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SPECIALTY SECTION  
This article was submitted to  
Geochemistry, a section of the journal  
Frontiers in Earth Science

RECEIVED 25 September 2022  
ACCEPTED 20 October 2022  
PUBLISHED 16 January 2023

CITATION  
Zhu Z, Song Y, Gao Q and Wang C  
(2023), The application of CO<sub>2</sub>-  
responsive materials on enhanced oil  
recovery for fractured tight  
oil reservoirs.  
*Front. Earth Sci.* 10:1053307.  
doi: 10.3389/feart.2022.1053307

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# The application of CO<sub>2</sub>-responsive materials on enhanced oil recovery for fractured tight oil reservoirs

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## KEYWORDS

CO<sub>2</sub>-responsive, foam, worm-like micelle, gel, enhanced oil and gas recovery (EOR and EGR), fractured oil reservoir

## Introduction

According to the statistics, about 38% of oil and gas fields in the world and 46% in China are contributed by low-permeability reservoirs. The effective development of low permeability oil and gas fields has important strategic significance to ensure the sustainable development and exploitation of oil and gas resources in China. Due to lack of natural energy in the formation and the difficulty of water injection, the oil recovery rate and factor of these reservoirs are fairly low (WANG, et al. 2007; LI, 2020).

CO<sub>2</sub> flooding is often used as a EOR technology to improve oil recovery in low permeability reservoirs due to its good solubility and strong extraction ability. It is mainly used to facilitate oil displacement by reducing the viscosity of crude oil, improving the mobility ratio, expanding the volume of crude oil, and reducing the interfacial tension (ZHAO, et al. 2017). However, due to the strong heterogeneity and the existence of natural and induced fractures, as well as the influence of injection-production well parameters and fluid properties, CO<sub>2</sub> is prone to channeling along the high seepage zone (LI, 2018; WANG, 2019). Avoiding gas channeling during the process of gas flooding has become a major issue. It is vital to increase the sweep volume and improve the performance of CO<sub>2</sub> flooding to reduce the heterogeneity of reservoir and plug the breakthrough channels such as fractures, throats and pores (LIU, et al. 2022).

Water-alternate-gas (WAG) injection, gas thickening, foam plugging and polymer gel plugging are common methods to address gas channeling (PENG, 2013; YUN, 2013; WEN, 2019; ZHAO, et al. 2020). However, these measures are generally one-time plugging, which limits the effectiveness on gas channeling. In this work, a variety of CO<sub>2</sub> responsive plugging systems are summarized and analyzed, including CO<sub>2</sub> responsive foams, surfactant solutions and gels. The main mechanism of these systems is that in saturated CO<sub>2</sub> solution, amine-containing compounds spontaneously or combine with surfactant molecules to form worm-like micelles (WLMs) after deprotonation, so as to improve the viscosity of the solution and achieve precise and efficient blocking of gas channeling.

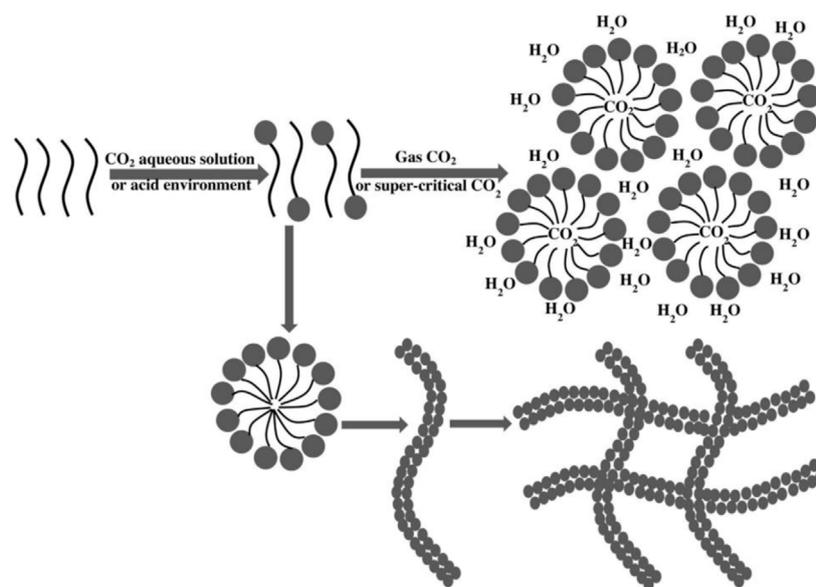


FIGURE 1

Schematic diagram of structure change of surfactant–amine system stimulated by CO<sub>2</sub> (LI, et al., 2015).

## Types of plugging agent

### CO<sub>2</sub>-responsive foam

A formula of CO<sub>2</sub> responsive foam system was proposed previously by (LV, et al. 2021). The system had obvious shear-thinning characteristics and was more viscoelastic than the conventional foam system. The FCI value of the foam system could be more than 11 times than that of the conventional foam system, which could effectively inhibit gas channeling in strongly heterogeneous reservoir, and improve the CO<sub>2</sub> flooding development efficiency. Li et al. screened the surfactant with the best performance from five surfactants (ODPTA, AC-1810, AC-1815, SDS, OTAC) and constructed a CO<sub>2</sub> sensitive and self-enhanced foam system for mobility control (LI, et al. 2017). ODPTA had a carbon chain consisting of an amine group and 18 carbon atoms, which could not be ionized in water. However, in the acidic environment caused by CO<sub>2</sub>, the amine group was protonated and ion pairs (C<sub>18</sub>H<sub>37</sub>-NH-(CH<sub>2</sub>)<sub>3</sub>-NH<sub>2</sub><sup>+</sup>-(CH<sub>2</sub>)<sub>3</sub>-NH<sub>3</sub><sup>+</sup> and C<sub>18</sub>H<sub>37</sub>-NH-(CH<sub>2</sub>)<sub>3</sub>-NH-(CH<sub>2</sub>)<sub>3</sub>-NH<sub>2</sub>-CO<sub>2</sub><sup>-</sup>) are formed. The results showed that the CO<sub>2</sub> foam prepared by ODPTA is sensitive to CO<sub>2</sub> and had good plugging and mobility control performance at low concentration. Even under the harsh conditions of 7.8 MPa and 160°C, the resistance factor could still reach 274.

### CO<sub>2</sub>-responsive surfactant

Some studies showed that the use of CO<sub>2</sub> as an external stimulus to transform surfactant micelles was currently a simple and environmentally friendly way to prepare micelles. (SU, et al. 2013; ZHENG, et al. 2015; ZHANG, et al. 2016). Su et al. prepared an anionic worm-like micellar system with CO<sub>2</sub> response using sodium octadecyl sulfate (C<sub>18</sub>H<sub>37</sub>SO<sub>4</sub>Na) and N, n-dimethylethanolamine (DMAE) at 60°C. DMAE was positively charged by protonation under CO<sub>2</sub> stimulation and then self-assembles with the anionic surfactant C<sub>18</sub>H<sub>37</sub>SO<sub>4</sub>Na under electrostatic attraction to form worm-like micelles. When N<sub>2</sub> was injected, the high viscosity system returned to the initial viscosity state. And this process could be repeated more than three times, and the maximum viscosity formed without a big deviation (SU, et al. 2013). Shen et al. screened ten compounds containing tertiary amine groups, and finally determined N, N-Dimethyl Erucamide tertiary amine (DMETA) as the research object. The results showed that the DMETA solution forms WLMs in saturated CO<sub>2</sub> solution, and the viscoelastic fluid could effectively reduce gas flow during CO<sub>2</sub> gas flooding in low-permeability fractured cores, and had a strong ability to withstand high temperature. WLMs had the ability of self-repair and had high residual resistance even after gas channeling (SHEN, et al. 2021).

## CO<sub>2</sub>-responsive gel

The mechanism of gel-blocking gas channeling was discussed in detail, and the future development direction of CO<sub>2</sub> trapping and interpenetrating gel system was prospected. CO<sub>2</sub> responsive intelligent gel can solve the problem of poor acid resistance of HPAM. The cross-linking formed a three-dimensional network structure after CO<sub>2</sub> treatment, with increased viscosity and volume, and remained stable for a long time under acidic CO<sub>2</sub> conditions (LIU, et al. 2022). A CO<sub>2</sub> responsive gel system mainly using small molecule amine (DMTA) and a modified long chain alkyl anionic surfactant (NADS) was prepared (DAI, et al. 2020). The experimental results showed that the DMTA-NADS system exhibited viscoelastic properties and shear thinning properties at high shear rates. The environment scanning electron microscope (ESEM) visually showed that the connection mode of its internal structure changed from lamellar to three-dimensional network structure. It was confirmed by NMR that amine molecules can bridge two anionic surfactant molecules by non-covalent electrostatic attraction after protonation. The core physical simulation experiment proved that the system could effectively block the CO<sub>2</sub> channeling channel, and the blocking efficiency was more than 90%, which increased the sweep volume of the subsequent CO<sub>2</sub> gas flooding and improved the recovery efficiency. It provided effective guidance for solving the practical problem of gas channeling and plugging in low permeability CO<sub>2</sub> gas flooding development reservoir.

## Comparative analysis of different materials

The mainly mechanism of CO<sub>2</sub> responsive materials involved in this paper is shown in Figure 1.

It is shown that CRMs are effective measures to prevent gas channeling during gas flooding. When the CRMs encounters CO<sub>2</sub>, its structure changes and the viscosity of the solution increases, which can be observed in both bulk and porous media. The three CRMs mentioned in this paper have essentially the same mechanism, but different plugging systems can be obtained by changing the type and concentration of surfactants, amines, and volume and rate of CO<sub>2</sub> injection according to different purposes of using.

Compared with other plugging agents, CRMs has a better application prospect in tight fractured reservoirs. Before CRMs gelling, the solution viscosity is low (1–2 mPa s), resulting in easy injecting. It can quickly form high viscosity gel after CO<sub>2</sub> injection and has strong blocking ability. Using suitable surfactants and amines, CRMs can maintain high stability under high temperature and high salt conditions.

## Conclusion

- 1) The mechanism of CO<sub>2</sub> responsive plugging system is that the molecular structure in aqueous solution changes upon CO<sub>2</sub> stimulation, forming worm-like micelles. The macroscopic behavior is that the viscosity of the system changes, which is reversible and controllable.
- 2) By using different materials to interact with amine compounds, CRMs are low viscosity solutions before injection and can be formed as CO<sub>2</sub> responsive blocking systems after reaction with CO<sub>2</sub> in porous media such as CO<sub>2</sub> responsive foam, CO<sub>2</sub> responsive surfactant solution and CO<sub>2</sub> responsive gel. With good injection ability, CRMs can effectively block the gas channeling, force the gas to turn to the unswept zone, and improve the degree of reservoir production. At present, it is necessary to develop a low cost and high tolerance CO<sub>2</sub> responsive plugging system for the development of fractured tight oil reservoirs, so as to improve the production capacity and benefit of oil fields. (LIU AND LIU, 2022), (LV et al., 2021).

## Author contributions

ZZ: investigation and research, writing manuscript draft; YS: resources and conceptualization; QG: modify analysis; CW: typesetting and supervision.

## Funding

This work is supported by PetroChina “Fourteenth Five Year” Significant Programs (No. 2021DJ3203).

## Conflict of interest

Author YS was employed by the company PetroChina Ji Dong Oilfield Company.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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