Corrosion Analysis of Rubber Sleeve during CO_2 Miscible Flooding Experiment

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Abstract. CO_2 miscible flooding is an important method of improving oil recovery in low permeability reservoirs. The most important parameter of CO_2 miscible flooding is the minimum miscibility pressure (MMP) between CO_2 and crude oil. In this paper, the coreflood method was used to measure MMP, but it was found that the rubber sleeve of the core holder was seriously corroded, which resulted in the rubber sleeve with ring pressure and worse safety of the experiment. Therefore, in this paper by the means of theoretical analysis, experiment observation and comparison of the rubber sleeves before and after corrosion process, the corrosion mechanisms were analyzed. The research results will give some advises for further similar experiments.

1. Introduction

The rubber sleeve of core holder is an indispensable tool for the indoor coreflood experiment [1, 2], which acts as a pressure seal on the core, prevents the formation of an annulus around the core, and improves the accuracy of the experiment [3, 4]. It also has the advantages of pressure resistance, high temperature resistance, corrosion resistance and acid resistance. In order to increase the service performance of the rubber, a certain amount of filler is usually added into rubber during the production process to improve its performance. For example, adding a reinforcing agent to increase the tensile strength, hardness and wear resistance of the rubber, or adding a filler to improve its processing properties. At present, the rubber products used in Chinese oil and gas fields mainly include nitrile rubber, neoprene rubber, tibetan rubber, fluorosilicone rubber, tetrapropylene rubber and hydrogenated nitrile rubber [5, 6].

The existing literature on the study of rubber corrosion is generally studied in a pure CO_2 environment or in a CO_2-containing and formation water environment, ignoring the effects of core and crude oil on rubber corrosion [7, 8]. However, the inside of the rubber sleeve contacts with the formation water, core and crude oil, the corrosion mechanism is more complicated, especially in the process of CO_2 miscible flooding [9, 10] experiment, the temperature and pressure are much higher than the critical temperature (31°C) and critical pressure (7.1MPa) of CO_2 [11]. At this time, CO_2 fluid is in a supercritical state, which is a high-density, solubility like liquid, which has a strong erosion effect on rubber sleeve. It can make the rubber sleeve fail, causing the rubber sleeve to have its own ring pressure, which affects the accuracy and safety of the experiment [12, 13]. So it is necessary to study the corrosion mechanism of the rubber sleeve in the CO_2 miscible flooding process was researched.
2. CO₂ coreflood experimental condition and flow

2.1. Experimental condition
The experimental temperature is 45℃. The water is the simulated formation aqueous solution which specific composition is shown in Table 1. The oil is the simulated oil mixed with crude oil (from Daqing oilfield) and appropriate amount of kerosene which viscosity measured at 45℃ is 9.8mPa·s. The model is cylindrical Berea core, length 30cm, diameter 2.5cm, permeability 70md, porosity 21%.

Table 1. Simulated formation aqueous solution preparation reagents and dosage

| Reagent name | NaHCO₃ | NaCl  | KCl  | MgSO₄ | Na₂SO₄ | CaCl₂ |
|--------------|--------|-------|------|-------|--------|-------|
| Reagent dosage (g/L) | 2.829 | 3.489 | 0.02 | 0.262 | 0.114 | 0.064 |

2.2. Experimental equipment and flow
The experimental equipments include ISCO pump, back pressure valve, CO₂ gas cylinder, piston container, six-way, core holder and rubber sleeve (nitrile rubber). The specific experimental process is shown in Fig.1.

3. Experimental phenomena

3.1. The change of production elements
Because CO₂ dissolves in water, its aqueous solution is more corrosive than hydrochloric acid under the same pH value. In order to avoid corrosion of the holder, the annular space pressure was pressurized by injecting white oil into the annular space before the experiment. During the experiment, it was found that the annular space pressure of the core holder increased continuously. The higher the experimental pressure is, the faster the annular space pressure increased. It was necessary to discharge the white oil from the connected six-way pressure to reduce the annulus pressure, as shown in Fig.2.

Fig.2 The production oil before and after CO₂ corrosion
From Fig.2, we can find the color difference of oil before and after CO₂ corrosion. With the pressure increasing, the CO₂ corrosion intensifies obviously, which leads to the annular space pressure exceeding the working pressure of the core holder. If the white oil is not discharged, an experimental accident will take place.
3.2. The change of rubber sleeves

When the experiment ended, during the process of pressure relief, it was found:

(1) The white oil in the annular space is completely discharged, and a large amount of gas is discharged, and the white oil is ejected in a foam form.

(2) After the gripper plug is opened, the inside of the gripper has a bust sound, and the inside of the rubber sleeve starts to bulge, even cracked and exploded, and the core is stuck in the rubber sleeve and is difficult to take out.

(3) After standing for 24h, the rubber sleeve expansion phenomenon is weakened. After the rubber sleeve was taken out, the rubber sleeve expands the bulge and some areas was broken, as shown in Fig.3.

(4) The length of the rubber sleeve increased by an average of 4cm, the diameter increased by an average of 5mm, and the shape of the rubber sleeve was bent, as shown in Fig.4.

From Fig.3 and Fig.4, it is obvious that the rubber sleeves swell and deform after high pressure CO2 miscible flooding experiment. As we know, if CO2 corrosion does not exist, the rubber sleeve can make the core fix in the holder and all the CO2 gas only flow through the core, not the annular space between core and rubber sleeve.

4. Rubber sleeve corrosion analysis

(1) The white oil in the annular space is all discharged and a large amount of gas is discharged, indicating that CO2 has passed through the rubber sleeve into the annular space. This phenomenon can be explained by the mechanism of the percolation of thermodynamic small molecular substances to high molecular polymers. When there are small molecular substances with different concentrations on both sides of the polymer material, the permeate on the high concentration side is first dissolved in the polymer material, and then diffused to the low concentration side in the polymer material, finally, it escapes on the side of low concentration[5].

In the experiment, different concentrations of CO2 exist on both sides of the rubber sleeve, and the CO2 on the high concentration side is first dissolved in the annular space, then diffused to the low concentration side in the rubber, and finally escapes in the annular space (as shown in Fig.5). So there is gas escape during the pressure relief process.

(2) The dissolution of gas in rubber generally follows Henry's law, and the influencing factors include ambient temperature and rubber properties.

Henry's law: \[ C=SP \]

Wherein, \( C \)-gas solubility; \( S \)-dissolution coefficient; \( P \)-pressure of gas medium.

It can be seen from the above formula that if the pressure of the gaseous medium increases, the solubility of the gas increases. Therefore, as the experimental pressure increases, the solubility of CO2 molecules in the rubber sleeve increases. The expansion volume of the rubber sleeve becomes larger, and the corresponding rubber sleeve pores also increase, by the way the diffusion
speed of CO₂ increases. Therefore, the higher the experimental pressure is, the faster the rising rate of CO₂ ring pressure is.

![Fig.5 Seepage process of CO₂ in the holder](image)

(3) After the end of the experiment, when the ring pressure was removed, the rubber sleeve will blast. The reason is that during the experiment, the rubber sleeve is in a high temperature and high pressure CO₂ environment. At this time the CO₂ dissolved in the rubber sleeve reaches a saturated state, and when the pressure dropped suddenly, the CO₂ in the rubber sleeve becomes supersaturated. Therefore the excess CO₂ will quickly drain from the rubber. During the experiment, supercritical CO₂ may react with the rubber molecules, causing the rubber polymer to break, creating gaps or voids inside the rubber sleeve, and CO₂ escaping in these positions will accumulate and form a bulge. When the pressure reaches a certain level, the bubble will break.

(4) After the rubber sleeve was taken out for 24 hours, the degree of expansion was reduced, and some of the bulges disappeared, but the deformation and expansion phenomenon still existed, and there was no significant change after another week. The reasons are: (1) CO₂ and rubber have some mutual solubility. During the high pressure experiment, some CO₂ is dissolved in the macromolecular grid of rubber, but the molecular structure of rubber is not destroyed. When the pressure was released, part of the CO₂ was discharged from the rubber, but some of the CO₂ was still dissolved in the rubber macromolecular crosslinked grid and did not diffuse out in time. Therefore, the rubber is still in an expanded state when the pressure is just removed. (2) After a period of pressure relief, because the CO₂ concentration in the rubber sleeve is higher than the CO₂ concentration in the outside air, the CO₂ dissolved in the rubber macromolecular grid gradually precipitates and is discharged into the air by diffusion, and the expansion degree of the rubber sleeve is gradually weakened. (3) Part of the CO₂ molecule may react with the rubber molecule at high temperature and pressure, causing the chemical bond of the inside rubber macromolecule to open, and the active functional group to be replaced or detached, resulting in permanent deformation, expansion and softening of the rubber, that is, rubber aging. The rubber sleeve used in this paper is made of nitrile rubber and its molecular structure is as follows:

![Molecular structure of rubber](image)

During the high temperature and high pressure experiment, the cross-linking bond of the nitrile rubber breaks, the macromolecular group degrades, and the broken molecular chain recombines with the C=C bond to produce a cross-linking reaction. Some of the molecular chains may be permanently broken and displaced, resulting in permanent changes in the properties of the rubber, resulting in different chemical aging phenomena such as chemical stress relaxation and hardness reduction. Rubber molecular chain changes are divided into three mechanisms: 1) Heterogeneous cracking: When a single bond breaks, two electrons are left on one fragment and two electron holes are formed.
on the other fragment. 2) Homogeneous cracking (free radical mechanism): When a single bond breaks, an electron is left on each fragment and an electron hole is formed. (The aging process of rubber is mainly based on this mechanism). 3) Cyclization reaction: Formation of cyclic compounds by synergistic chain transfer [8].

![Diagram of Reaction Mechanism](image)

1) Heterogeneous cracking  
2) Homogeneous cracking  
3) Cyclization reaction

Fig. 6 The Reaction Mechanism of Molecular Chain Change

(5) During the CO₂ miscible flooding experiment, the generated carbonic acid reacts with the carbonate cement in the core, generating a large amount of hydrogen ions, increasing the acidity of the solution and accelerating the corrosion of the rubber sleeve. The reaction process is as follows:

\[
\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3 \\
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HCO}_3)_2\downarrow
\]

With the injection of CO₂, the content of carbonate ions in the solution is getting higher and higher, causing the dissolution of carbonate such as calcium feldspar, dolomite and iron dolomite in cores. Resulting the content of magnesium ions, ferrous ions and calcium ions in the solution to increase, and they react with bicarbonate ions to produce large amounts of hydrogen ions.

\[
\text{Mg}^{2+} + \text{HCO}_3^- \rightarrow \text{MgCO}_3\downarrow + \text{H}^+ \\
\text{Fe}^{2+} + \text{HCO}_3^- \rightarrow \text{FeCO}_3\downarrow + \text{H}^+ \\
\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{CaCO}_3\downarrow + \text{H}^+
\]

At the same time, the bicarbonate produced also blocks the pores of the rock, reduces the permeability of the core, increases the partial pressure of CO₂, and accelerates the dissolution and diffusion of CO₂ molecules in the rubber sleeve. As the experimental pressure increases, the concentration of dissolved CO₂ in the water increases, and the acidity increases, which causes certain acid corrosion to the rubber sleeve.

(6) After CO₂ is dissolved in water, the CO₂ aqueous solution is more corrosive than hydrochloric acid under the same pH condition, which can be electrochemically corroded with the holder.

Cathodic reaction:

\[
2\text{H}_2\text{CO}_3 + 2\text{e}^- = 2\text{HCO}_3^- + \text{H}_2
\]

Anodic reaction:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \\
\text{Fe} + \text{HCO}_3^- \rightarrow \text{FeCO}_3\downarrow + 2\text{e}^- + \text{H}^+ \\
\text{Cr} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3\downarrow + 3\text{e}^-
\]

During the experiment, a small amount of electrochemical corrosion occurred in the core holder, which increased the acidity in the annular space and accelerated the corrosion on the outside of the rubber sleeve.

5. Conclusions

Through above research, below conclusions can be got.

1) During the experiment, CO₂ dissolved, diffused, and escaped into the annular space of the core holder to cause an increase in ring pressure.
(2) During the CO\(_2\) miscible flooding process, the higher the pressure is, the greater the solubility of CO\(_2\) is in the rubber sleeve. A part of CO\(_2\) is dissolved in the macromolecular grid of rubber, but the rubber molecular structure is not destroyed, and a part of CO\(_2\) reacts with the rubber to make a rubber sleeve aging and failure.

(3) During the CO\(_2\) miscible flooding process, the generated carbonic acid reacts with the core and the core holder to increase the acidity of the solution and exacerbate the corrosion of the rubber sleeve.

(4) During the CO\(_2\) miscible flooding process, the ring pressure of rubber sleeve is rising continuously. It is necessary to observe the ring pressure. When the limit pressure is exceeded, we need to relieve pressure. After the experiment, the CO\(_2\) will escape in the rubber sleeve, and the experimental device should be disassembled after 24 hours.

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