The Progress of Offshore CO₂ Capture and Storage

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Abstract. With the development of the offshore oil and gas fields, more and more offshore oil and gas fields are found to have high carbon dioxide. In addition, as peaking carbon dioxide emissions and carbon neutrality were written into the government work report for the first time, the correct separation and emission of CO₂ have become a key issue that needs to be solved by offshore oil and gas fields. In this paper, we studied two CO₂ separation methods suitable for offshore platforms and the current status of CO₂ offshore storage and application. Moreover, the development of offshore carbon dioxide storage application was investigated in detail, and the technical characteristics and application prospects of CO₂-EOR and CO₂ replacing combustible ice were analysed and discussed. This paper analyses the challenges and countermeasures of offshore CO₂ storage from many aspects. It provides a theoretical reference for future CO₂ treatment in offshore oil and gas fields.

1 Introduction

With the development of the offshore oil and gas fields, more and more offshore oil and gas fields are found to have high carbon dioxide (CO₂), and the carbon dioxide content of some offshore field is up to 40%[1]. Especially in offshore gas fields, the high content of CO2 have a potential corrosion risk to the upper structures and pipeline. But CO₂ cannot be emitted directly into the atmosphere, it is considered to be a major contributor to the greenhouse effect and climate change. Therefore, the correct separation and emission of CO₂ have become the key problem to be solved by offshore oil and gas fields. At the fourth Plenary Session of the 13th CPC Central Committee (2021), peaking carbon dioxide emissions and carbon neutrality were written into the government work report for the first time, which pointed out that peaking carbon dioxide emissions should be reached before 2030 and achieve carbon neutrality before 2060[2]. The latest assessment report of Intergovernmental Panel on Climate Change (IPCC) also shows that to achieve the global temperature limit of 1.5 °C, global CO₂ emissions will need to be reduced by about 45% in 2030 compared to 2010, and "net zero" emissions will need to be achieved in 2050[3]. Carbon capture and storage (CCS) is a methodology to separate CO₂, then to store the CO₂, commonly originating from power generation, industrial processes, and from CO2 gas fields. IPCC report[4] has indicated that in the absence of CCS implementation, the required total cost to mitigate global climate change may escalate up to 138%. CCS has been recently known to play a vital role in global climate change. Therefore, the further development of CO₂ separation and capture technology in offshore oil and gas fields conform to the basic requirements of the country in the field of energy.

Meanwhile, as the carbon-rich matrix, the successful recovery and reuse of CO_2 can also solve the fuel supply problem of the offshore drilling platform and make preparation for the next step of offshore CO_2 storage.

2 The technology of CO₂ capture

At present, the technologies used for CO₂ capture mainly include adsorption capture technology, absorption capture technology, membrane separation technology, chemical cycle combustion capture technology, cryogenic, electrochemical capture and so on[5]. However, due to the complex and compact structure, small space and strict weight requirements of the offshore platform, on-site CO₂ separation on the offshore platform required that the CO₂ separation device can be installed in the limited space of the platform and the weight of the platform can bear the weight range. Considering the characteristics of offshore platform and various separation technologies, membrane separation technology and supergravity chemical absorption separation technology are suitable for offshore platform.

2.1 Membrane separation technology

Membrane separation is a kind of technology which uses the different permeability of gases to realize the separation. The gas separation membrane is mainly composed of polymeric materials and permeates the membrane by gas dissolution and diffusion[6].

The CO₂ membrane separation system used in offshore platforms consists of pre-treatment and membrane separation system (Figure 1). The pre-treatment part mainly includes gas-liquid separation system and heating

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system. Under a given pressure, CO_2 has better permeability than CH_4 . It leaves through the membrane to the low pressure side as permeable gas, and most of CH_4 remains in the high pressure side as residual gas. The residual gas is enriched in CH_4 , and the permeated gas is enriched in CO_2 .

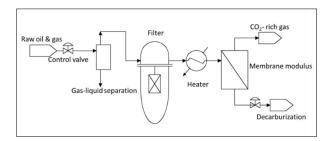


Figure 1. Process diagram of CO2 removal by first membrane separation

In order to reduce the loss rate of hydrocarbon and improve the purity of CO₂, two-stage membrane separation technology can be used. The process of two-stage membrane separation and decarbonisation device is shown in Figure 2. The membrane separation part is divide into two stages, and the raw gas is separated into the first stage membrane separator M-01. Decarbonized gas (residual gas) is obtained at the high first pressure side, and CO₂-rich gas (permeable gas) is obtained at the low pressure side. The primary permeable gas enters the compressor and compresses to a certain pressure, then enter the secondary membrane to separate M-02. The residual gas returns to the inlet of raw gas, and the CO₂-rich permeable gas is discharged and collected uniformly[7].

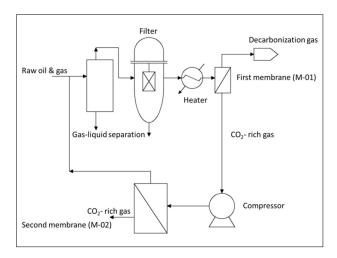


Figure 2. Process diagram of CO2 removal by second membrane separation

Membrane separation has the advantage of simple process, less equipment, less floor space, less operation and maintenance workload and low system energy consumption. Its greatest advantage lies in the combination of flexible membrane, easy to expand.

2.2 Supergravity chemical absorption separation technology

Supergravity removal CO₂ technology is a comprehensive CO₂ removal technology combining chemical absorption and supergravity technology. It generate a gravitational field of 10~1000g by high speed rotating to greatly strengthen gas-liquid mass transfer during CO₂ capture and improve CO₂ capture effect. The supergravity device equipment was shown in Figure 3[8]. CO₂ supergravity chemical absorption technology is to use rotating packed bed (RPB) instead of the vertical static tower, make a fully contact between gas and liquid in RPB. Mass and heat transfer are carried out under the condition of high dispersion of liquid phase, rapid updating of surface and strong disturbance of phase interface, so that the chemical reaction process of adsorbent and CO2 in mixed gas is strengthened, so as to realize the technology of CO2 and natural gas separation[9]. Meanwhile, the efficient mass transfer effect of RPB is beneficial to reduce the size of the equipment, reduce the occupying space, reduce the investment cost of the equipment, and the operation of RPB is flexible, easy to assemble into skid-mounted equipment, and easy to move, all of these performance are far superior to the traditional tower equipment [8].

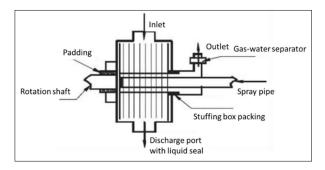


Figure 3. Schematic diagram of supergravity device equipment

Absorbent commonly used for CO₂ absorption include monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), ammonia, diethylene glycol amine, methyldiethanolamine (MEDA), etc.. However, the focus of current research on supergravity chemical absorption technology is to select effective CO₂ absorbent. It can react with CO₂ quickly and efficiently to form intermediate compounds in a supergravity environment. MEA is a kind of absorbent which has been studied more, but its combination with supergravity action needs further experimental verification and optimization. In addition, the development of new absorbent is also the focus of current research.

The process of supergravity absorption technology is complicated, and the energy consumption of the moving equipment is high, the stability needs to be improved. Meanwhile, the matching selection of the supergravity machine with CO₂ absorbent is being studied and tested, and further screening tests are needed to improve the separation efficiency and meet the requirements of industrial use.

3 Offshore carbon storage and application

In addition to conventional CO₂ separation and reprocessing through industrial processes, offshore CO₂ can be sequestering directly in subsea or used as a driving force for enhanced oil and gas recovery or gas hydrate exploitation.

3.1 Offshore CO₂ storage

The CO₂ produced by offshore gas field can be buried on land or subsea. From the engineering and economic point, it is ideal to inject CO₂ on land or near shore. Generally, before the exploration of the offshore gas field, the appraisal well and seismic data were limited on the sea, the geology surrounding the gas field area is clear, including the type of structure, reservoir-cap conditions. Therefore, if inject on land or near shore, relevant exploration needs to be carried out to determine the thickness, occurrence and distribution range of high permeability salt water layer and cap layer. In consequence, CO₂ in offshore gas field is more suitable for deep saline water storage mode.

According to the method of carbon dioxide capture, the geological storage in salt water layer can be divided into primary capture and secondary capture. Primary capture is the sequestration of carbon dioxide directly blocked by geological traps. Secondary capture means that carbon dioxide is dissolved in salt water and chemically reacts with salt water and reservoir minerals to produce new minerals and achieve permanent storage of carbon dioxide. According to the reservoir site, it can be divided into geological traps and monocline structures.

In 1996, the Sleipner Gas field[10] in the North Sea of Norway started the CO2 geological storage on offshore salt water layer for the first time, and proposed that the injection and storage of CO2 in the underground aquifer must meet the following physical and chemical conditions[11]: (1) The top of the aquifer is at least 800 m below the seafloor. Below this depth, the hydrostatic pressure will exceed the critical pressure of CO₂, which will exist as a supercritical fluid, facilitating the storage of more CO₂. And the deep aquifer is mostly saline water with high salinity, which cannot be used as drinking water and will not affect groundwater resources. (2) A waterproof or weakly permeable layer shall be covered above the aquifer to ensure the separation of the aquifer from shallow potable water and surface water to prevent possible contamination of water quality due to the release of CO₂. (3) The aquifer is near the injection well, the surrounding area should have maximum porosity and permeability. (4) The permeability of the entire storage area should be relatively low to ensure long-term CO2 separation in the aquifer. (5) Injection point should be as close as possible to CO₂ emission source, so as to reduce CO₂ transport costs.

Considering the geological characteristics of offshore gas fields in China, the following conditions should be met for CO₂ offshore storage: (1) The layers must be relatively stable in distribution. Shallow mudstone is not good for

sealing as cap layer and does not conform to the requirements of supercritical temperature and pressure. Therefore, it is ideal for cap layer depth to be at least 500 m. (2) the most suitable burial depth is $600\sim1000$ m, where the temperature is about $25\sim30^{\circ}$ C and the pressure is $6\sim12$ Mpa, meeting the requirements of supercritical temperature and pressure of carbon dioxide. The thickness of sandstone is more than 100 m, with high porosity and high permeability. The porosity is more than 30%, and the permeability is more than $500\times10-3$ µm.

CO2 offshore sequestration is similar to the land, also includes carbon dioxide capture, purification, transportation, injection and other processes, among which the mode of CO₂ transport at sea is the key to determine the sequestration scheme. There are two options for carbon dioxide transport by sea: one is by ship, the other is by subsea pipeline. When using ship transportation, in order to make the ship effective load, reduce the transportation cost, it is advisable to liquefied carbon dioxide for transportation, which requires the installation of liquefaction device in the platform. Pipeline transportation can be carried out in three phases, gas, liquid and supercritical state. The actual conditions of heat tracing, insulation, construction, pressure, operation and maintenance and investment of submarine pipelines should also be considered.

3.2 Offshore CO₂ storage used for enhanced oil and gas recovery (EOR)

Offshore CO2-EOR can be seen as a way to facilitate offshore storage. Over the past four decades, CO2-EOR technology has been in operation onshore[12], particularly in North America, but the large amount of CO₂ produced by offshore has not been used on a large scale. According to the report, the key obstacle of offshore CO₂-EOR projects are the investment in facility modifications, loss of revenue during the modifications, emission of CO₂, uncertainty in reservoir performance, and lack of transportation infrastructure. In order to prevent the release of CO₂, Norway has been put offshore CO₂ storage into practice since 1996[10], and Brazil is also working on a project related to offshore CO₂-EOR. The world's first project to implement offshore CO₂-EOR was launched in 2011(so-called Lula-pilot) and a second one in 2013 (Lula-NE).

In the CO2-EOR process, CO2 is injected into an oil reservoir under high pressure. Oil displacement by CO2 injection relies on the phase behaviour and properties of the mixture of CO2 and oil, which are strongly dependent on reservoir temperature, pressure and oil composition. There are two main types of CO2-EOR processes[13]: Miscible CO2-EOR is a multiple contact process involving interactions between the injected CO2 and the reservoir's oil. Figure 4 provides a one-dimensional schematic showing the dynamics of the miscible CO2-EOR process. Immiscible CO2-EOR occurs when insufficient reservoir pressure is available or the reservoir's oil composition is less favourable (heavier) [14].

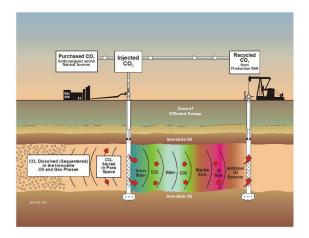


Figure 4. The principles of miscible CO2-EOR

In a CO₂-EOR operation floodable hydrocarbons (mainly oil), CO₂ and brine are produced to surface are production well. The elements involved in a typical offshore CO₂-EOR are indicated in Figure 5[15]. The production mechanisms are principally the same in onshore and offshore CO₂-EOR setting, and future CO₂-EOR operation offshore will mimic and utilise technologies known from the more matured onshore business. However, the following challenges remain for offshore CO₂-EOR implementation: (1) Due to the limited space and weight of offshore platforms, large equipment cannot be placed. (2) Offshore oil and gas Wells tend to be directional and farther away than onshore Wells. (3) Compared to onshore fields, offshore oil fields have typically achieved higher recovery rates prior to the use of CO₂-EOR. (4) On the sea, carbon dioxide must be transported by ship or subsea pipelines, both of which incur additional costs compared to onshore solutions. (5) The reservoir dynamic management model is inconsistent with that of onshore oil and gas fields. All of these challenges and differences will result in higher investment and operating costs of offshore CO₂-EOR [15].

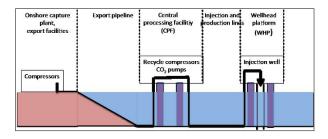


Figure 5. Schematic diagram of offshore CO2-EOR project facilities

3.3 Offshore CO_2 storage used for combustible ice exploitation

Based on CO₂ geological storage technology and CO₂ replacement gas hydrate technology, the co-combustion ice mining technology is a new technology that comprehensively uses CO₂ and obtains multiple benefits. It is also a useful complement to Carbon Capture, Utilization and Storage (CCUS).

Ebinuma and Ohgaki first proposed the idea of CO₂ replacement for combustible ice[16]. After long term research and demonstration, CO₂ replacement of combustible ice has been proved to be highly feasible in terms of dynamics and thermodynamics, and its replacement reaction is shown in Equation (1)[17]. Compared with other exploit technologies, the biggest advantage of CO₂ replacement of combustible ice is that it can maintain the stability of the original reservoir structure and reduce some geological disasters such as earthquakes. The schematic diagram of replacement exploitation is shown in Figure 6[18].

 $CH_4 \cdot nH_2O + CO_2(g) \rightleftharpoons CH_4(g) + CO_2 \cdot nH_2O(n \ge 5.75)(1)$

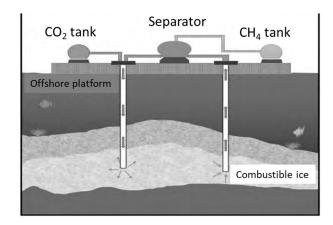


Figure 6. Schematic diagram of CO2 replacement of combustible ice

The research shows that if liquid CO₂ is injected into combustible ice reservoir, the hydrophilicity of CO2 is better than CH4, and the pressure required to generate CO₂ hydrate is lower than that required to maintain the stability of combustible ice at the same temperature. Therefore, in a certain pressure range, natural gas hydrate (NGH) will decompose into water and CH₄, CO₂ will combine with water generated by decomposition to form hydrate and remain stable, so CO₂ will drive away CH₄. In this displace process, the formation of CO₂ hydrate is exothermic, while the decomposition of combustible ice is endothermic. It can be seen from Equations (2) and (3) that the exothermic is greater than the endothermic, so this process can also occur spontaneously [19].

 $nH_2O + CO_2(g) \rightarrow CO_2 \cdot nH_2O(\Delta H_f = -57.98 \text{ kJ/mol})$ (2) $CH_4 \cdot nH_2O \rightarrow CH_4 + nH_2O (\Delta H_f = 54.49 \text{ kJ/mol})$ (3) The technology of CO₂ storage combined with combustible ice exploit is beneficial in many aspects. The combustible ice reserves are huge, which is undoubtedly an important follow-up energy source in the future. The CO₂ offshore storage combined with combustible ice exploit can accelerate the development of combustible ice, which is of great significance to alleviate the current situation of energy shortage in the world. Although CO₂ storage combined with combustible ice have broad prospects, it still faces some challenges. Firstly, the replacement of CH₄ by CO₂ is not complete, and the water cages wrapped with CH₄ molecules in combustible ice have different sizes. CO₂ molecules can only enter large holes, but not small ones, resulting in the retention of CH4

molecules in small holes. For this problem, it is necessary to combine other exploit methods to fully release CH₄. Secondly, the rate in CO₂ replace CH₄ of combustible ice is low, and the reaction rate will be lower and lower as the replacement reaction progresses, which requires to find conditions or catalysts to accelerate the replacement rate.

4 Conclusion

In summary, with the large scale development of offshore oil and gas fields, how to deal with CO2 emission is a major problem and challenge that needs to be treated seriously at present. A series of factors such as investment cost, platform space and system energy consumption should be considered for CO2 processing in offshore platforms. Subsea geological conditions and CO₂ gathering and transportation should also be considered in the process of further CO₂ offshore storage. China is a Marine big county whose the sea area is vast and salt water layer is all over the ocean, which is the favourable condition for the implementation of CO₂ offshore storage. In addition, further application of CO₂ offshore storage can be considered, such as offshore CO2-EOR and combine with combustible ice exploitation. This paper provides theoretical reference for further offshore CO₂ capture and storage.

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