

# Profile improvement during CO<sub>2</sub> flooding in ultra-low permeability reservoirs

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**Abstract:** Gas flooding such as CO<sub>2</sub> flooding may be effectively applied to ultra-low permeability reservoirs, but gas channeling is inevitable due to low viscosity and high mobility of gas and formation heterogeneity. In order to mitigate or prevent gas channeling, ethylenediamine is chosen for permeability profile control. The reaction mechanism of ethylenediamine with CO<sub>2</sub>, injection performance, swept volume, and enhanced oil recovery were systematically evaluated. The reaction product of ethylenediamine and CO<sub>2</sub> was a white solid or a light yellow viscous liquid, which would mitigate or prevent gas channeling. Also, ethylenediamine could be easily injected into ultra-low permeability cores at high temperature with protective ethanol slugs. The core was swept by injection of 0.3 PV ethylenediamine. Oil displacement tests performed on heterogeneous models with closed fractures, oil recovery was significantly enhanced with injection of ethylenediamine. Experimental results showed that using ethylenediamine to plug high permeability layers would provide a new research idea for the gas injection in fractured, heterogeneous and ultra-low permeability reservoirs. This technology has the potential to be widely applied in oilfields.

**Key words:** Ethylenediamine, organic amine, profile improvement, ultra-low permeability reservoirs, mitigation of gas channeling, CO<sub>2</sub> flooding

## 1 Introduction

Carbon dioxide (CO<sub>2</sub>) displacement was developed in the 1950s. It is the most widely used enhanced oil recovery (EOR) process. Many laboratory studies and field tests were conducted in USA, Canada, China, etc. (Moritis, 1990; Manrique, et al 2010; Koottungal, 2008; Shen, 2010). CO<sub>2</sub> EOR technology may be CO<sub>2</sub> huff and puff and CO<sub>2</sub> flooding (including miscible and immiscible CO<sub>2</sub> flooding). Several researchers investigated the phase behavior between CO<sub>2</sub> and crude oil. Whether CO<sub>2</sub> can be miscible with crude oil or not depends on the reservoir temperature, pressure and the components of crude oil (Jaubert et al, 2002; Ju et al, 2012; Li, 2012; Bon et al, 2005; Luo et al, 2012; Cao and Gu, 2013). In addition, CO<sub>2</sub> is soluble in formation water and crude oil, so the components of crude oil and formation water would be changed, which leads to asphaltene deposition in reservoirs. Also, the pore structure, permeability and wettability may change. Hamouda et al (2009) investigated the effect of CO<sub>2</sub> flooding on asphaltenic oil recovery and reservoir wettability. Alemu et al (2011), Oldenburg and Rinaldi (2011), and Wang and Gu (2011) studied the influence of CO<sub>2</sub> on rock physical properties including permeability

reduction. Tang et al (2011) and Huang et al (2002) studied CO<sub>2</sub> dissolution and mass transfer in formation water. Yao and Ji (2010) and Ju et al (2013) proposed prediction models for CO<sub>2</sub> flooding and CO<sub>2</sub> sequestration, which can be used for parameter optimization. Meanwhile, Xue et al (2001), Qin et al (2010), Okuno et al (2001), Moreno et al (2011), and Torabi et al (2012) discussed CO<sub>2</sub> flooding mechanisms. The known mechanisms of CO<sub>2</sub> flooding include oil swelling, oil viscosity reduction, miscibility at the specified temperature and pressure, interfacial tension (IFT) reduction, vaporization and extraction of oil components, etc.

Due to fractures, serious heterogeneity and unfavorable mobility ratio between CO<sub>2</sub> and oil, the major problem in the use of CO<sub>2</sub> flooding is severe gas cross-flow and gas channeling, which leads to small swept volumes and low oil recovery. Therefore, mitigating gas cross-flow and gas channeling is particularly critical to enhance oil recovery (Hou and Yue, 2010; Wang and Gu, 2011; Chen et al, 2010). Previous studies show that successful mitigation of gas channeling or bypassing in reservoirs depends on three factors, including fine reservoir engineering studies, blocking agents matching reservoir conditions and reasonable implementation schemes and technology. Among these factors, selection of blocking agents matched with reservoirs is the most critical. CO<sub>2</sub> displacement is commonly used in conventional reservoirs, and the gas channeling can be

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controlled by conventional technologies, such as water alternating gas (WAG). In China, CO<sub>2</sub> displacement is mainly applied in low/ultra-low permeability reservoirs, but research into reduction and mitigation of gas channeling in these reservoirs are still immature around the world. Therefore, it is necessary to develop some new blocking agents applicable to mitigate gas channeling in ultra-low permeability reservoirs (Reid and David, 2002; Enick et al, 2012; Zhang et al, 2012).

The reaction between organic amines and CO<sub>2</sub> was firstly reported in the late 1920s, mainly about using organic amine solution to absorb CO<sub>2</sub>. Nowadays, absorption of CO<sub>2</sub> by organic amines have been become a leading method for CO<sub>2</sub> capture in the chemical industry (Zhao et al, 2012; Patil et al, 2012). According to the above reaction mechanism, ethylenediamine can be used as blocking agent to mitigate CO<sub>2</sub> channeling in ultra-low permeability reservoirs. Hou et al (2007) first proposed the idea and Yu et al (2009) provided some primary experimental results about feasibility of using organic amines to mitigate CO<sub>2</sub> channeling. In this paper, the reaction mechanism between CO<sub>2</sub> and ethylenediamine, reaction conditions, profile control mechanism and techniques and plugging performance in cores with micro-fractures are further discussed, providing some information to field application.

## 2 Experimental

### 2.1 Experimental equipment and materials

A static evaluation device including an air bath, reaction and pressure containers, and a pressure pump was used to study the reaction between organic amine and CO<sub>2</sub> (shown in Fig. 1). A high temperature, high pressure (HTHP) gas displacement apparatus (including an air bath, a injection pump, a high temperature container, a core holder, pressure sensors and a data recording computer, shown in Fig. 2) was used to evaluate the plugging performance of ethylenediamine and the follow-up CO<sub>2</sub> displacement performance.

Natural outcrop cores with dimensions of 4.5 cm×4.5 cm×30 cm were used in the tests. Crude oil taken from the Yanchang Oilfield has a viscosity of 11.54 mPa·s at surface conditions (dead crude oil) and 4.87 mPa·s under reservoir conditions (live crude oil). The oil sample used was a mixture of Yanchang crude oil and aviation kerosene, and its viscosity

was adjusted to 4.87 mPa·s to simulate crude oil under reservoir conditions. Produced formation water from the Yanchang Oilfield with a salinity of 70,000 mg/L was used.

Ethylenediamine (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, chemical purity, >98%) is a colorless liquid with an odor of ammonia. Its melting point and boiling point are 8.5 and 116.5 °C, respectively. The relative density of ethylenediamine is 0.8995. It is soluble in water and ethanol. CO<sub>2</sub> used was of 99.9% purity.

### 2.2 Experimental methods

When the reservoir temperature is near or at the boiling point of ethylenediamine, the reservoir has good injectivity for ethylenediamine, so ethylenediamine may enter gas channels in ultra-low permeability reservoirs and then react with CO<sub>2</sub> to form a chemical reaction product to block these channels.

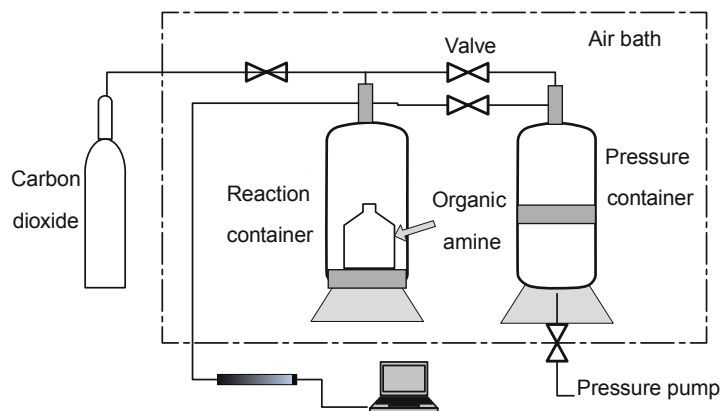
#### 2.2.1 Chemical reaction of ethylenediamine with CO<sub>2</sub>

Different volumes of ethylenediamine were measured and put into beakers, and then the beakers were placed in a high temperature container (100 °C, Fig. 1). CO<sub>2</sub> was then injected into the intermediate container to maintain a pressure of 3 MPa. The beakers were taken out after 24 h, and the characteristics of the reaction products were observed.

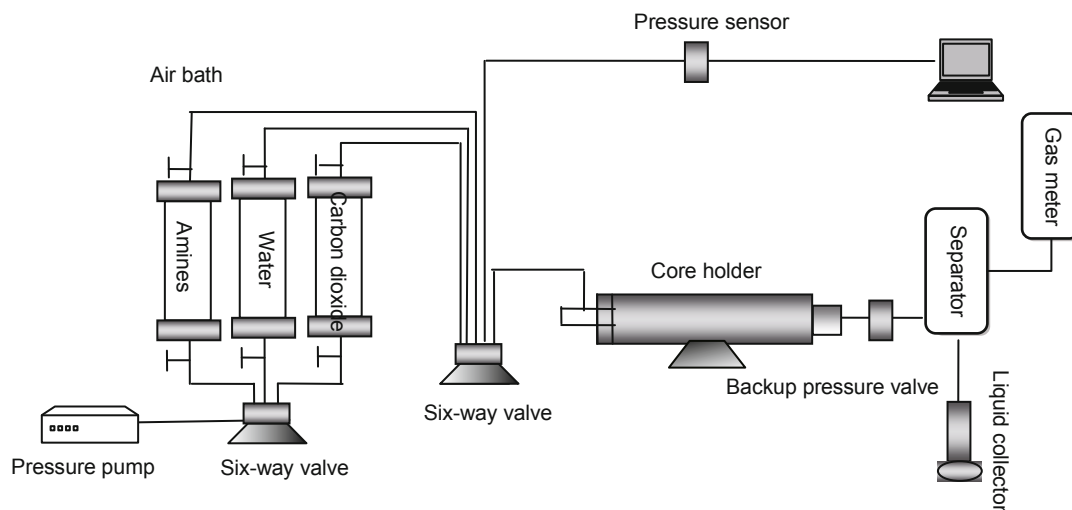
#### 2.2.2 Measurement of ethylenediamine injectivity

For mitigating gas channeling in ultra-low permeability reservoirs, blocking agents could be injected into and flow in the reservoirs. In order to evaluate injectivity of ethylenediamine at different temperatures, oil displacement tests were conducted at 45, 65, 85, and 100 °C, respectively, in a HTHP gas displacement apparatus (Fig. 2). These tests were divided into two groups. In the first group of tests, ethylenediamine was directly injected into the core; and in the other group, protective slugs of ethanol were injected into the core before and after injection of ethylenediamine. In these tests, the permeability of cores used was  $6 \times 10^{-3} \mu\text{m}^2$ . The test procedures are as follows:

- 1) The test temperature was set at 45 °C.
- 2) The prepared natural outcrop core was placed in the core holder. After evacuation the core was saturated with formation water. Then, the water permeability was measured. Subsequently, CO<sub>2</sub> was injected into the core at 3 MPa until gas channeling was observed at the outlet.



**Fig. 1** A static evaluation device for reaction between organic amine and CO<sub>2</sub>



**Fig. 2** High temperature, high pressure gas displacement apparatus

3) Ethylenediamine was injected into the core and the inlet pressure was recorded until the pressure reached a constant.

4) The test temperature was set at 65, 85 and 100 °C, respectively, Steps 2 through 3 were repeated.

It should be noted that in the second group of tests, protective ethanol slugs (0.1 PV) were injected into the core before and after injection of ethylenediamine.

### 2.2.3 Measurement of swept volume by ethylenediamine

Large swept volume is the premise of high enhanced oil recovery. Natural outcrop cores with permeability of  $6 \times 10^{-3} \mu\text{m}^2$  were used to investigate the migration of ethylenediamine under formation conditions. The experimental apparatus and core parameters were the same as those described in above injectivity evaluation. In the test, protective slugs (0.1 PV) were injected before and after ethylenediamine injection and the swept volume was analyzed at different injection volumes of ethylenediamine. Finally, the cores were cut through, and the core sections were observed. Here, the temperature was set at 100 °C.

### 2.2.4 Oil displacement tests before and after profile improvement

The effect of channeling blocking and flooding was determined based on enhanced oil recovery from blocking high-permeability layers by injecting ethylenediamine. The heterogeneous model consisted of two parallel cores of permeability of  $1.4 \times 10^{-3}$  and  $10 \times 10^{-3} \mu\text{m}^2$ , respectively. The model containing sealed fractures was prepared by fracturing (the core was put on a bench press and pressure was applied on it along the axis until the core was split in half) and letting the fractures close naturally without proppants, and the matrix permeability was  $1 \times 10^{-3} \mu\text{m}^2$ . The tests were conducted at 100 °C and the test procedures are as follows.

1) Before test, the core dimensions were measured and then its apparent volume was calculated.

2) After drying, the core was evacuated and then saturated with formation water, so the pore volume and porosity were calculated.

3) Water was injected into the core and then the water

permeability was measured. Oil was then injected to displace water, according to the oil volume and water volume in cores, the initial oil saturation was calculated.

4)  $\text{CO}_2$  was pumped into the core and the volumes of gas and liquid collected at the outlet and the gas breakthrough time were recorded.

5)  $\text{CO}_2$  was continuously injected into the core until the outlet gas/liquid ratio reached 6,000, and the produced oil volume was recorded and the gas recovery and the cumulative gas volume were then calculated.

6) Three slugs used for profile control (0.1 PV ethanol (pre-slug), 0.2 PV ethylenediamine, 0.1 PV ethanol (post-slug)) were injected in turn into the core and then the inlet and outlet valves of the core holder were closed. After 24 h,  $\text{CO}_2$  was pumped into the core and the test was terminated when gas breakthrough occurred. The oil production was measured and total oil recovery was calculated.

## 3 Results and discussion

### 3.1 Chemical reaction of ethylenediamine with $\text{CO}_2$

#### 3.1.1 Morphologic characteristics of reaction products

The reaction products of ethylenediamine and  $\text{CO}_2$  are shown in Fig. 3. It can be seen that the reaction products existed in two phase states. One was in the form of white particles attached to the wall of the beaker and the other was a light yellow viscous liquid. The color of the viscous liquid would deepen with an increasing volume of ethylenediamine.

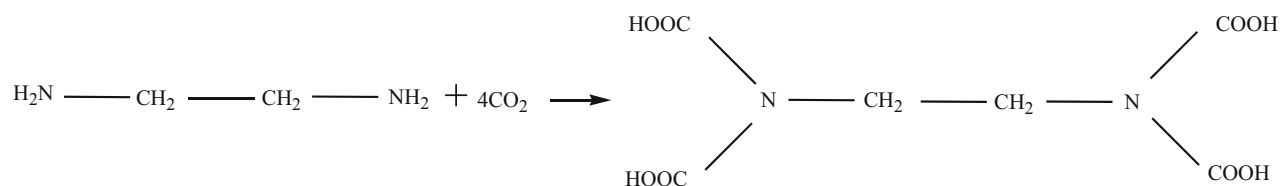
#### 3.1.2 Reaction mechanism of ethylenediamine and $\text{CO}_2$

Ethylenediamine has two equivalents of primary amine per mole and reacts with  $\text{CO}_2$  to generate amino acid-like substances. On the other hand, the structure of ethylenediamine makes the reaction product have some particular properties. It can be inferred from the forms of reaction product that the reaction occurs in two stages, complete reaction and incomplete reaction.

1) Complete reaction of ethylenediamine with  $\text{CO}_2$

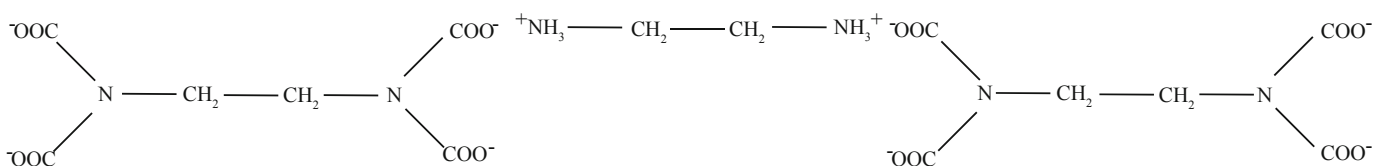
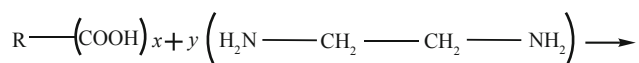
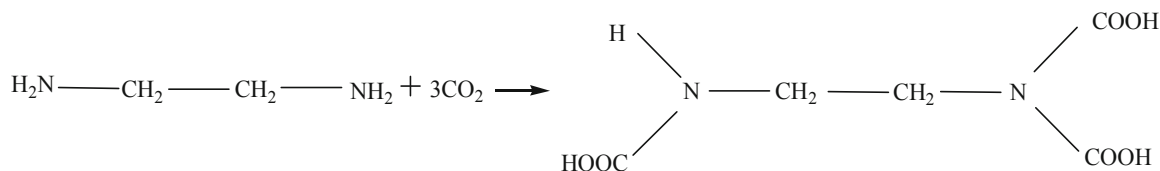
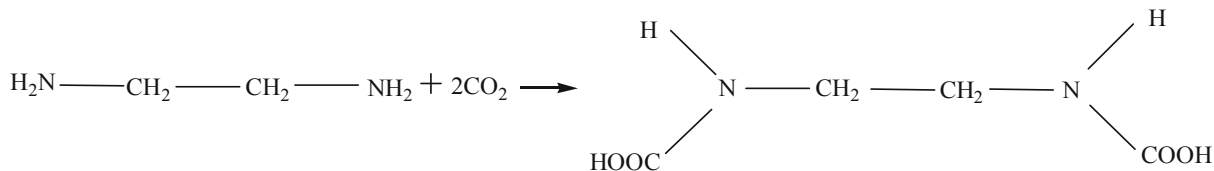
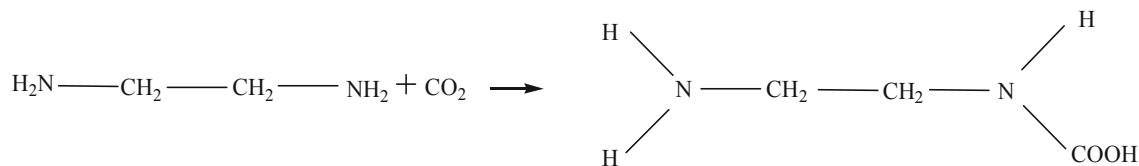


**Fig. 3** Reaction products of ethylenediamine and CO<sub>2</sub> at 3 MPa



The complete reaction product, carbamic acid, is in the form of white particles, which are shown as the white solids attached to the wall of the beaker in Fig. 3.

2) Incomplete reaction of ethylenediamine with CO<sub>2</sub>



The incomplete reaction product, carbamate, is a light yellow and viscous liquid of macromolecular structure.

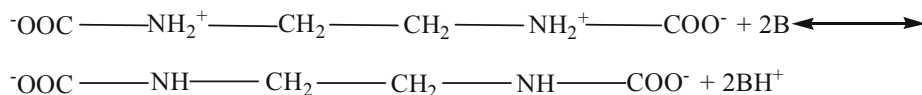
Reaction products and equations show that the

ethylenediamine diffusing in CO<sub>2</sub> or being on the solution surface contacts completely with CO<sub>2</sub> at first, and then reacts to generate solid particles, which may prevent CO<sub>2</sub>



from contacting with ethylenediamine in the solution. Subsequently, CO<sub>2</sub> and ethylenediamine react incompletely. Therefore, the reaction products exist in two phase states. Moreover, the greater the amount of ethylenediamine, the higher the probability of incomplete reaction, and the deeper the color of products will be, which can be seen in Fig. 3.

3) Reaction analysis of ethylenediamine and CO<sub>2</sub> in the



Intramolecular cross-linking of  $^-\text{OOC}-\text{NH}_2^+-\text{CH}_2\text{CH}_2\text{NH}_2^+-\text{COO}^-$  occurs due to multivalent ions present in the solution, leading to solution thickening. Therefore, the viscosity of the product created in formation water is significantly higher than that without formation water, as shown in Fig. 4. This proves that formation water is helpful to improve plugging performance.

When the light yellow viscous liquid was continually exposed to CO<sub>2</sub> the final product was a white crystal, as shown in Fig. 5. Also, the white crystal and light yellow liquid are mutually soluble.

The reaction between ethylenediamine and carbon oxide is in fact a rapid acid-base reaction, with stable reaction products. Compared with other carbon dioxide absorbents such as alkylol amine, the desorption proportion and desorption rate of CO<sub>2</sub> from ethylenediamine are relatively

presence of formation water

In actual formations, except for the crude oil and injected ethylenediamine and CO<sub>2</sub>, the formation water always exists, so it is necessary to analyze the reaction of ethylenediamine and CO<sub>2</sub> in the presence of formation water. From the above reaction mechanism, the zwitterion will be deprotonated by other anions such as Cl<sup>-</sup> in the solution, and then form carbamate, for example,

low at 110 °C, hence the high-viscosity reaction products may effectively block the high-permeability zones in the reservoirs.

### 3.2 Injectivity of ethylenediamine

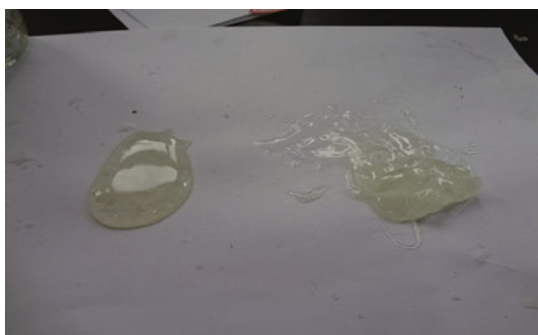
For the first group of injectivity evaluations, the injection pressure increased dramatically in the process of direct ethylenediamine injection. When 0.08 PV ethylenediamine was injected into the core, the pressure reached 2 MPa; when 0.12 PV ethylenediamine was injected, the corresponding pressure reached 4 MPa. This means that the injection pressure was not proportional to the injection volume, as a result the test had to be terminated. The core was taken out for observation after the pressure was released. It was found that the core inlet was blocked by a black substance, so the volume swept by ethylenediamine was very small, shown in Fig. 6. The main reason is that CO<sub>2</sub> injected into the core reacted with ethylenediamine so early and rapidly that the pores were blocked by the reaction product, which hindered the subsequent injection.

To prevent ethylenediamine and CO<sub>2</sub> from reacting too rapidly, 0.1 PV of ethanol was injected as a protective slug (pre-slug) before injecting ethylenediamine to isolate ethylenediamine and CO<sub>2</sub>. After injection of ethylenediamine, 0.1 PV of another protective ethanol slug (post slug) was injected to prevent subsequent reaction between ethylenediamine and CO<sub>2</sub>. The relationship between injection pressure and injection volume is shown in Fig. 7.

Fig. 7 shows that the protective slug injected into the core could greatly reduce the injection pressure. Note that increasing test temperature also reduced the injection pressure. This is because with the increase in temperature, ethylenediamine was close to its boiling point and the reaction product viscosity reduced significantly, thus ethylenediamine and its reaction product may easily flow into the core. The injection pressures were relatively lower at 85 and 100 °C, while the pressures were high at 45 and 65 °C. This demonstrates that ethylenediamine is more suitable for high-temperature reservoirs. Injection of a protective ethanol slug helps the penetration of ethylenediamine into the formation more easily and deeply.

### 3.3 Swept volume

0.1, 0.2, 0.3 PV of ethylenediamine was respectively injected into the natural outcrop cores whose permeability was



**Fig. 4** Reaction products without formation water (left) and with formation water (right)

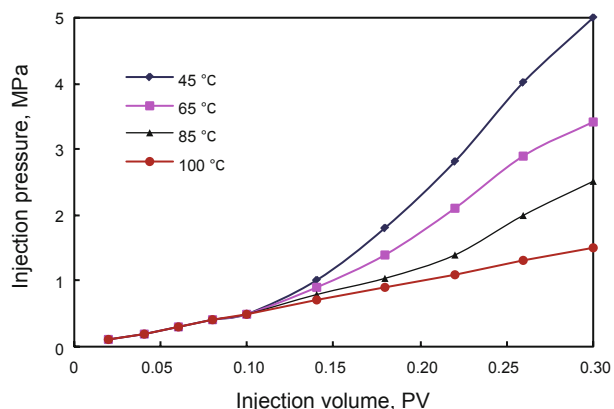


**Fig. 5** The final product of the yellowish-brown viscous liquid continually exposed to CO<sub>2</sub>



**Fig. 6** Head face and profile of the core after direct injection of ethylenediamine

$6 \times 10^{-3} \mu\text{m}^2$ . After the tests were completed, the cores were taken out and split, as shown in Fig. 8. It can be seen that after injection of 0.1 PV ethylenediamine, the swept volume was estimated to be 1/3 of the whole core volume, but after injection of 0.3 PV ethylenediamine, the core was wholly swept. The reason is that the low molecular weight amine is volatile, and its diffusion and migration ability is very strong in cores at high temperatures. This shows that injection



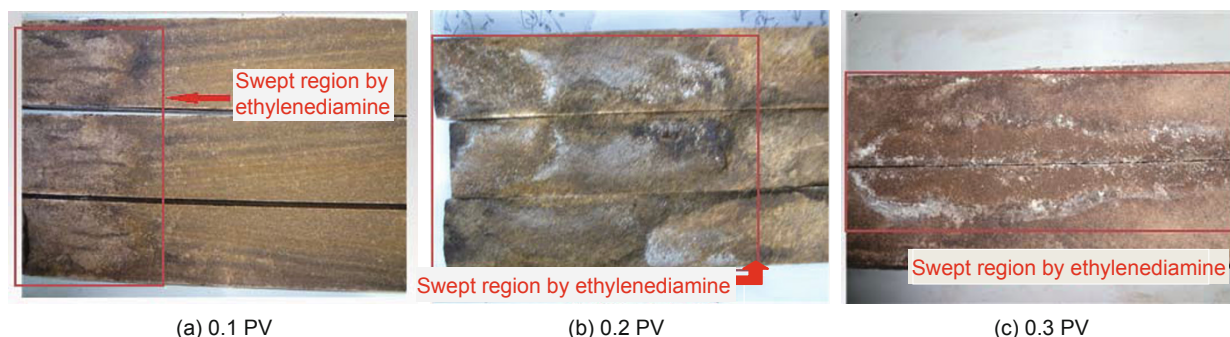
**Fig. 7** Relationship between injection pressure and injection volume of ethylenediamine after injection of 0.1 PV protective ethanol slug

of ethylenediamine into reservoir formations may greatly improve the CO<sub>2</sub> swept volume.

### 3.4 Oil displacement results of the plugged cores

#### 3.4.1 Heterogeneous cores

The physical parameters and experimental results of oil displacement tests on heterogeneous cores are listed in Table 1. It can be seen that injection of ethylenediamine could effectively mitigate gas channeling in high-permeability layers and improve oil recovery from subsequent CO<sub>2</sub> injection. The gas channeling rate reduced significantly, and after gas breakthrough the gas flow rate at the outlet of the high-permeability core decreased to be consistent with that of the low-permeability core. On the other hand, the swept volume by ethylenediamine increased, and the oil recovery of the low-permeability core increased by 13%-25%, and that of the high-permeability core increased by 4%-5% during subsequent flooding after the profiles of the heterogeneous cores were modified. This indicates that the gas channels were blocked and remaining oil may be displaced from the low-permeability layers. Experimental results demonstrate that ethylenediamine



**Fig. 8** Swept volume by ethylenediamine of different injection volumes

**Table 1** Oil displacement results of heterogeneous cores before and after being plugged by ethylenediamine

Heterogeneous cores	Permeability $10^{-3} \mu\text{m}^2$	Permeability ratio	Oil recovery before plugging, %	Gas flow rate before plugging, mL/min	Increased oil recovery after plugging, %	Gas flow rate after plugging, mL/min	Cumulative oil recovery, %
Core 1	1.4	7.1	10.0	65	25.5	105	35.5
Core 2	10		43.5	1860	4	180	47.5

may flow into the high-permeability zone and reacted with subsequently injected CO<sub>2</sub> to form high-viscosity reaction products to block this zone and then divert CO<sub>2</sub> to the low-permeability zone, thus the oil recovery was enhanced.

### 3.4.2 Sealed fracture core

In ultra-low permeability reservoirs, micro-fractures are commonly well-developed, which may improve oil recovery, but these fractures also become the dominant open channels to fluid flow and often cause early gas breakthrough

during production. Therefore, it is very important to study how to effectively plug these micro-fractures. Analysis and observation of the reaction product of ethylenediamine with CO<sub>2</sub> indicate that the light yellow viscous liquid had high viscosity, and the final product—the white solid was very dense, so ethylenediamine can be used to block micro-fractures. In experiments, sealed fractures were used to simulate micro-fractures in the real formation. The displacement results are shown in Table 2.

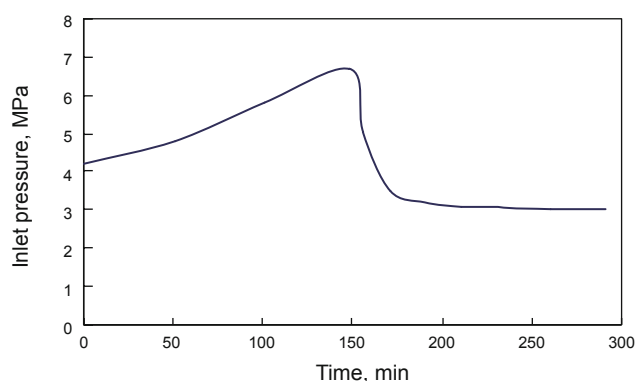
**Table 2** Experimental results of the sealed fracture core before and after being plugged by ethylenediamine

Matrix permeability 10 <sup>-3</sup> μm <sup>2</sup>	Gas flow rate before plugging, mL/min*	Oil recovery before plugging, %*	Injection sequence	Gas flow rate after plugging, mL/min*	Oil recovery after plugging, %*
1	5000	0	1 mL ethanol pre slug +8 mL ethylenediamine +1 mL ethanol post slug	55	32

Notes: \* these values were measured when gas breakthrough occurred.

It can be seen that ethylenediamine could effectively plug the closed fractures. Before plugging, no oil was displaced from the core by gas (oil recovery was 0). While, after injection of 8 mL ethylenediamine, the oil recovery was improved greatly, and the final recovery increased to 32%. Besides, the gas flow rate reduced significantly, from 5,000 mL/min to 55 mL/min, which proved that fractures had been effectively plugged.

In former displacement tests, the pressure was kept constant. In the following test, the gas flow rate was kept constant and then the breakthrough pressure was measured for the plugged fracture core, as shown in Fig. 9. The threshold (or displacement) pressure of ethylenediamine in the sealed fractures was 4 MPa, and the pressure stabilized at 3 MPa after breakthrough. Therefore, ethylenediamine can be used to plug sealed fractures.



**Fig. 9** Injection pressure of ethylenediamine in the sealed fracture cores

## 4 Conclusions

1) The reaction products of ethylenediamine with CO<sub>2</sub> were in two forms: white crystal from the complete reaction and light yellow viscous liquid from the incomplete reaction. The reaction products could be used to block channels.

2) Injection of a protective slug of ethanol could greatly reduce the injection pressure of ethylenediamine in high temperature reservoirs, which would meet the injection

requirements for ultra-low permeability reservoirs. Under high temperature conditions, ethylenediamine had good mobility in the formation, and the swept volume was enlarged.

3) Oil displacement tests in heterogeneous models indicated that reaction product of ethylenediamine and CO<sub>2</sub> had good plugging performance and could plug high-permeability layers and divert the fluid flow to low-permeability layers. For the sealed fracture model, the breakthrough pressure of the blocking agent reached 4 MPa, and the injection pressure after breakthrough maintained at about 3 MPa.

4) Ethylenediamine can be used to mitigate CO<sub>2</sub> channeling, which provides a feasible technical approach for CO<sub>2</sub> injection in heterogeneous fractured reservoirs of ultra-low permeability. For field application, some parameters need to be further optimized according to reservoir characteristics.

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