

Mineralization Reaction Behavior during CO₂ Flooding in Reservoirs

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Abstract

CO₂ flooding is a promising technology for enhancing oil recovery while achieving geological CO₂ storage. Under high-temperature and high-pressure reservoir conditions, CO₂ dissolves in formation water to form carbonic acid, which reacts chemically with the reservoir rock minerals to achieve safe CO₂ storage. Currently research on mineralization reactions during CO₂ flooding in oil reservoirs remains limited, the characteristics of such reactions under different conditions and their impact on rock physical properties are not well understood. This study conducted static dissolution experiments to investigate the effects of various factors such as reservoir temperature, pressure, salinity, and oil saturation on the reaction behavior of the CO₂-crude oil-water-rock system. The results indicate that CO₂ dissolved in water can dissolve minerals such as calcite in the rock samples, leading to increased porosity and permeability. Although higher temperature promotes mineralization reactions, it also reduces the solubility of CO₂ in water, resulting in an overall weakening of reaction intensity. As reservoir pressure rises or formation water salinity decreases, the extent of mineralization intensifies and the rock dissolution rate increases. However, the presence of crude oil inhibits the mineralization reaction between CO₂ and rock, increasing oil saturation from 20% to 70% reduced the mineral dissolution rate by roughly 94% (from 3.77% to 0.22%), indicating a significant shielding effect.

Keywords: CO₂ flooding and storage, mineralization reaction, oil recovery, dissolution

1. Introduction

CO₂ flooding and storage represents a crucial technology for significantly enhancing crude oil recovery while contributing to the strategic “net-zero carbon emissions” goals^[1]. Following CO₂ injection into the reservoir, complex chemical reactions occur with formation water and rock minerals^[2,3]. These reactions subsequently alter the physical properties of the reservoir, thereby impacting both oil recovery efficiency and the long-term safety of CO₂ sequestration. Consequently, understanding the behavior of CO₂ mineralization reactions has attracted increasing attention.

Upon injection into oil reservoirs, CO₂ dissolves into formation water, forming carbonic acid and releasing a substantial amount of hydrogen ions, which leads to the acidification of the formation water^[4,5]. This acidic environment accelerates mineral dissolution, particularly for minerals such as feldspar and calcite that are susceptible to dissolution, thereby altering reservoir porosity and permeability^[6,7,8]. Simultaneously, CO₂ can react with certain reservoir minerals to generate new precipitates, such as calcite and dolomite^[9-13]. These reactions are governed by multiple factors, including temperature, pressure, oil saturation, and formation water composition. For instance, different types of formation water exhibit distinct influences on mineral dissolution and precipitation. Currently, studies on the behaviors of CO₂-rock mineralization reactions under varying reservoir conditions remain unsystematic, the influencing mechanisms of different factors are still unclear.

This study investigates the mineralization reaction characteristics of the CO₂-oil-water-rock system under varying reservoir conditions through static dissolution experiments. The findings aim to provide fundamental insights into the mechanisms of CO₂ storage in oil reservoirs, thereby supporting the broader application of this technology.

2. Experimental Methodology

Natural core samples with homogeneous mineralogical composition from the same region were used for the static dissolution experiments, and their mineral composition is presented in Table 1. The static dissolution experiments

were conducted using a high-pressure, high-temperature reactor system, consisting of the reactor vessel, a CO₂ injection vessel, and an injection pump. The experimental procedure comprised the following steps:

- (1) The core samples were cleaned, oven-dried, weighed, and its initial porosity and permeability were measured.
- (2) The sample was placed into the reactor, the system was evacuated, and formation water injected into the reactor.
- (3) An excess volume of CO₂ was injected, after which the inlet valve was sealed. The reactor was then heated and pressurized to the target conditions. The temperature was maintained at the set point by a temperature control system, and the system was left static for 15 days.
- (4) Upon completion, the system was depressurized. The core was retrieved, thoroughly cleaned, and oven-dried. Its dry weight, final porosity, and final permeability were measured to analyze the changes induced by the chemical reactions.

It is worth noting that in order to investigate the effect of oil saturation on mineralization reactions in core samples, this study employed a displacement method to saturate cores with crude oil, thereby obtaining cores with varying oil saturation levels. Mineralization experiments were subsequently conducted based on these prepared samples.

Table 1. The mineral composition of the samples

Component	Quartz	K-feldspar	Plagioclase	Argillaceous	Calcite	Dolomite	Quartz overgrowth
Content(%)	45.8	16.8	20.9	5.6	5.36	5.78	0.91
	44.5	17.5	17.2	3.3	5.38	10.73	0.65
Average(%)	45.4	17.2	19.1	4.5	5.37	8.23	0.78

3. Results and Discussions

The dissolution rate of the core is defined as the mass difference before and after the reaction divided by the initial core mass. This rate is used to evaluate the extent of mineral dissolution caused by the reactions.

3.1 Effect of Temperature

Dissolution experiments on the CO₂-water-rock system were conducted at different temperatures. The changes in porosity, permeability, and dissolution rate are shown in Figure 1-2. The results indicate an increase in both porosity and permeability of the core samples after the reactions. The extent of this increase initially rose and then declined with elevating temperature.

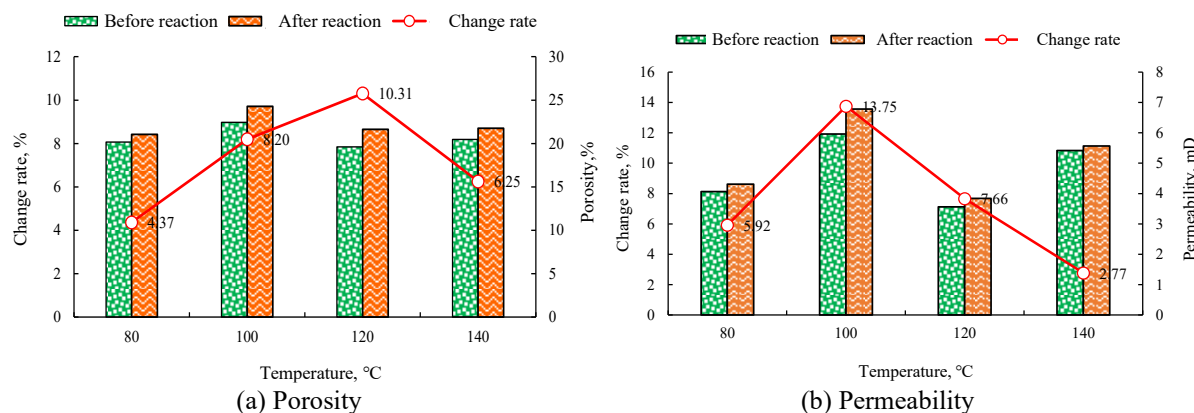


Figure 1. Changes in porosity and permeability before and after reactions at different temperatures

This trend is attributed to the temperature dependence of CO₂ solubility in formation water. Generally, CO₂ solubility decreases with increasing temperature. However, under conditions exceeding 100°C and 22 MPa, the solubility exhibits an increase with further temperature rise, which is consistent with previous research results^[14]. It is caused by the evaporation effect of formation water, where more CO₂ dissolves into the formation water, resulting in abnormal solubility of CO₂^[15]. Consequently, the acidity of the carbonated water first strengthens and then weakens as temperature increases. At lower temperatures, the mineralization reaction is dominated by the

dissolution of calcite. In contrast, at higher temperatures, the precipitation of calcite becomes predominant. The dissolution behavior of other minerals, however, opposes that of calcite. Their dissolution rates increase significantly with temperature, leading to an overall increase in the total core dissolution rate. When the temperature becomes excessively high, the promoting effect of temperature on mineral dissolution diminishes, resulting in a decrease in the dissolution rate.

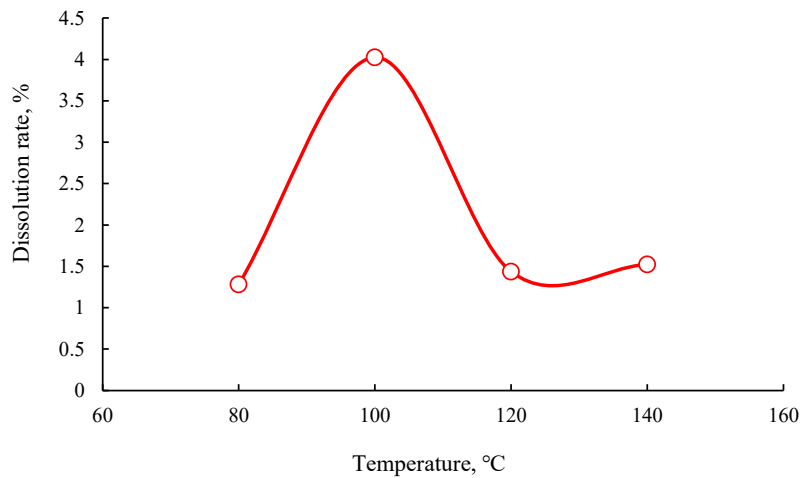


Figure 2. Relationship between temperature and dissolution rate

3.2 Effect of Pressure

Figures 3-4 present the variations in porosity, permeability, and dissolution rate of the core samples after mineralization reactions under different pressures. As shown in the figures, both porosity and permeability increased after the reactions, with the extent of increase growing as pressure rose. Specifically, the porosity increase ranged from 0.50% at 26 MPa to 10.73% at 44 MPa, while the permeability increase expanded from 0.02% to 7.43% over the same pressure range. These results indicate that higher pressures intensify the CO₂-water-rock interactions, leading to greater enhancements in porosity and permeability.

This behavior can be attributed to the increased solubility of CO₂ in formation water under elevated pressure, which raises the acidity of the carbonated water and accelerates the mineralization rate. When pressure was increased from 26 MPa to 32 MPa, the core dissolution rate rose from 1.29% to 1.43%. At 44 MPa, the increases in porosity and permeability, along with the dissolution rate reached their maximum values of 10.73%, 7.43%, and 1.97%, respectively.

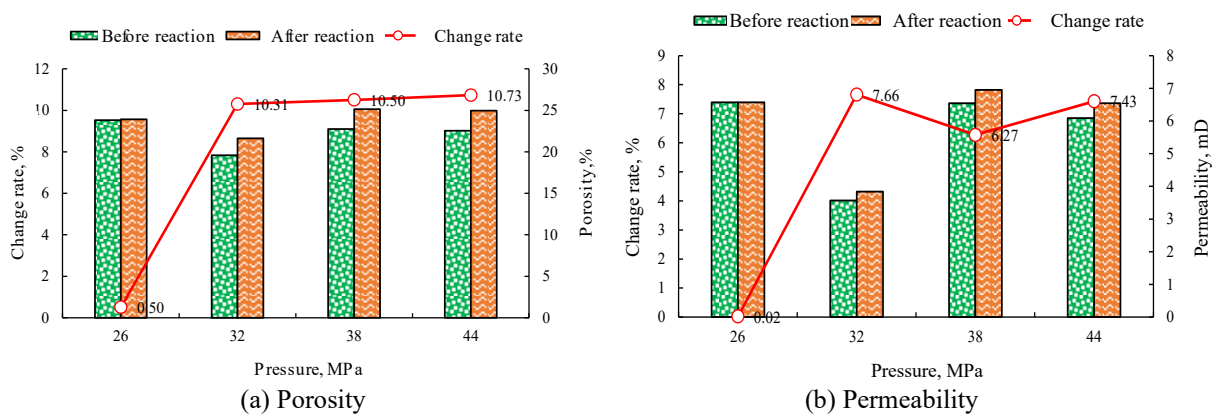


Figure 3. Changes in porosity and permeability before and after reactions at different pressures

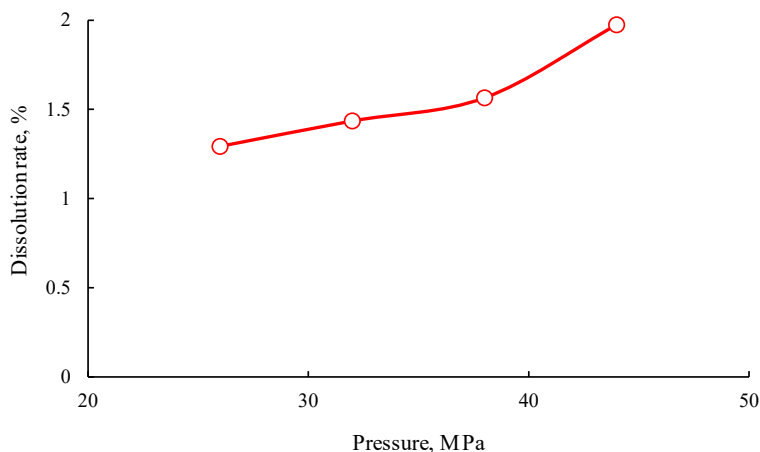


Figure 4. Relationship between pressure and dissolution rate

3.3 Effect of Oil Saturation

The variations in porosity, permeability, and dissolution rate before and after mineralization under different oil saturation conditions are illustrated in Figures 5-6. The results indicate that as oil saturation increases, the dissolution rate decreases, and the extent of improvement in both porosity and permeability is reduced. At an oil saturation of 20%, the dissolution rate was 3.77%, porosity increased from 15.85% to 22.61% (a 42.65% increase), and permeability rose to 3.80 mD (a 46.95% increase). In contrast, at 70% oil saturation, the dissolution rate dropped to 0.222%, while the increases in porosity and permeability decreased by 37.22% and 37.56%, respectively.

Under reservoir conditions, when CO₂-acidized fluid enters the rock core, it preferentially reacts with minerals that are more reactive, such as mineral surfaces not coated by oil film or partially dissolved low-energy barrier surfaces^[16]. In oil-wet reservoirs in particular, portions of carbonate minerals are coated by oil film, which significantly reduces the contact area available for the CO₂-acidized fluid. Only the carbonate mineral surfaces that remain free from oil coverage can directly react with the CO₂-acidized fluid. Those coated with oil film can react only after CO₂ has dissolved into the oil, thereby reducing the overall reaction intensity.

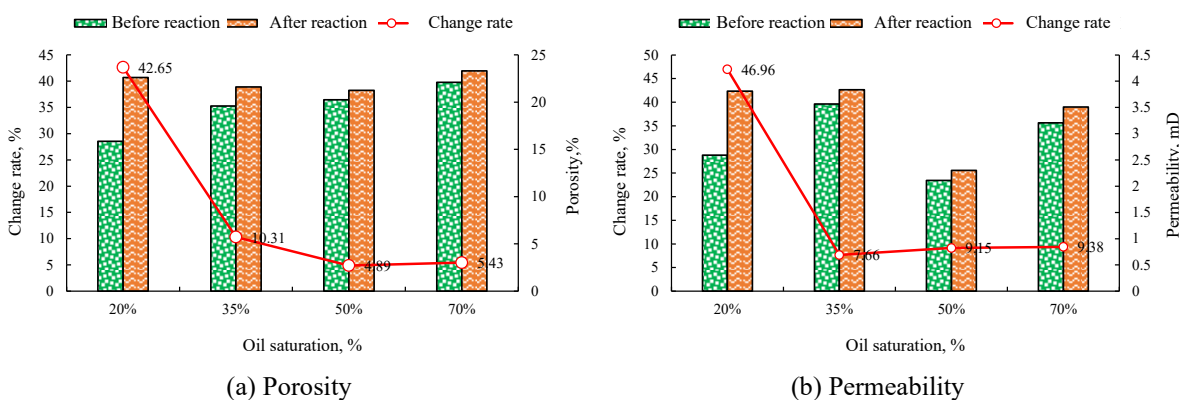


Figure 5. Changes in porosity and permeability before and after reactions at different oil saturations.

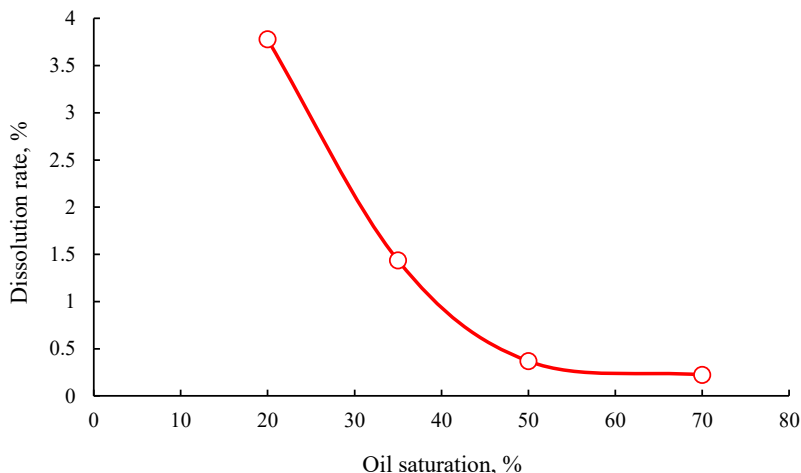


Figure 6. Relationship between oil saturation and dissolution rate

3.4 Effect of Water Salinity

Water salinity influences the solubility of CO₂ in formation water, thereby affecting the acidity of the water and consequently the dissolution of minerals within the core. The changes in porosity, permeability, and dissolution rate after the mineralization reaction under three different salinity conditions are shown in Figures 7-8. At a salinity of 20617 mg/L, the core dissolution rate was 1.47%, with porosity and permeability increasing by 10.82% and 22.96%, respectively. When the salinity was raised to 83237 mg/L, the dissolution rate decreased to 1.18%, while the increases in porosity and permeability dropped to 5.63% and 4.24%, respectively. This reduction is attributed to the decreased amount of CO₂ dissolved in the formation water at higher salinity levels. Specifically, as salinity increases, less CO₂ dissolves into the aqueous phase, resulting in a lower concentration of hydrogen ions and thus a weaker reaction between the core minerals and the carbonated water, leading to a decline in the dissolution rate.



Figure 7. Changes in porosity and permeability before and after reactions at different salinity.

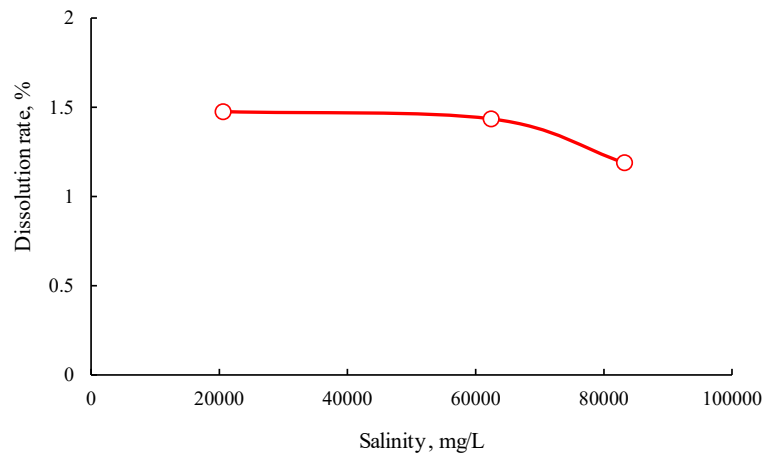


Figure 8. Relationship between salinity and dissolution rate

4. Conclusions

Dissolution experiments on the CO₂-oil-water-rock system were conducted to investigate the influence of key factors such as temperature, pressure, oil saturation, and salinity on reservoir mineralization reactions. The main findings are summarized as follows:

- (1) After the reaction, the porosity, permeability, and dissolution rate of the cores generally increased, with the extent of improvement being jointly influenced by temperature, pressure, and other factors.
- (2) The increase in porosity and permeability initially rose and then declined with increasing temperature, which correlates with the non-monotonic variation of CO₂ solubility in water as temperature increases.
- (3) Higher pressure enhanced the growth of porosity and permeability and dissolution rate due to the increased solubility of CO₂ in water under elevated pressure.
- (4) Both the increase in porosity and permeability decreased with higher oil saturation and higher water salinity.

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