1 Introduction

1.1 Background and motivation

With the intensification of human activities, particularly due to industrialization and the extensive use of carbon-intensive fossil fuels, greenhouse gas emissions have increased significantly. According to the International Energy Agency (IEA), global energy-related carbon emissions reached a record high of 37.4 Gt in 2023 (Figure 1.1). Among these, China was the largest emitter, with carbon emissions reaching 12.6 Gt, an increase of 565 million tonnes compared to 2022 (IEA, 2024). The massive emission of carbon dioxide (CO_2) has led to a significant increase in global temperatures compared to pre-industrial levels, causing a series of adverse effects (Kweku et al., 2018). These consequences include more frequent and severe extreme weather events, such as rainstorms, hurricanes, droughts, and heatwaves. Additionally, the melting of polar glaciers contributes to rising sea levels, while ecosystem degradation impacts biodiversity and food supply. Consequently, global warming has become a critical factor affecting human survival and development.

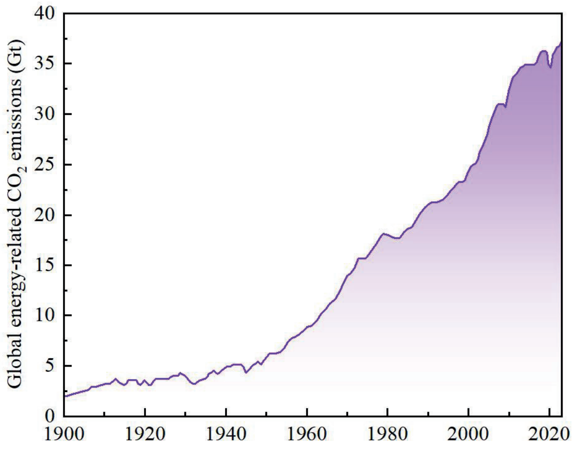


Figure 1.1 Global energy-related CO_2 emissions (Data from IEA, 2024).

In response to global climate change, governments have negotiated and adopted a series of international agreements, such as the Kyoto Protocol in 1997, the Copenhagen Accord in 2009, and the Paris Agreement in 2015. The Paris Agreement, in particular, serves as the cornerstone of current global climate policy, aiming to limit the rise in global average temperature to well below 2 °C, with efforts to further restrict it to 1.5 °C (Dimitrov, 2016). Furthermore, nearly 200 countries and regions have pledged to achieve carbon neutrality between 2030 and 2070, implementing various measures to reduce carbon emissions (Hou et al., 2023c; Hou et al., 2025a). These measures primarily focus on optimizing the energy structure by decreasing reliance on carbon-intensive fossil fuels and transitioning to renewable energies such as wind and solar. Additionally, efforts are being made to enhance energy efficiency and promote energy conservation (Ascione, 2017). Enhancing natural carbon sinks through afforestation and expanding vegetation areas are also key strategies being pursued. Moreover, the large-scale promotion and implementation of artificial carbon-negative technologies are crucial, particularly in China. Recent forecasts indicate that, to maintain carbon neutrality, China will need to rely on these technologies to reduce CO_2 emissions by more than 2 billion tonnes annually after 2060 (Zhang et al., 2023b).

Currently, artificial carbon-negative technologies primarily include CCU (Carbon Capture and Utilization), CCS (Carbon Capture and Storage), and CCUS (Carbon Capture, Utilization, and Storage). CCU focuses on using captured CO_2 in various industries (Zhang et al., 2020), such as producing carbonated beverages, coolants, and chemicals like synthetic methanol and urea. Additionally, CO_2 can be applied in firefighting equipment, metal manufacturing, and other fields. These technologies are relatively mature and can provide economic benefits, yet the scale of CO_2 utilization remains relatively limited. Compared to CCU, CCS is an artificial carbon-negative technology capable of large-scale implementation. It primarily involves injecting captured CO_2 directly into geological formations for storage, such as depleted oil and gas reservoirs, deep saline aquifers, or salt caverns (Lengler et al., 2010; Bui et al., 2018). The most notable drawback of CCS is its requirement for substantial investment without yielding direct financial returns. CCUS primarily employs CO_2 as a working fluid to enhance the extraction efficiency of underground energy and resources, such as oil, gas, and geothermal energy, while concurrently achieving geological storage of CO_2 (Liu et al., 2017). As a combination of CCU and CCS, CCUS can partially address the issues of CCU's limited scale and CCS's high costs, thereby offering significant development potential (Cao et al., 2020b).

In recent years, the rapid advancement of renewable energy has introduced greater challenges for energy storage (Hou et al., 2024; Huang et al., 2024). A promising technology that combines CCUS with large-scale underground storage of renewable energy, specifically through the underground bio-methanation (UBM) of CO_2 and H_2, was proposed (Panfilov, 2010; Strobel et al., 2020) (Figure 1.2). In this approach, during periods of low energy demand, CO_2 and H_2 are injected into porous formations such as depleted oil and gas reservoirs and saline aquifers. The wells are then shut down, and methanogens, either naturally present in the formation or introduced from external sources, are used to biochemically convert CO_2 and H_2 into CH_4. During this process, a portion of the CO_2 can also be geologically sequestered through dissolution, mineralization, or as a cushion gas (Xiong et al., 2023a). Subsequently, during high energy demand periods, renewable natural gas (RNG), primarily composed of CH_4, is extracted to ensure a stable energy supply.

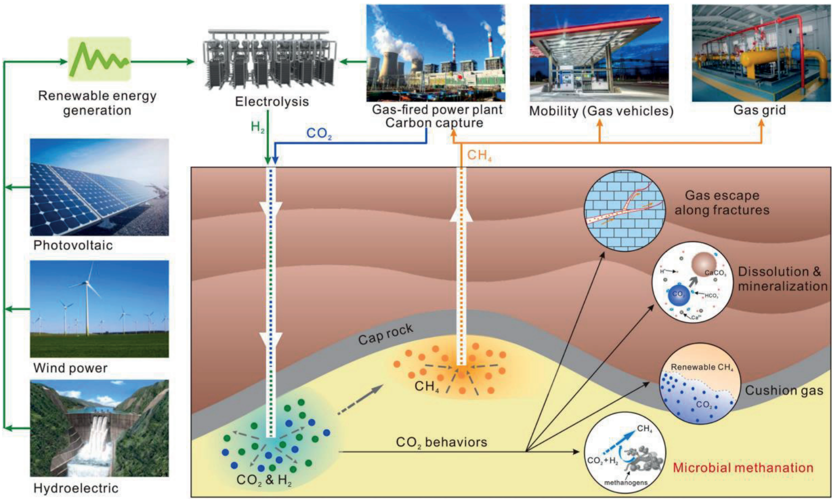


Figure 1.2 Simplified concept of underground bio-methanation (Adapted from Xiong et al., 2023a).

Compared to conventional CCUS technologies, UBM differs significantly in the modes of carbon utilization and carbon existence (Hou et al., 2025b; Wu et al., 2025a). In UBM, CO_2 is directly converted into valuable RNG, whereas in conventional CCUS methods, CO_2 primarily functions as a working fluid to extract existing resources or energy. Additionally, CO_2 captured from RNG utilization can be reinjected into the ground to synthesize more RNG, thereby enabling a circular conversion between CO_2 and CH_4. In contrast, traditional CCUS technologies primarily retain carbon in the form of CO_2. Due to these notable differences from conventional CCUS approaches, and its potential role in developing a carbon circular utilization system, Hou et al. have termed this approach Carbon Capture, Circular Utilization, and Sequestration (CCCUS) (Hou et al., 2022; Wu et al., 2023c).

As previously noted, UBM technology performs multiple functions simultaneously, such as CO_2 utilization and sequestration, alongside large-scale energy storage. The biocatalyst methanogens, which are vital for converting CO_2 and H_2, are sensitive to environmental factors like temperature, pH, and salinity (Thaysen et al., 2021; Thaysen et al., 2023). Therefore, conducting systematic research on UBM site selection, which serves as a bridge from theoretical research to field application, is crucial for the successful implementation of UBM technology, as well as for promoting sustainable development, enhancing economic benefits, and mitigating safety risks.

Moreover, in addition to methanogens, acetogens and sulfate-reducing bacteria (SRB) present in the subsurface also compete for the consumption of injected CO_2 and H_2 (Konegger et al., 2023). As a result, complex gas-water-rock-microbe interactions (biogeochemical reactions) occur during cyclic UBM, influencing the efficiency of converting CO_2 and H_2 to CH_4. Consequently, biogeochemical modelling to elucidate these intricate mechanisms can provide valuable theoretical guidance for the field implementation of UBM.

1.2 State of the art

1.2.1 Carbon geological utilization and storage technologies

This subsection primarily introduces the following carbon geological utilization and storage technologies: CO_2 enhanced oil recovery (CO_2-EOR), CO_2 enhanced gas recovery (CO_2-EGR), CO_2 fracturing, CO_2 geothermal system, CO_2 as cushion gas, and CO_2 replacement of natural gas hydrate.

1.2.1.1 CO_2 enhanced oil recovery (CO_2-EOR)

CO_2-EOR refers to the technology of enhancing oil recovery by injecting CO_2 into oil reservoirs. The primary mechanisms involved are as follows (Sambo et al., 2023; Jia et al., 2024): i) reduction in density and viscosity of crude oil, improving flow characteristics; ii) expansion of crude oil volume, increasing elastic energy of the formation; iii) reduction of interfacial tension and flow resistance of crude oil; iv) mixed-phase extraction and vaporization of light hydrocarbons in crude oil; v) dissolution gas drive; and vi) formation of weak acid from CO_2 dissolution in water, enhancing reservoir permeability. Based on the mixing conditions of CO_2 and crude oil, the process can be categorized into miscible flooding and immiscible flooding. In miscible flooding, CO_2 is able to completely mix with oil to form a single phase, leading to higher recovery rates. This method, however, demands higher pressure conditions.

Numerous factors influence the effectiveness of CO_2 flooding, primarily including fluid properties, reservoir properties, and gas injection methods (Jia et al., 2019a; Kumar et al., 2022). Among these, the gas injection method is more easily controlled during field implementation. Currently, there are three primary methods for injecting CO_2: continuous injection, water alternating gas injection, and cyclic injection (Cao et al., 2020b). Continuous injection rapidly enhances oil recovery but results in early gas channeling, which reduces CO_2 utilization efficiency. Water alternating gas injection can effectively improve CO_2 mobility; however, in reservoirs with significant vertical heterogeneity, CO_2 tends to migrate upward, leading to accelerated gas breakthrough. Cyclic injection, such as the CO_2 huff-and-puff process that includes three stages of CO_2 injection, well soaking, and oil production, can effectively mitigate the issue of gas channeling.

The United States and Canada initiated research on CO_2-EOR as early as the 1950s. Over the decades and have since become primary contributors to large-scale implementations. Currently, the United States has developed a highly mature CO_2-EOR industrial infrastructure, achieving an annual CO_2 capture capacity exceeding 15 million tonnes (Yuan et al., 2022). In China, related research began in the 1960s. Following years of exploration and innovation, China has developed the theory of CO_2-EOR and sequestration in terrestrial sedimentary reservoirs. Additionally, China has established reservoir engineering design technology and formed an initial comprehensive supporting technology system that includes injection and extraction processes, full-system anti-corrosion technologies, and monitoring techniques (Yuan et al., 2022; Song et al., 2023). At present, PetroChina has conducted over 10 CO_2-EOR field tests and established four pilot test areas suited for various reservoir types. The company aims to achieve an annual CO_2 injection of 5 million tonnes and an annual increase in oil production of 1.5 million tonnes by 2025. Sinopec has also performed CO_2-EOR tests in several oil fields, resulting in a cumulative oil production increase of over 250,000 tonnes. In 2022, the Qilu Petrochemical-Shengli Oilfield million-ton CO_2-EOR project was completed, anticipating the injection of 10.68 million tonnes of CO_2 and an oil production increase of 2.965 million tonnes over the next 15 years. Moreover, demonstration areas established by Yanchang Oilfield have collectively injected 216,000 tonnes of CO_2.

1.2.1.2 CO_2 enhanced gas recovery (CO_2-EGR)

CO_2-EGR refers to the technology of injecting CO_2 into gas reservoirs to enhance gas recovery (Zhang et al., 2023a). Depending on the type of gas reservoir, CO_2-EGR can be further categorized into CO_2-enhanced natural gas recovery (CO_2-ENGR), CO_2-enhanced shale gas recovery (CO_2-ESGR), and CO_2-enhanced coalbed methane recovery (CO_2-ECBM), among others. CO_2-ENGR technology primarily increases the recovery rate of gas reservoirs through pressurization and displacement. Pressurization is achieved by injecting CO_2 to supplement reservoir energy, while displacement involves the continuous convective movement of CO_2 to displace CH_4. In comparison, the mechanisms for enhancing recovery in CO_2-ESGR and CO_2-ECBM also include competitive adsorption. CO_2 has a stronger adsorption affinity on shale or coal seams compared to CH_4, and the adsorption of CO_2 facilitates the desorption of CH_4, thereby enhancing its flow performance.

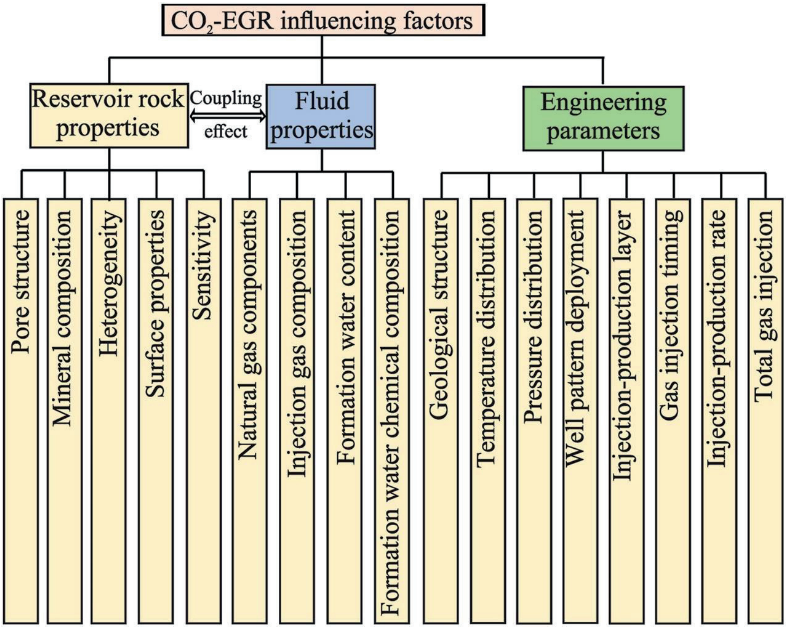


Figure 1.3 Factors influencing CO_2-EGR (Zhang et al., 2023a).

The effectiveness of CO_2-EGR is influenced by many factors (Figure 1.3). Several engineering methods can be employed to improve the recovery rate of gas reservoirs, such as: i) injecting CO_2 into the lower part of the reservoir while extracting CH_4 from the upper part, or regulating the injection rate of CO_2 to be lower than the production rate of CH_4 to delay CO_2 breakthrough; ii) increasing the injection pressure, raising the injection temperature, and initiating injection at the onset of the CH_4 production decline to maintain CO_2 in a supercritical state. For specific gas reservoirs, optimizing operational parameters is essential to enhance the effect of CO_2-EGR.

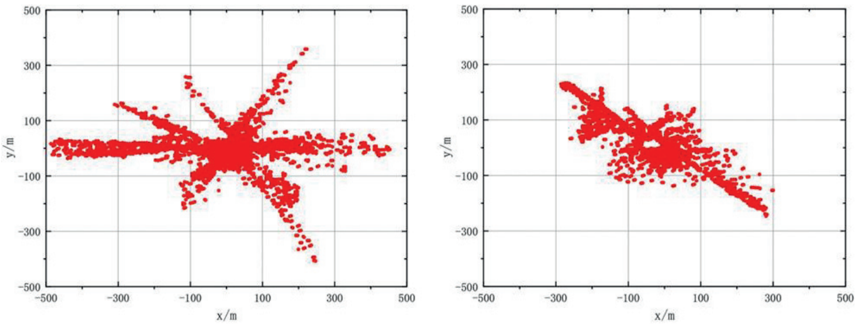
Global CO_2-EGR efforts are largely limited to the stages of mechanistic exploration and small-scale pilot tests. Notable projects include the Australian CO_2 CRC Otway project, the Canadian Alberta project, and the Dutch K12-B project (Zhang et al., 2023a). China's CO_2-EGR field tests are primarily focused on coalbed methane and condensate gas reservoirs. In 2004, China initiated its first pilot test for CO_2-enhanced coalbed methane recovery in the southern Qinshui Basin (Zhang et al., 2022a). Between 2011 and 2012, China and Australia collaborated on intermittent single-well injection and production tests in shallow coalbed methane in Liulin, Shanxi. Field tests for CO_2 cyclic injection and pressure maintenance, aimed at enhancing condensate gas reservoir recovery, are primarily concentrated in the Tarim Oilfield. Recently, PetroChina Southwest Oil & Gasfield Company has been preparing to launch China's first pilot test project exploring CO_2 injection to enhance recovery from carbonate reservoirs in the Wolonghe gas field (Yong, 2024). The pilot test is scheduled to last three years, with an estimated affected geological reserve of over 1.5 billion cubic meters.

1.2.1.3 CO_2 fracturing

CO_2 fracturing is a method used to enhance oil and gas production by using CO_2 as a fracturing fluid to create fractures in the reservoir that improve fluid flow capacity. Compared to traditional hydraulic fracturing, CO_2 fracturing offers several advantages (Mojid et al., 2021; Wu et al., 2023b): i) CO_2 has low flow resistance, which results in lower rock breakdown pressure during fracturing, making it easier to connect natural fractures and form a complex fracture network. ii) CO_2 fracturing fluid contains no water phase, preventing issues such as water blockage and clay swelling once it enters the reservoir, and leaves no residue, thereby minimizing reservoir damage. iii) CO_2 does not cause rock softening upon contact, reducing the likelihood of proppant embedding. iv) CO_2 exhibits excellent expansion properties, effectively replenishing formation energy after entering the reservoir. v) CO_2 is capable of displacing crude oil or competing with CH_4 for adsorption on rock surfaces, facilitating CO_2 sequestration while enhancing oil and gas recovery. Due to the unique properties of supercritical CO_2, such as its high density and low viscosity, supercritical CO_2 fracturing offers a more effective production enhancement compared to liquid CO_2 fracturing (Middleton et al., 2015; Wu et al., 2023d). To achieve the supercritical state of CO_2 in the fracture , techniques such as wellhead heating and low-rate injection can be employed (Wu and Luo, 2022; Wu et al., 2022a; Wu et al., 2023e).

In the 1980s, liquid CO_2 fracturing was first field-tested in North America. Today, the United States has developed a comprehensive liquid CO_2 fracturing process technology system, which has been applied to enhance production in over 3,000 low-permeability oil and gas reservoirs. This method typically results in a production increase of 3 to 5 times, with an efficiency improvement of more than 50% (Zhang et al., 2018). China was a late adopter of CO_2 fracturing technology. In 2011, the Sulige gas field in China conducted its first field test of CO_2 dry fracturing, utilizing rock cuttings generated during fracturing as proppant. This method reduced the post-fracturing flowback duration by more than 50% compared to hydraulic fracturing, leading to an average production rate of 5,000 m^3/d. In 2015, Jilin Oilfield implemented a field test of CO_2 energy storage fracturing in six wells. By incorporating thickeners into the liquid CO_2 fracturing fluid and increasing the injection rate (up to a maximum of 8 m^3/min), the maximum sand ratio during the fracturing process reached 14%. Given the effectiveness of this fracturing technology in replenishing formation energy, it has been further promoted and applied in both Jilin Oilfield and Xinjiang Oilfield. In 2017, Shaanxi Yanchang

Petroleum Group conducted China's first field test of supercritical CO_2 fracturing in Yan 2011 well (Wang et al., 2020). Since supercritical CO_2 has low viscosity and filtrates easily (Luo et al., 2021), its ability to carry sand is limited. Consequently, during the early stages of fracturing, a 3% volume fraction of ceramsite frequently caused sand plugging. As a result, conventional fracturing fluid was used later in the process to carry the sand. Despite this challenge, on-site microseismic signals confirmed that supercritical CO_2 fracturing can facilitate the formation of complex fracture networks (Figure 1.4). Since then, more than 10 field tests have been conducted in the area. Overall, CO_2 fracturing technology remains at the small-scale testing stage in China.



(a) Supercritical CO_2 fracturing (b) Hydraulic fracturing

Figure 1.4 Comparison of microseismic fracture monitoring data (Adapted from Li et al., 2021).

1.2.1.4 CO_2 geothermal system

CO_2 geothermal systems using CO_2 as a working fluid to extract underground heat (Figure 1.5). For hydrothermal geothermal resources, the natural high porosity and permeability of the reservoir's geological conditions can be exploited, allowing CO_2 to serve as the displacement medium to extract high-temperature formation water (Fleming et al., 2022). This type of geothermal system is commonly referred to as a CO_2 plume geothermal system (CPG), and the heat extracted is primarily used for applications such as building heating and aquaculture. For hot dry rock geothermal resources, where the natural porosity of the formation is low, CO_2 is typically used to create a complex fracture network during geothermal extraction, thereby enhancing the heat exchange efficiency (Liao et al., 2023). This approach is known as a CO_2-enhanced geothermal system (CO_2-EGS), and the extracted heat is primarily utilized for power generation. Compared to geothermal systems that use water as the working fluid, CO_2 geothermal systems offer several key advantages (Esteves et al., 2019; Schifflechner et al., 2024): i) CO_2 has a greater heat-carrying capacity and fluidity, leading to higher heat exchange efficiency; ii) The significant density difference between CO_2 in the injection well and the production well generates buoyancy, which can reduce the power requirements for circulation pumps; iii) The issue of scaling, resulting from mineral dissolution and migration, can be eliminated; iv) CO_2 geothermal systems facilitate the underground sequestration of CO_2.

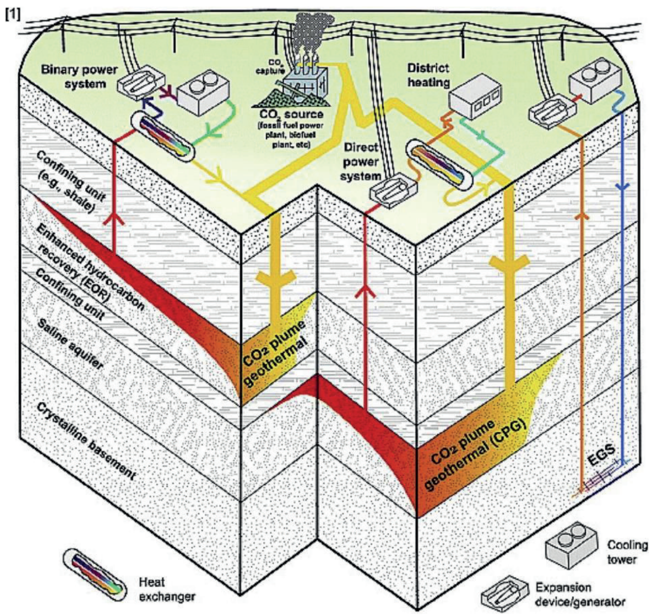


Figure 1.5 Schematic of CO_2 geothermal systems (Randolph and Saar, 2011).

In 2019, the ECO2G™ project in the United States conducted a pilot test to extract shallow geothermal heat using CO_2 as a heat exchange medium. The test well, 34A-20, is located in the Coso KGRA in California (Amaya et al., 2020). During the test, CO_2 circulated within a 330-meter-long downhole tube-in-tube heat exchanger to evaluate its heat exchange efficiency and power generation potential in a closed-loop system. The results demonstrated a strong thermal siphon effect in the CO_2 circulation, and showed that increasing the inlet pressure while reducing the inlet temperature and flow rate could effectively enhance power generation. As CO_2 does not actually enter the formation, this geothermal system is neither a CPG nor a CO_2-EGS, and CO_2 sequestration cannot be achieved.

1.2.1.5 CO_2 as cushion gas

In underground gas storage operations, a portion of cushion gas is generally required to maintain adequate pressure and volume in the reservoir. This is essential to inhibit the flow of formation water, prevent water intrusion, and ensure gas storage stability. Typically, natural gas is used as the cushion gas. Oldenburg (2003) first proposed using CO_2 as a cushion gas in depleted gas reservoir-type storage facilities (Figure 1.6), noting that under underground gas storage conditions, CO_2 has a viscosity more than 10 times that of natural gas. Utilizing CO_2 as a cushion gas allows its high compressibility to provide more storage capacity during gas injection and deliver a greater gas drive effect during production. Compared to using natural gas as a cushion gas for storage, CO_2 offers several additional advantages (Shoushtari et al., 2023). For instance, CO_2 can replace natural gas at the bottom of the reservoir due to the gravitational gradient, thereby reducing residual natural gas. Supercritical CO_2's high density significantly enhances the driving force for gas-driven water during multi-cycle injection and production, facilitating capacity expansion of gas storage. Additionally, CO_2 is low-cost, and its use as cushion gas enables geological CO_2 storage, thus improving economic benefits and contributing to environmental protection.

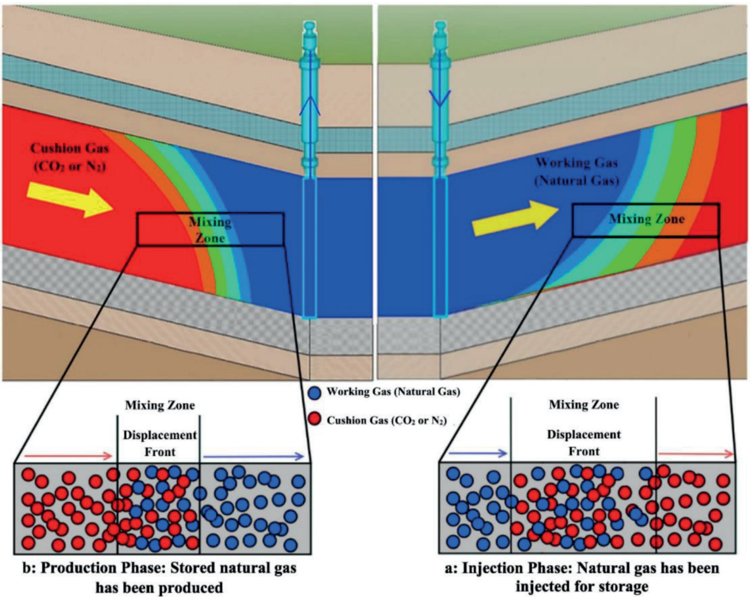


Figure 1.6 Schematic diagram of CO_2/N_2 used as cushion gas (Shoushtari et al., 2023).

Current research on employing CO_2 as a cushion gas remains predominantly at the exploratory stage, with relatively limited studies conducted to date. The primary focus has been on the mixing of CO_2 and natural gas, as well as the impact of geological and operational parameters on natural gas withdrawal. For example, in laboratory settings, Hu et al. (2018) utilized a self-developed CO_2-CH_4 mixing device to simulate the interaction of working gas with cushion gas under near-critical and far-