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# Experimental study on a new plugging agent during CO<sub>2</sub> flooding for heterogeneous oil reservoirs: A case study of Block G89-1 of Shengli oilfield



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#### ABSTRACT

In oilfield operations,  $CO_2$  has been applied to enhance oil recovery (EOR). However,  $CO_2$  injection in heterogeneous oil reservoirs lacks acceptable sweep efficiency due to the high mobility of  $CO_2$ . A suitable composite organic granule plugging agent was developed to control  $CO_2$  mobility and hence, improve sweep efficiency and oil recovery. The reaction mechanism involved hydroquinone, formaldehyde, furfural and heptyl alcohol catalyzed by p-toluene sulfonic acid at supercritical  $CO_2$  to initiate carbonyl addition and condensation reaction via sol-gel polymerization to form granulated polymer. This system is suitable for low permeability and low water-cut oil reservoirs. The core experiments show that the system is easy for injection, and the plugging ratio is more than 98% after injecting 1PV. The parallel sand pack model experiments show that the system can enter the high permeability reservoirs first and as the increase of permeability ratio, the profile modification becomes better. The core flooding experiment shows that the system had good performance of sealing for  $CO_2$  and the EOR can be further improved 11.9% at the same time.

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# 1. Introduction

CO<sub>2</sub> has been used commercially to recover oil from geologic formations by enhanced oil recovery (EOR) technologies for over 40 years (Enick et al., 2012), and CO<sub>2</sub> flooding has been gaining wide recognition in recent times of China, such as Shengli (Lv et al., 2015; Zhang et al., 2009), Tahe and Jilin oilfield (Ren et al., 2015; Zhang et al., 2015). The main mechanisms behind conventional CO<sub>2</sub> EOR are oil swelling, viscosity reduction, vaporization and extraction (Riazi et al., 2011). The CO<sub>2</sub> EOR process could be improved if the high mobility of CO<sub>2</sub> relative to reservoir oil and water can be effectively reduced. Different CO<sub>2</sub> injection techniques, namely continuous/slug CO<sub>2</sub> injection (Zhou et al., 2012), simultaneous water and gas injection (SWAG) (Ma et al., 1995), and water alternating gas process (WAG) (Nidia et al., 2002) have been developed. However, for high heterogeneous oil reservoirs, the continuous/slug CO<sub>2</sub> injection, SWAG and WAG techniques have not been very effective (Chang et al., 1998; Dong et al., 2011). The results of non-aqueous sealing agent and profile modification

http://dx.doi.org/10.1016/j.petrol.2016.04.017 0920-4105/© 2016 Elsevier B.V. All rights reserved. properties under high-temperature conditions are scarce in the literatures, the plugging agent was produced by condensation reaction which was used hydroquinone, formaldehyde, furfural, p-toluene sulfonic acid, poly(dimethylsiloxane) and heptyl alcohol then crosslinking create net structure in the end, this reaction along with produce, grow up and crosslink of the organic granule at the same time. In this paper, we took the Block G89-1 of Shengli Oilfield as an example.

The Block G89-1 of Shengli oilfield belongs to high temperature, low permeability and heterogeneous oil reservoir. The temperature is 126 °C and the permeability is 0.077–23.8 × 10<sup>-3</sup> µm<sup>2</sup>, the depth of the reservoir is 2350–3400 m. Because of the fracturing technology, many wells in Block G89-1, the permeability between matrix and crevice have big difference, and the swept volume factor may be lower. So, before CO<sub>2</sub> flooding we should do some plugging work.

No matter  $CO_2$  flooding was deemed to secondary oil recovery or the way of EOR after water flooding, it was highly regarded by this industry, so, the technology of  $CO_2$ -EOR can continuous renewal and mature (Zain et al., 2001). In the real oil reservoir, the factor of the heterogeneous and detrimental mobility ratio of oil reservoir cause viscous fingering, then lead to gas premature break

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through and increased gas-oil ratio and low viscosity made CO<sub>2</sub> easier to enter the high permeability reservoir, that made the field test bad (Desch and Larsen, 1984). ChunLei et al. (2009) studied ethylenediamine plugging in extra-low permeability oil reservoir during CO<sub>2</sub> flooding, the experiment showed that the system was easy for injection, and had good performance of sealing for CO<sub>2</sub> and the EOR can be further improved 19.8% at the same time. Fan and Luo (2013, 2014) researched a sealing agent for high temperature and low permeability oil reservoirs, the intake volume was small, the gelling time can control, the performance of resisting temperature, resisting shearing and resisting acids was good. Shusheng et al. (2013) researched the effect of Ca(OH)<sub>2</sub> plugging CO<sub>2</sub> flooding, the result showed that Ca(OH)<sub>2</sub> can effective improve the heterogeneous of low permeability reservoir, adjust gas and water injection profile of this reservoir, prevent gas channeling, increase oil recovery of low permeability reservoir, effectively prolong gas flooding time, and then achieved the result of EOR.

This paper proceeds with experimental apparatus, materials and procedures. Next, we discuss the effect of pressure, temperature, stirring on plugging agent property. The results of sand packs flooding experiments are presented in detail and discussed. We studied the plugging performance through the injection volume, permeability ratio, plugging experiment of  $CO_2$  flooding and displacement efficiency of  $CO_2$ .

#### 2. Experimental

## 2.1. Materials and equipment

Details of the materials and equipment used to do the experiment and their specification are tabulated below in Table 1.

# 2.2. Preparation

The hydroquinone, formaldehyde, furfural, p-toluene sulfonic acid, heptyl alcohol and solvent were introduced into the high temperature and high pressure steel vessel equipped with transparent glass window and stirred to complete homogeneity. The steel vessel was sealed up and  $CO_2$  injected until the required pressure was attained. Stir the solution or not, observing the formation of organic granule through the glass on the steel vessel. The objective was to study the effect of mole ratio of reactants, reaction pressure and reaction temperature on the formation of organic granule. After reaction, organic granule was poured out, filtered, dried and the yield calculated. The yield ( $\eta$ ) defined by Eq. (1),

$$\eta = \frac{M}{M_1 + M_2 + M_3} \times 100\%$$
(1)

where  $\eta$  is the yield of the organic granule, and M is the total mass

of organic granule after reaction and dried (g), and  $M_1$  is the initial dosage of hydroquinone in reaction (g), and  $M_2$  is the initial dosage of formaldehyde in reaction (g), and  $M_3$  is the initial dosage of furfural in reaction (g).

After preparing the sample, Scanning electron microscopy was used to examine the particle morphology (Fig. 1).

# 2.3. Plugging agent stability tests

The organic granule produced at 126 °C was divided into 5 equal parts and labeled A, B, C, D, E. Samples B, C, D and E were placed in aging tank containing 200 mL of synthetic water of Shengli oilfield Block G89-1, the pH was adjusted to 3 and in order to simulate the super critical  $CO_2$  system. The aging tank was then sealed up and hot-aged in a GRL-9 roller oven at 126 °C for 7 days, 14 days, 30 days, 60 days and 90 days. The organic granule produced was also aging in kerosene for 7 days, 15 days, 20 days, 30 days and 50 days. The organic granule was then filtered and dried after the aging test, and its mass retention ratio calculated (Table 2).

#### 2.4. Physical simulation experiment

# 2.4.1. The effect of injection volume on plugging performance

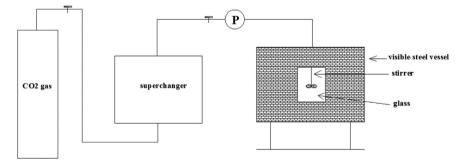
A 30 cm length of core was placed into core holder and maintained at a temperature of 126 °C during the entire test. The test involved water flooding, CO<sub>2</sub> flooding, injecting different volume plugging agent using the best recipe into the core, closed the tail valve of the core holder and injected CO<sub>2</sub> to 10 MPa, keep the temperature at 126 °C and 48 h. The tail valve was then opened and water flooded and plugging ratio calculated. The fluids injection were performed at a constant flow rate of 0.5 mL/min. The best injection volume of the plugging agent can be characterized by plugging ration (Pr), resistance factor (R<sub>f</sub>) and residual resistance factor (R<sub>ff</sub>). The plugging ration (Pr), resistance factor (R<sub>f</sub>) and residual resistance factor (R<sub>ff</sub>) defined by Eqs. (2), (3) and (4).

$$P_{\rm r} = \frac{K_{wb} - K_{wa}}{K_{wb}} \tag{2}$$

$$R_{\rm f} = \frac{K_w/\mu_w}{K_p/\mu_p} \tag{3}$$

$$R_{\rm ff} = \frac{\kappa_{wb}}{K_{wa}} \tag{4}$$

where  $K_w$  is the permeability of injection water,  $\mu_w$  is the viscosity of water,  $K_p$  is the permeability of injection plugging agent,  $\mu_p$  is the viscosity of plugging agent.  $K_{wb}$  is the permeability of the core or sandpack plugging before,  $K_{wa}$  is the permeability of the core or sandpack plugging after (Fig. 2).



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Fig. 1. The visual steel vessel of high temperature and high pressure.

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