[Journal of Natural Gas Science and Engineering 32 \(2016\) 59](http://dx.doi.org/10.1016/j.jngse.2016.03.073)–[65](http://dx.doi.org/10.1016/j.jngse.2016.03.073)

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Experimental study on the mechanism of carbon dioxide removing formation paraffin deposits

Xue Sun ^a, Hongjian Ni ^{a,} *, Hongshi Qiao ^b, Xueying Wang ^c, Bo Ma ^c, Ruihe Wang ^c, Zhonghou Shen ^a, Mengyun Zhao ^d

a Research Institute of Unconventional Oil & Gas and New Energy, China University of Petroleum, Qingdao 266580, China

^b CNPC Bohai Directional Drilling Service Company, Tianjin 300280, China

^c School of Petroleum Engineering, China University of Petroleum, Qingdao 266580, China

^d Research Institute of Production Engineering, SINOPEC Exploration & Production Research Institute, Beijing 100083, China

article info

Article history: Received 3 November 2015 Received in revised form 21 March 2016 Accepted 22 March 2016 Available online 25 March 2016

Keywords: Carbon dioxide Formation paraffin deposits removal Adsorption-induced swelling Experiment

ABSTRACT

Formation paraffin deposits cause serious productivity damage during the process of oil production. As an effective, economical and environmentally friendly organic solvent, $CO₂$ has many advantages in removing formation paraffin deposits. In this paper, the mechanism of action for CO₂-mediated removal of formation paraffin deposits is analysed. An indoor simulation of CO₂-mediated removal of formation paraffin deposits is conducted. The feasibility of removing formation paraffin deposits by $CO₂$ is investigated and the effect of injection parameters on plug removal efficiency is discussed. The experimental results show that $CO₂$ adsorption-induced swelling and paraffin thermal expansion are the main factors that facilitate CO_2 -mediated removal of formation paraffin deposits. Plug removal using CO_2 requires a long injection time. As the injection temperature increases, plug removal efficiency increases. As the injection pressure increases, plug removal efficiency first increases and then decreases, which allows for determination of the optimal injection pressure.

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1. Introduction

Crystallization and deposition of paraffin are common problems encountered during crude oil production and transportation. Paraffin deposits are solid mixtures of wax crystals precipitated from crude oil. They are hydrocarbons with long linear and branched chains, including C18H38~C60H122 ([Newberry and Baker,](#page--1-0) [1985\)](#page--1-0). Paraffin deposition can occur on tubing, pipelines and other equipment, which causes blockages of the flowline and may result in surface equipment failure ([Misra et al., 1995\)](#page--1-0). Paraffin deposition can also occur in formations, which leads to serious formation damage and a decrease in productivity [\(Santos, 1997\)](#page--1-0). There are two main causes of paraffin deposition in an oil reservoir. First, if the treating fluids injected into a reservoir are cold, they may cause the crude oil to cool below its cloud point. Consequently, paraffin crystals precipitate out of the oil and aggregate on the surface of the rock pores ([Yao et al., 2009](#page--1-0)). Second, the loss of dissolved gas in crude oil can reduce the solubility of paraffin in

E-mail address: nihj@upc.edu.cn (H. Ni).

crude oil; the loss of dissolved gas is induced by a decrease in formation pressure. The decreased solubility of paraffin in crude oil causes paraffin precipitation [\(Mei et al., 2001\)](#page--1-0). Therefore, it is necessary to develop effective and economical methods for removing paraffin deposits to facilitate the stable production of oil.

Many methods have been studied and applied to the removal of paraffin from tubing and pipelines ([Alian et al., 2013; Ahn et al.,](#page--1-0) [2005\)](#page--1-0). Two such methods include a mechanical method and a surface preventing method. The mechanical method for removing paraffin uses scrapers to mechanically remove paraffin deposits on the surface of tubing or other parts of the equipment being used. The surface preventing method places a glass lining or epoxy phenolic coating on the inner wall of tubing; such coatings or linings prevent paraffin deposition by changing the tubing's surface properties. However, neither the mechanic paraffin removing method nor the surface preventing method can be applied in formation pores ([Wang and Dong, 1995](#page--1-0)).

Removing paraffin deposits from formation pores is more difficult than removing paraffin from tubing or pipelines ([Ju et al.,](#page--1-0) [2001\)](#page--1-0). Thermal removal and paraffin removal chemicals are Corresponding author. The removal of formation paraffin deposits.

However, the thermal removal technology that injects hot oil or hot water to remove formation paraffin deposits has the disadvantage of large energy consumption ([Wang et al., 2003\)](#page--1-0). The chemical method uses two types of chemicals for removing paraffin: water-soluble dispersants and solvents. Water-soluble dispersants do not dissolve paraffin but rather disperse the paraffin particles to prevent wax crystal aggregation ([Mohammed,](#page--1-0) [2011\)](#page--1-0). Solvents remove paraffin deposits by dissolving the paraffin; the two types of solvents used are aliphatic solvents (such as diesel, kerosene or condensate) and aromatic solvents (such as xylene or toluene) ([Barker et al., 2001](#page--1-0)). The use of solvents is undesirable due to their toxicity and flammability. Although thermal removal and paraffin removal chemicals are widely applied in the removal of formation paraffin deposits and achieve good performance, more effective, environmentally friendly and economical formation paraffin removing technologies are still necessary in the development of oil and gas.

Carbon dioxide $(CO₂)$ is widely used as an extraction solvent in the chemical industry because it is nontoxic, nonexplosive, cheap, and solubilizes organics (Friedrich and Pryde, 1984). CO₂ injection has also been applied in enhanced oil recovery (EOR) methods in the petroleum industry due to its ability to swell the crude oil and reduce oil viscosity ([Fernø et al., 2015](#page--1-0)). Stauffer et al. used CO₂ under 30 MPa of pressure at 100 \degree C to clean the wax coating of corrugated board; a paraffin removal rate of 70-98% was achieved ([Stauffer et al., 2002](#page--1-0)). These studies indicate that $CO₂$ may be an effective and environmentally friendly solvent for removal of paraffin deposits located in formations. To date, the use of $CO₂$ to remove paraffin deposits from formations has not been studied. The mechanism of action for $CO₂$ -mediated removal of formation paraffin deposits was unknown prior to this current study. In this paper, the mechanism of action for $CO₂$ -mediated removal of paraffin deposits in formations is analysed, along with the microstress of the paraffin particle. An indoor simulation of $CO₂$ -mediated removal of paraffin deposits from formations was conducted, and the effect of the injection parameters on plug removal efficiency was studied.

2. Mechanism of $CO₂$ -mediated removal of paraffin deposits in formations

When the formation temperature is lower than the cloud point, paraffin particles begin to precipitate out from crude oil. Under the action of shear diffusion and molecular attraction, the precipitated paraffin particles stick to the pore surface or the formed paraffin deposition layer, thus reducing formation permeability [\(Yue and](#page--1-0) [Dong, 1987\)](#page--1-0). When $CO₂$ is injected into the formation below the paraffin melting temperature, the mechanism of paraffin removal occurs as follows: (1) CO₂ fluid exhibits a hydraulic washing effect on paraffin deposits; (2) paraffin deposits expand spontaneously when heated by $CO₂$ fluid, reducing the van der Waals forces between paraffin particles; and (3) paraffin swell due to $CO₂$ adsorption on the surface of paraffin particles, which is facilitated by paraffin's branched and porous structures. Under one or more of these mechanisms, paraffin particles will fall off from the surface of the deposition layer and be flushed out of the formation by the $CO₂$ fluid, leading to increased formation permeability.

To analyse the micro-stress of paraffin particles, a paraffin particle was modelled as a hard sphere model of diameter D_p as shown in Fig. 1. The stress state of paraffin particles on a deposition surface is shown in Fig. 1. The primary forces exhibited by the $CO₂$ fluid that cause the migration of the paraffin particle are: the fluid drag force F_d , gravity force F_g , buoyancy force F_f and van der Waals force F_{vh} .

The flow state of $CO₂$ in porous media exhibits an interstitial flow with a low Reynolds number, so the fluid drag force F_d can be

Fig. 1. Micro-stress analysis diagram of formation paraffin deposits.

calculated by the spherical particle drag force formula using a low Reynolds number ([Stokes, 1850](#page--1-0)):

$$
F_d = \frac{\pi D_p^2}{8} C_D \rho_f V_f^2 \tag{1}
$$

where C_D is the drag force coefficient, $C_D = \frac{24}{\text{Res}}$; Res is the particle diameter;
Reynolds number, Res = $\frac{\rho_f V_f D_p}{\mu_f}$; D_p is the paraffin particle diameter; ρ_f , V_f , μ_f stands for the density, flow rate and dynamic viscosity of the $CO₂$ fluid, respectively.

The gravity force F_g and buoyancy force F_f can be calculated by the following formulas:

$$
F_g = \frac{\pi D_P^3}{6} \rho_d g \tag{2}
$$

$$
F_f = \frac{\pi D_P^3}{6} \rho_f g \tag{3}
$$

where ρ_d is the density of paraffin particle.

In consideration of the effect of $CO₂$ adsorption, the van der Waals force between two particles can be represented as ([Xie,](#page--1-0) [2003](#page--1-0)):

$$
F_v = \frac{AD_P}{24Z^2} + \frac{BD_P}{12Z^3} \tag{4}
$$

where A is the Hamaker constant; B is the Van der Waals adsorption constant; Z is the shortest distance between two particles.

It is assumed that two adjacent particles in the surface layer of the paraffin deposits are subjected to van der Waals forces in different directions. So the resultant van der Waals force on the surface particle F_{vh} can be calculated as:

$$
F_{vh} = 2F_v \cdot \sin \theta \tag{5}
$$

where θ is the angle formed from the line between the centre points of two adjacent particles and the pore wall.

The easiest way to break the paraffin particle from the paraffin deposition layer is probably via the roll mode. The following conditions should be satisfied when the paraffin particle is separated from the deposition layer via the roll mode:

$$
F_d \cdot L_d \ge F_g \cdot L_g - F_f \cdot L_f + F_{vh} \cdot L_{vh} \tag{6}
$$

where L_d , L_g , L_f , L_{vh} respectively stand for the force moment of drag Force, gravity, buoyancy and van der Waals force. $L_d = \frac{1}{2}(D_P + Z) \cdot \cos \theta$; $L_g = L_f = L_{vh} = \frac{1}{2}(D_P + Z) \cdot \sin \theta$.

Then, we can deduce the max diameter of paraffin particles available for removal by $CO₂$ flow from formulas (1)–(6).

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