was taken in a two-dimension lengthways-heterogeneous physical model with a relatively high permeability (26×10^{-3} μm^2) layer and a relatively low permeability (5×10^{-3} μm^2) layer. The core was put into a core holder with circling pressure, pumped to vacuum for 48 hours until -0.1MPa, saturated with water, and then displaced with CO_2 at a uniform speed of 5ml/min by the constant speed and pressure pump (HXH-100B) until no liquid came out from the output end. Then, 0.1PV of preposed N_2 slug, 0.2PV of ethylenediamine slug and 0.1PV of post N_2 slug were injected in turn, after that, CO_2 were injected continuously(5ml/min).

2.4 Oil displacement experiment in heterogeneous core

The core was put into a core holder with circling pressure, pumped to vacuum for 48 hours until -0.1MPa, saturated with oil, and then displaced with CO_2 at a uniform speed of 5ml/min by the constant speed and pressure pump (HXH-100B) until no liquid came out from the output end. Then, 0.1PV of preposed N_2 slug, 0.2PV of ethylenediamine slug and 0.1PV of post N_2 slug were injected in turn, after that, CO_2 were injected continuously (5ml/min).

3. DISCUSSIONS ON THE RESULTS

3.1 plugging strength

Pressure data and gas-test permeability (fig1, table1) in single sand pack experiment show that this plugging system has a breakthrough pressure of 22MPa,a big pressure drop can be observed within the 60cm distance from the injection point, while the largest pressure drop accrued in 20～40 cm distance, reached 13.5MPa. The permeability is reduced significantly within the 60cm distance from the injection point, which is in good conformity with the pressure result. Hence, it is suggested that this system has a good plugging strength and can meet the requirement of CO_2 breakthrough control.

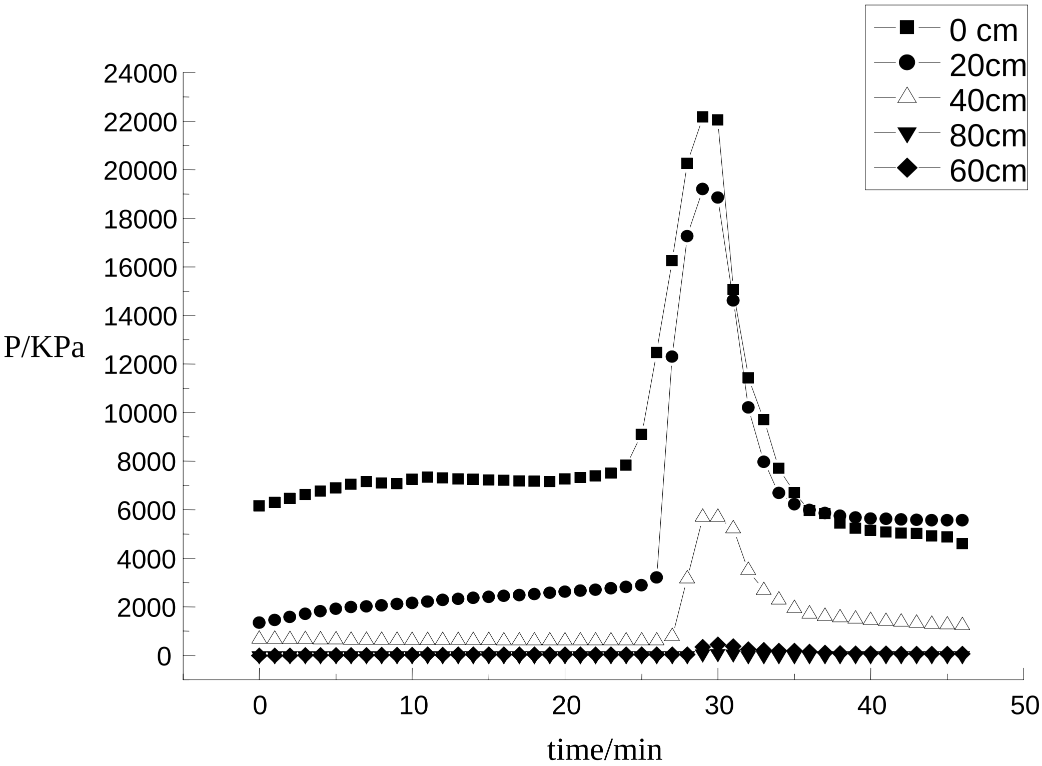

Figure 1. Pressures of CO_2 flooding in different distances after injecting ethylenediamine

Table 1. Gas-test permeability in different distances before and after plugging

distance/cm		10	30	50	70	90
Permeability/$10^{-3}\mu m^2$	Before plugging	38.8977	6.6000	0.3205	9.7800	30.6189
	After plugging	3.7680	0.1228	0.1178	12.5215	25.1232

Injection pressure of ethylenediamine at the input end (Fig2) show that this system has a perfect mobility, the injection flow rate is 0.1 mL/min.

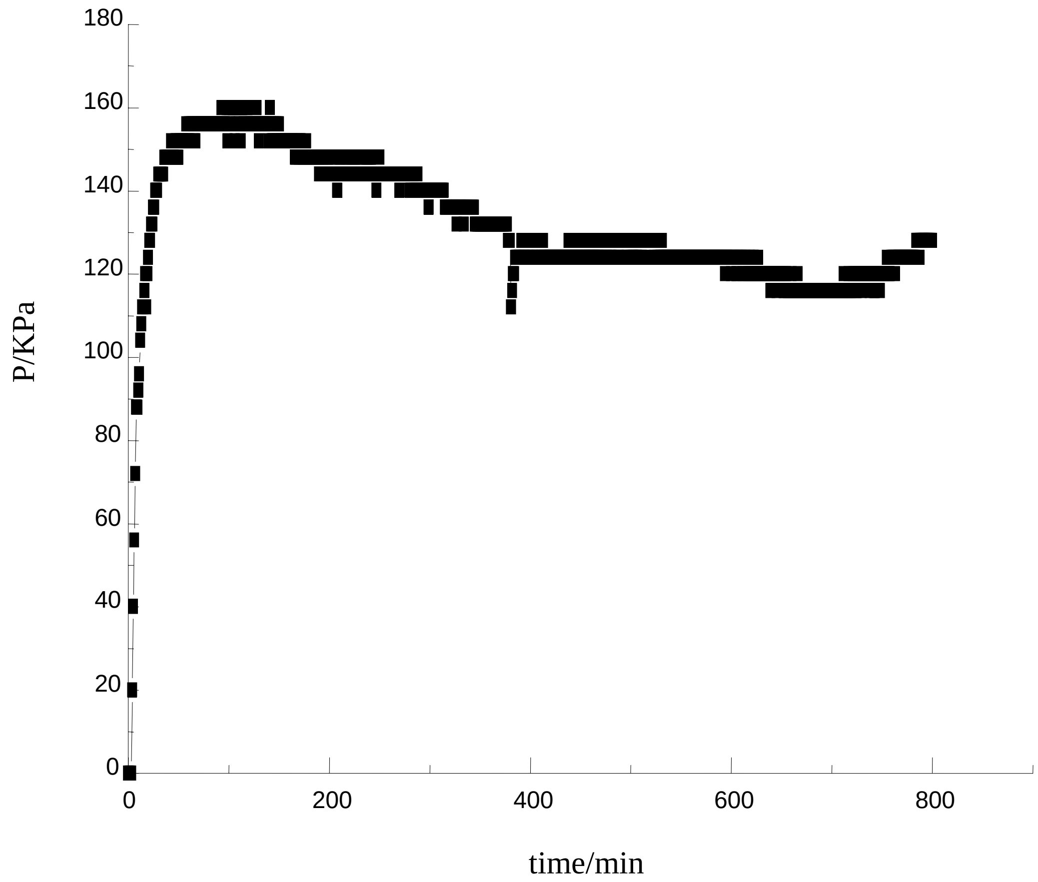

Figure 2. Injection pressure of ethylenediamine at the input end

3.2 Stability of plugging

The sand pack of plugging strength experiment was provided with constant temperature and constant pressure (102℃, 4MPa),gas flow rate at different time was recorded, and the corresponding permeability was obtained(fig 2). The results show that this system has good resistance of high temperature and CO_2 corrosion. For 25 days, the average gas-test permeability was of little variation, with time passing by it became quite stable, this was because the ethylenediamine and CO_2 reacted gradually and generated carbonate without mobility.

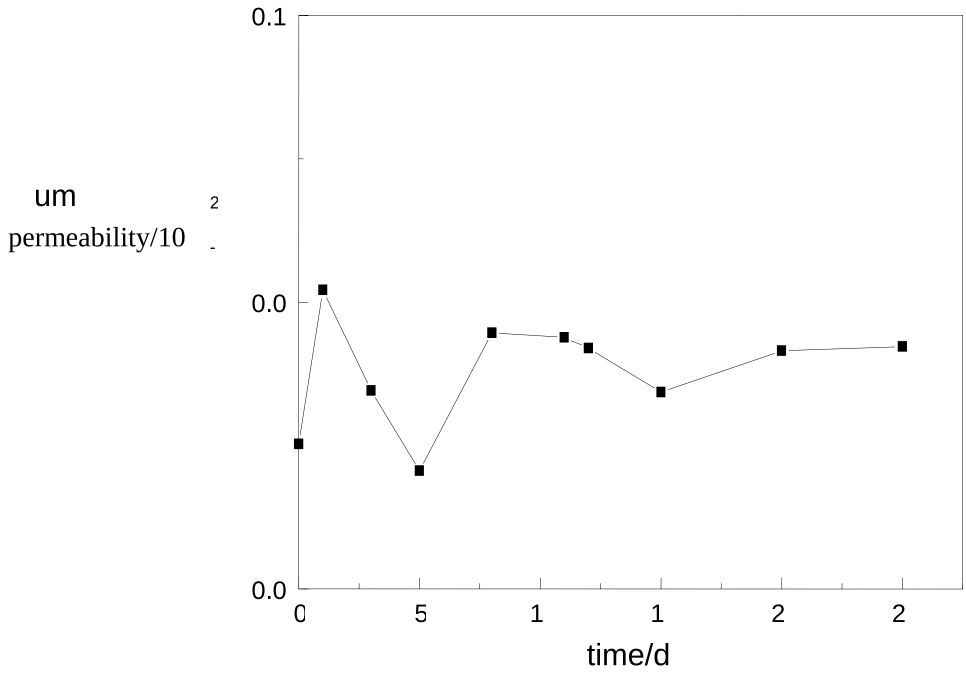

Figure 3. Average permeability after plugging

3.3 Selective plugging performance

3.3.1 Result of Parallel sand packs

Permeability values before plugging (table 2) are tested during the stable period of gas displacement with saturated water, and values after plugging are tested during the stable CO_2 injection after post slug (0.1PV) was injected. The values show that the permeability of high permeability pack was reduced distinctly, from $18.3723\times10^{-3}\,\mu m^2$ to $0.1652\times10^{-3}\,\mu m^2$; while the low permeability pack was not reduced, and even increased for water saturation decreased.

Different changes between two packs' permeability provide a convenience for ethylenediamine flooding in the high permeability pack,in certain flow rate, ethylenediamine would flow along the CO2 channel, selectively plugging the high permeability channel, while the area with low permeability would not be hurt.

3.3.2 Water displacement with two-dimension heterogeneous model

For the CO_2 displacement of water, pressure at different distances before plugging show that pressure along the high permeability layer was high, while it was low along the low permeability and nearly zero after 15cm, which suggests that most of CO_2 flooded into high permeability layer, while the low permeability layer was not swept. After plugging, the pressure of injecting CO_2 was significantly increased, a big pressure drop was observed in the distance from 30cm to 60cm where plugging happened, while pressure along the low permeability pack after plugging had little change. Vertically splitting the core after experiment, flow crack of ethylenediamine was quit clear in the high permeability layer, but not in low permeability layer.

Table 2. Gas-test permeability of high and low permeability sand packs before and after plugging

	Before plugging			***After plugging***		
	Pressure in input end /MPa	Gas flow rate /mL min^{-1}	Permeability /$10^{-3}\mu m^2$	Pressure in out put end /MPa	Gas flow rate /mL min^{-1}	permeability /$10^{-3}\mu m^2$
High Permeability pack	0.2640	18	17.6420	4.8	34	0.1709
	0.2600	18	18.0682	5.28	39	0.1627
	0.4480	44	18.2277	6.36	56	0.1620
	0.3120	26	19.5511	average		0.1652
	average		18.3723			
low Permeability pack	20.6	16	0.0045	19.4	16	0.0051
	21.3	16	0.0042	27.0	18	0.0030
	28.0	17	0.0026	average		0.0040
	average		0.0038			

Table 3. Gas injection pressure of high and low permeability packs before and after plugging

distances/cm	Gas injection pressure in High Permeability pack /KPa		Gas injection pressure in low Permeability pack /KPa	
	Before plugging	after plugging	Before plugging	after plugging
0	164.0	2464.3	164.0	2464.2
15	140.0	1940.2	148.0	1620.2
30	164.0	2320.2	0.0	582.1
45	102.0	22.5	17.5	285.0
60	84.0	646.1	15.0	752.6
70	109.0	196.0	13.0	477.0

3.4 Oil displacement experiment in heterogeneous core

According to the results of oil displacement experiment in heterogeneous core, the recovery factor was increased by 19.8% after plugging, with 17.1% in high permeability layer and 2.7% in low permeability layer (figure 3).

Two effects increased the recovery factor of high permeability layer, one was that the reaction caused reduction in the permeability of the flooded region in the high permeability layer, improving the conformance of the injected CO_2, the other was that higher pressure after plugging made CO_2 an ideal displacement fluid for multiple contact miscibility, high microscopic sweep efficiency was approached.

The increased recovery in the low permeability layer was mainly because the heterogeneity between two layers was reduced after plugging, thus the sweep volume was enlarged.

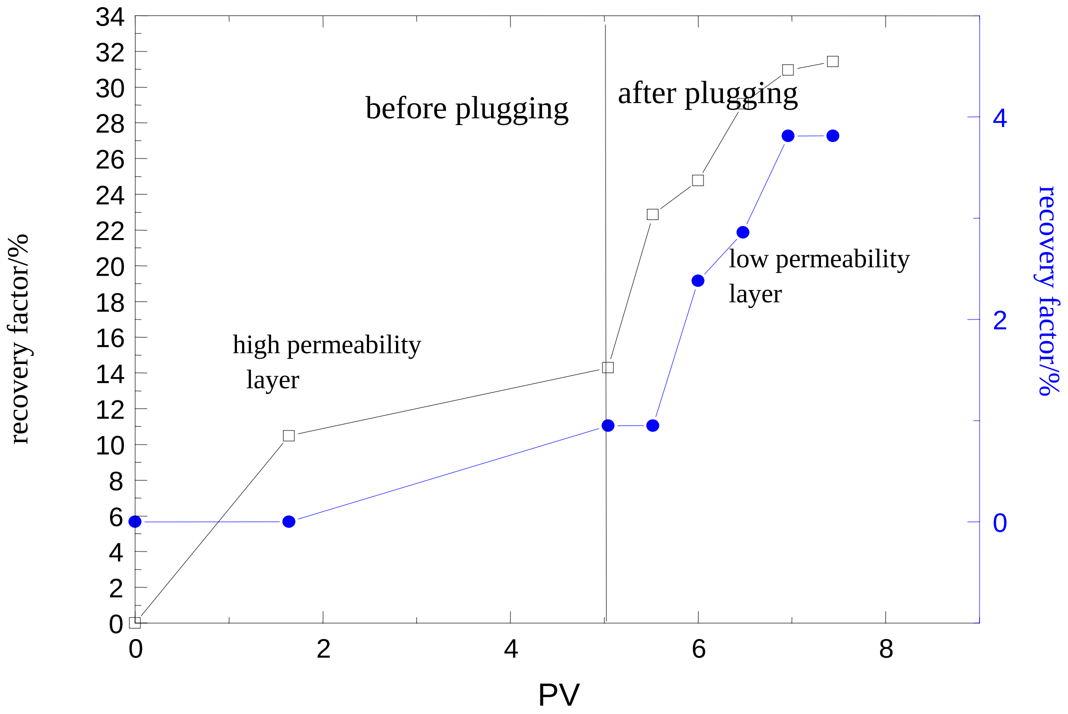

Figure 4. Recovery factor～injection volume in high and low permeability layers

4. CONCLUSIONS

The following conclusions have been made based on the experiments conducted throughout this study:

1st. The ethylenediamine system has a good mobility, can be injected easily; this system have a good plugging strength and can reduce the permeability of a sandstone porous medium during CO_2 flooding.

2nd. This system has good resistance of high temperature and CO_2 corrosion.

3rd. Ethylenediamine can be injected in an absolutely environment-friendly manner, improve reservoir heterogeneities, such as fractures or high-permeability streaks that could intensify viscous fingering of CO_2 and cause early breakthrough of injected CO_2, which will reduce oil recovery efficiency.

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