The potential of coupled carbon storage and geothermal extraction in a CO₂-enhanced geothermal system: a review

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Abstract

The increasing demand for energy makes it difficult to replace fossil fuels with low-carbon energy sources in the short term, and the large amount of CO₂ emitted by fossil fuel combustion increases global warming. Carbon capture and storage (CCS) technologies for reducing CO₂ emissions in power plants and industrial processes have been developed. High costs and security issues limit industrial applications of these technologies, so an alternative for carbon reduction is needed, i.e., CO₂ as a working fluid for coupled carbon storage and geothermal extraction in an Enhanced Geothermal System (EGS). We describe the status of global carbon emissions, CCS technologies, and their challenges. The characteristics of CO₂ as a working fluid are compared from thermophysical and thermodynamic perspectives, and the solubility of CO₂ in reservoir fluids with different ionic strengths, pressures, and temperatures is analyzed. The influence of artificial stimulation on the permeability of an EGS reservoir is described. Through heat extraction experiment of water alternating supercritical CO₂ (SCCO₂) cycle injection, the effects of CO₂–fluid–rock interactions on the reservoir’s structure and of mineral dissolution and precipitation on geological CO₂ storage are analyzed. We summarize the application prospects for this alternative and the challenges of future application.

Keywords: Alternative technology, Carbon dioxide, Enhanced geothermal system, Renewable energy, Storage potential

Introduction

The continuous consumption of fossil fuels has led to severe environmental and ecological problems, which make the use of low-carbon energy and carbon emission reduction technologies an important step in ensuring sustainable global development. As a clean renewable energy, geothermal energy has gradually received more attention worldwide (Sanyal 2018; Abas et al. 2017). Compared with other renewable energies, e.g., solar energy and wind energy, geothermal energy has the advantages of high stability (not affected by season or sunshine), high utilization rate (up to 73%, i.e., 5.2 times that of solar photovoltaic power generation and 3.5 times that of wind power generation), safety, low operating costs, comprehensive utilization (Li and Wang 2015). According to the occurrence state, the geothermal resources can be divided into hydrothermal,
magmatic, and hot dry rock (HDR). HDR is a high-temperature rock (about 150–650 °C) that does not contain water or contains only a small amount of water. It is estimated that an HDR at a depth of 3–10 km contains approximately 30 times the energy of global fossil fuels (Guo et al. 2016; Xu et al. 2016a, b).

The low permeability and porosity of natural HDRs restrict heat extraction, so an enhanced geothermal system (EGS) was created to artificially stimulate (hydraulic, chemical, and thermal) HDRs. An injection well is used to inject high-pressure cold fluids into the artificial reservoir. The working fluid absorbs thermal energy when passing through the reservoir’s fractures, and then, the fluid returns to the surface through the production well, and the energy it carries is used for power generation. The cooled working fluid is reinjected into the thermal reservoir to form a closed loop (see Fig. 1). Theoretical calculations indicate that a 20 °C reduction in the temperature of 1 km³ of HDR can provide enough thermal energy to operate an electric generator with a 10 MWe capacity for 20 years, which is equivalent to 1.3 million tons of oil (Baria et al. 2012). Conventional EGS uses water as the working fluid, but there is a 10–20% water loss during EGS stimulation and operation (Wang et al. 2012a, b). Because of this, studies have been conducted to find alternative working fluids. CO₂ is currently a promising alternative due to its thermodynamic and hydrodynamic properties (Pruess 2008).

Global warming is one of the largest challenges we face in this century. It has brought extreme precipitation and extended the duration of regional drought periods, which in turn reduces crop yields and increases forest vegetation mortality (Adams et al. 2017; Liu et al. 2020; Zhang and Zhou 2020). In addition, the extreme climate caused by global warming will also trigger violent conflicts in certain areas (Breckner and Sunde 2019). Seventy-six percent of the greenhouse gases that cause climate warming is CO₂, and 65% of this CO₂ is derived from fossil fuel combustion and industrial emissions (Abas et al. 2017). Carbon capture and storage (CCS) can effectively reduce CO₂ emissions. Current carbon capture technologies include chemical absorption, polymer membrane separation, porous material adsorption, and chemical looping separation. The first two technologies have been applied at the commercial-scale level, while the latter two are still at the experimental level (Al-Mamoori et al. 2017). For captured CO₂, target storage

![Diagram depicting the EGS process (Olasolo et al. 2016)](image-url)
options include deep-ocean storage, mineralized storage, depleted oil/gas field storage, and saline storage (Bui et al. 2018). The specific application methods for the above technologies will be introduced in Part 2. In addition, the CO₂ compression process is also a link that cannot be ignored in CCS, which will greatly affect the overall efficiency of CCS. Therefore, it is necessary to consider the impact of CO₂ capture pressure, post-compression pressure, temperature and other parameters on system performance (Muhammad et al. 2020). However, the high cost of CO₂ capture and the potential CO₂ leakage and ecological pollution due to CO₂ geological storage techniques have constrained the promotion of CCS. Therefore, using CO₂ as the working fluid instead of water, which combines EGS geothermal extraction with CO₂ geological storage, is a promising alternative solution. Compared with water, the loss of CO₂ during the heat extraction process is conducive to the reduction of greenhouse gases, and the CO₂ used to obtain thermal energy is used for power generation, which can compensate for the high cost of CCS. Although the combination of geothermal extraction, energy production, and carbon storage can improve the economic feasibility of CO₂ storage, the solubility of CO₂ under various pressure–temperature–molarity ($P$–$T$–$m$) conditions, the stimulation's effect on the reservoir, and the CO₂–fluid–rock interactions after CO₂ injection and during reservoir stimulation and operation of the EGS are key challenges that affect the long-term storage of CO₂.

In this paper, we review the use of CO₂ as a working fluid in EGS, the global carbon emission status, the challenges encountered in current CCS projects, and the potential for combining carbon storage and EGS geothermal recovery, providing technical insights for addressing global warming and energy stress.

**Carbon emission reduction challenges**

**Emission reduction pressure and measures**

From 1990 to 2019, global CO₂ emissions from energy utilization increased (see Fig. 2), reaching approximately 33.3 billion tons in 2019 (IEA 2020). In 2016, the major CO₂
emitting countries included China, the United States, India, Russia, Japan, and the countries of the European Union. These nations accounted for 68% of the total global emissions. Figure 3 shows the greenhouse gas emissions for the various countries and regions of the world as well as the fact that the trend in CO₂ emissions is similar to that of the amount of greenhouse gases (Olivier et al. 2017). In recent years, global warming has triggered disasters such as floods, heat waves, hurricanes, and wildfires. This indicates that it is imperative to significantly reduce global carbon emissions in the future. It is necessary to maintain a global temperature rise of 1.5–2 °C in order to maintain a relatively stable climate (Peters et al. 2013; Knutti et al. 2016; Rogelj et al. 2016). In response to global warming, appropriate policies and technical measures have been adopted worldwide to reduce CO₂ emissions (Grant et al. 2014; Mackey et al. 2013; Peters et al. 2017; Haszeldine 2009). This mainly involves two goals: one is to vigorously develop renewable energy such as wind energy, solar energy, biomass energy, and geothermal energy; and the other is to implement CCS.

World energy demands continue to rise and will grow by 30% by 2040 (IEA 2017a, b). In terms of global energy sources, the International Energy Agency predicts that the share of coal will fall to 26% in 2022 (27% in 2016). However, coal-fired power generation is still growing at a rate of 1.2%, will still account for nearly 36% of the power structure in 2022, and the global demand for coal will reach ~ 380 million tons of oil equivalent by 2022 (IEA 2017a, b). In addition, before 2040, the demand for oil will still have a growth rate of 1.05 million barrels per day, and by 2040, we will still need 67 billion barrels of new resources. The growth of natural gas will accommodate 25% of the global energy demand under this new policy scenario. Even in the context of sustainable development, fossil fuels still account for nearly 60% of the global energy mix (IEA 2017a, b). According to the research of World Intellectual Property Organization, from 2006 to 2011, the number of patents for renewable energy technologies such as biofuels and solar energy decreased. Although the number of new energy technology patents has increased, there are fewer core technology patents. In addition, the sharing and diffusion of low-carbon technologies between developed and developing countries are insufficient, and there are large regional differences and industry differences in low-carbon technologies (Huang...
et al. 2017). This indicates to some extent that the supply of renewable energy will not be sufficient to replace fossil fuels in the near future (Jiang et al. 2017).

Thus, it has become extremely important to find a way to control global warming by controlling the atmospheric CO$_2$ content using CCS technology. CCS is considered to be the most promising measure for mitigating carbon emissions. It can serve as a bridge for the transition from fossil fuel combustion to renewable energy and can provide solutions for global green sustainable development (Bains et al. 2017).

CCS technology principle

Biological approach to CCS

CCS methods can be divided into biological approaches and artificial approaches. There are two common methods of biological carbon storage. The first is to use the photosynthesis of microalgae, cyanobacteria, and green plants to capture and convert atmospheric CO$_2$ into organic biomass with higher chemical energy (Cheah et al. 2016); however, this process is far from applicable on an industrial scale (Zhu et al. 2017; Psarras et al. 2017; Saunders et al. 2014). The second is the use of thermo-alkali-stable carbonic anhydrases (CAs, EC 4.2.1.1) to catalyze the hydration reaction and biomineralization. The aqueous solution containing immobilized carbonic anhydrase absorbs CO$_2$ from high-temperature flue gas to form bicarbonate, which absorbs 25 times more CO$_2$ than the non-catalytic method. When carbonic anhydrase is used for biomineralization, it can mineralize the CO$_2$ in the flue gas from power plants into calcite with a high thermal stability. Electron microscopy was used to scan the crystal morphology of the calcium carbonate formed in the presence and absence of CA. It was observed that the former forms a stable phase of rhombohedral calcite crystals (Fig. 4a), while the latter forms a metastable phase of spherical vaterite crystals (Fig. 4b) (Bose and Satyanarayana 2016). However, the use of thermo-alkali microorganisms to produce the corresponding CAs involves biotechnology such as genetic optimization, and the conditions are demanding, e.g., temperature, oxygen environment, and pH control, making it difficult to produce CA on an industrial scale (Bose and Satyanarayana 2017).

Artificial approach to CCS

The artificial approach to CCS involves two methods: CO$_2$ capture and geological storage. Figure 5 illustrates the technology used for carbon (CO$_2$) capture, utilization, and geological storage (CCUS) (Abu Ghalia and Dahman 2017; Al-Mamoori et al. 2017; Service 2008; Schrag 2009; de Coninck et al. 2009; Yang et al. 2017; Yaumi et al. 2017; Fridahl 2017). CCUS is a process that includes separating CO$_2$ from related sources through a series of technical means, compressing it for geological storage or utilization in the life and the production, and thereby achieving the purpose of long-term separation of CO$_2$ from the atmosphere. Moreover, CO$_2$ utilization and storage are two independent processes.

The CO$_2$ sources utilized by the CCUS method are derived from the combustion of fossil and biomass fuels in power plants, industrial processes (cement manufacturing, steelmaking, ammonia synthesis, etc.), the separation of associated gas after oil extraction, and the separation processes that take place after natural gas extraction (Smit 2016).
The geological storage of CO₂ is a very complicated technical process, which includes the selection of a storage site, the mechanism of CO₂ capture by a geological reservoir, the assessment of the CO₂ storage capacity of the reservoirs, and CO₂ monitoring after storage. In addition, the CO₂ storage capacity of the geological reservoirs, the CO₂ injection capacity, the local environmental and regulatory requirements should be taken into consideration before site selection. The geological reservoir used to store CO₂ is usually a porous and permeable rock mass containing fluids such as water, gas, and oil. The storage space in the rock mass is the pores of the rock matrix or the natural (or artificial) fractures within the rock mass. The CO₂ capture methods used in geological storage can be divided into the following five categories (BP Corporation North America Inc. 2019). Figure 6 shows a schematic diagram of the geological storage mechanisms:

**Fig. 4** Scanning electron microscope images of calcium carbonate crystals. **a** Rhombohedral calcite crystals formed in the presence of CA, **b** spherical vaterite crystals formed in the absence of CA (Bose and Satyanarayana 2017)
Fig. 5 CCUS technology system
a) Structural trapping is the main trapping mechanism. After the gas phase or super-critical CO$_2$ (SCCO$_2$) is injected into the formation, its buoyancy is greater than that of the other liquids that may be present in the pores or fractures of the reservoir. Therefore, CO$_2$ will seep through the porous rock mass until it reaches the top of the geological reservoir where it encounters an impermeable cover layer. When the motion is balanced, CO$_2$ will be stored in immiscible and immobile plumes below the cap rock (see Fig. 6a).

b) Residual trapping is also known as capillary trapping (Gershenzon et al. 2017). When the CO$_2$ is injected into the reservoir, it flows into the porous rock and replaces the fluid in that location. As the CO$_2$ continues to flow, the liquid will replace it again. Due to discontinuities in the pore space of the reservoir, some CO$_2$ is trapped as residual static droplets (Fig. 6b).
c) Solubility trapping and mineral trapping: when the formation into which the CO₂ is injected contains water (such as a saline reservoir), the structurally and residually trapped CO₂ will gradually dissolve, changing the chemical properties of the pore water. With the acidification of pore water, some of the minerals (feldspar) in the cap rock and reservoir will gradually dissolve, and new minerals (carbonates) will form.
The type of carbonate formed depends on the pressure, temperature, pH, and other geochemical conditions of the reservoir (Fig. 6c and d).

d) Adsorption trapping is mainly used for the injection of CO₂ into coal seams. The CO₂ diffuses into the coal matrix through fractures in a free state and is adsorbed onto the micro-porous walls of the matrix (Wu et al. 2010). The adsorption of CO₂ can lead to the desorption of CH₄, providing conditions for the exploitation of coal-bed methane. At suitable pressures and temperatures, 95% of the CO₂ stored in the coal seam will exist in an adsorbed form. The CO₂ storage form under each scenario is shown in Table 1.

**CCS application challenges**

Forecasts for CCS technology and demand indicate that by 2025, the number of patent applications for CCS technology worldwide will increase to 16,156. The US has the most competitive CCS technology (Shin et al. 2016). However, there are two prominent challenges in the field of CCS: cost and safety (Rahman et al. 2017). The processes of CO₂ separation, capture, purification, compression, transportation, and storage have high investment and operating costs. The capture and compression of CO₂ is the most cost-intensive part of the CCS process and can be as much as 50–80% of the total cost of CCS. This hinders the large-scale use of CCS technology (Al-Mamoori et al. 2017; Kolster et al. 2017). Therefore, it is necessary to rationally optimize the transportation of CO₂ from the carbon source to the storage or utilization sites (Mechleri et al. 2017). Further research and development is needed to create low-cost capture technology (Garg et al. 2017).

Geological storage is the main choice for CO₂ storage. CO₂ is injected into a deep saline reservoir, oil/gas reservoir, coal seam, or seabed sediment layer for storage. Combining CO₂ storage with oil/gas production (CO₂ enhanced oil/gas recovery, CO₂-EOR/EGR) has the potential to reduce the total cost of CO₂ storage (Zhang and Huisingh 2017). Deep saline reservoirs are a potential carbon sink, but large-scale CO₂ storage in saline reservoirs will increase reservoir pressure. When pressure builds to a certain threshold, it could cause saline water to migrate continuously into the freshwater reservoir through the leaking wellbore (Birkholzer et al. 2011). Saline water extraction is an effective depressurization strategy (Cihan et al. 2015; Birkholzer et al. 2012), but the extracted water contains high concentrations of dissolved solids, suspended solids, and various toxic substances (Kaplan et al. 2017). Therefore, adopting this approach brings new environmental problems and additional costs. In addition, the storage of CO₂ into deep saline aquifers, depleted oil/gas reservoirs, and seabed sediments has a potential risk of leakage.

Leakage of offshore geological storage may affect surface sediment circulation within 5 cm (Rastelli et al. 2015, 2016), and the mixture of acidified sediment and seawater causes the leaching of pollutants into sediments, releasing elements such as Zn, Pb, Cd, Ni, and As (Martín-Torre et al. 2016). Long-term large-scale continuous leakage of CO₂ onto the seabed would damage the environment (Lichtschlag et al. 2015; Blackford et al. 2014). For onshore geological storage, CO₂ injected into depleted oil/gas reservoirs and saline reservoirs through large-scale industrialization will result in increased reservoir
pressure and lateral CO₂ migration. Because of this, a number of CO₂ and/or saline plumes may pass through the fractures, fault zones, and poorly closed injection wells. This could be followed by vertical migration, resulting in leakage and the contamination of shallow aquifers (freshwater layers) (Porter et al. 2015; Carroll et al. 2014; Birkholzer et al. 2015). During the leakage process, the fluid undergoes discontinuous flow shrinkage at the heterogeneous interface with the low permeability layer, which may cause CO₂ dissolved in the saline water to escape, allowing it to enter the soil or even the atmosphere (Plampin et al. 2014). Direct mineralization and industrial utilization of captured CO₂ is also a desirable option considering the potential adverse effects of leakage from geological CO₂ storage sites. However, this solution still has the disadvantages of high costs and high energy consumption.

In addition, injecting CO₂ into the mafic and ultramafic reservoirs (basalt formation) and achieving mineral carbonation based on the reaction of calcium oxide or magnesium oxide with CO₂ is also a promising method of CO₂ storage. CO₂ is fixed in basalts by the form of carbonate, which prevents it from escaping and migrating to shallow aquifers or even entering the atmosphere, enhancing the safety of CO₂ storage (Liu et al. 2019; McGrail et al. 2017). To explore this form of CO₂ storage, there are already several commercial-scale operation and pilot projects (e.g., CarbFix project, Wallula project, Oman Drilling Projects, etc.) (Kelektsoglou 2018; Kelemen et al. 2018; McGrail et al. 2014). In the CarbFix project of Iceland, more than 95% of the injected CO₂ formed carbonate within 2 years (Matter et al. 2016). The Wallula project test found that Fe and Mn were enriched in the carbonate formed in the basalt formation after CO₂ injection. This indicates that the part carbonation of the minerals in the injection area comes from the dissolution of basalt (McGrail et al. 2017). Based on the CO₂ storage of mineral carbonation, this paper considers another alternative to achieve geological storage of CO₂, namely, the use of CO₂-EGS geothermal extraction, which uses CO₂ as both a heating fluid and a storage object.

### Working fluid selection of EGS

#### Comparison of water and CO₂ in EGS

High costs make it difficult to widely apply these methods of geological CO₂ storage in deep saline aquifers in a short period of time, resulting in the combination of geological CO₂ storage and methane/geothermal energy extraction. The methane and geothermal energy produced by a saline water reservoir with an abnormally high pressure and temperature can compensate or even offset the cost of CCS, but this solution is currently limited to intermediate-low temperature hydrothermal aquifers (Ganjdanesh et al. 2012; Liu et al. 2015; Ganjdanesh and Hosseini 2016; Randolph and Saar 2011).

During the implementation of an EGS project with water as the circulating working fluid, maintaining the thermal reservoir’s pressure to ensure the successful and continuous operation of the EGS equipment requires a large amount of water (about 870.64–15,898.68 L/MWh) (Harto et al. 2014). Although EGS can use lower quality water sources than traditional power plants, in many dry areas, groundwater and fresh surface water are inevitably consumed. In 2000, Brown (2000) first proposed the use of SCCO₂ as an alternative working fluid, instead of water, to achieve geological CO₂ storage.
during geothermal extraction. The report pointed out that using SCCO$_2$ as a working fluid had three advantages:

1. The large difference in the density of the CO$_2$ in the injection well (cold SCCO$_2$) and in the production well (hot SCCO$_2$) provides a large buoyancy difference that reduces power requirements of the circulating pump compared to the power requirements of the water-based system.
2. Minerals in geothermal reservoirs cannot be dissolved by SCCO$_2$ and transported to the surface, decreasing or eliminating scaling problems in pipelines and heat exchange equipment.
3. Problems such as dissolved silica in water-based systems do not occur when the reservoir temperature exceeds 647 K (the critical point temperature of water).

Numerous studies have been conducted on the feasibility of using CO$_2$ to replace water as a working fluid and the difference in the extraction efficiency of the two fluids. However, there is some disagreement between these different studies.

SCCO$_2$ has greater expansion and compressibility than water, resulting in a strong buoyancy force between the injection and production wells. CO$_2$ is roughly equivalent to water as a heat transfer fluid, while the former has considerable advantages on wellbore hydraulics. For a given driving pressure, CO$_2$ has approximately 4 times the mass flow and 1.5 times the net heat recovery rate of water. In addition, as shown in Fig. 7, the advantages of CO$_2$ in accelerating thermal recovery become greater at lower reservoir temperatures (Pruess 2006). Pan et al. (2017) and Wang et al. (2018) also obtained similar findings through numerical calculations. The net heat recovery rate and the mass productivity of CO$_2$-EGS were higher than that of H$_2$O-EGS. When the surrounding formation had a high permeability, the CO$_2$-EGS extraction efficiency was significantly greater. A lower average reservoir permeability and initial temperature enhance the thermal recovery rate of the CO$_2$-EGS and reduce the CO$_2$ loss rate. Therefore, in order to
obtain the best thermal recovery rate and fluid loss rate, the reservoir stimulation effect as well as initial temperatures of different reservoirs should be considered.

However, Pritchett (2009) found that for the same conditions, the heat extraction efficiency was the greatest when using water as the working fluid. Assuming that the in situ fluid in the reservoir was water or CO₂, water and CO₂ were used as the working fluids, with cold water replacing hot water or hot CO₂, and cold CO₂ replacing hot water or hot CO₂. In these processes, the extraction efficiencies when water was injected into a CO₂-containing system and when water was injected into a water-containing system were quite similar, whereas the efficiency when CO₂ was injected into a CO₂-containing system was lower. However, the injection of CO₂ into a water-containing system led to a faster thermal breakthrough in the production well, resulting in the lowest heat recovery rate.

The CO₂ thermosiphon design for thermal extraction and power generation is an alternative to H₂O-EGS. The system was evaluated by Atrens et al. (2009), but the wellbore friction, turbulence, pressure drop in the equipment, and the effects of the water in the system were ignored in the evaluation model. Based on the above assumptions, the net power generation of the CO₂ thermosiphon system (CO₂-EGS power generation) was comparable to that of the conventional method, but the design was much simpler. Comparing the thermal recovery capacity of the two systems, the low specific heat capacity of CO₂ and the lower density of CO₂ in the production well resulted in less thermal energy being extracted by the CO₂ thermosiphon system than by the H₂O-EGS. In high-impedance reservoirs and shallow EGS, the effective energy of the CO₂ extraction was close to that of water. When using a large diameter wellbore, the thermal extraction efficiencies of the two systems were similar (Atrens et al. 2010). Because of the low specific heat capacity of CO₂, Pruess (2008) believed that the higher mass flow rate resulting from the low viscosity of the SCCO₂ could compensate for this disadvantage.

At present, the CO₂ used in EGS is obtained by capture purification, and the direct use of unpurified CO₂ (containing impurities such as nitrogen, oxygen, and solid particles) as a working fluid can offset the CO₂ capture cost. However, impure CO₂ cannot be directly expanded in the turbine, so the Organic Rankine Cycle must be used in combination with the impure CO₂-EGS. An increase in the impurities decreases the thermal extraction efficiency of impure CO₂-EGS, so the impure fraction should not exceed 10% (Zhang et al. 2016).

In addition, alternative working fluids other than CO₂ have been proposed. Phuoc et al. (2018) evaluated and compared the thermodynamic and transmission properties of air, water, and CO₂ as working fluids for EGS, arguing that air can extract more thermal energy and carry more effective energy. The thermal extraction rate and effective energy of both CO₂ and water decrease with time, while those of air remain unchanged, which can extend the thermal extraction life. Olasolo et al. (2018) suggested that single supercritical phase nitrous oxide (N₂O) could be a substitute for the two working fluids currently used. Its thermodynamic properties were superior to those of CO₂ and were closer to the thermodynamic properties of an ideal EGS working fluid. However, this result was limited to plants that matched the assumptions and parameters used in the study and could not be extended to other EGS plants. Overall, whether air or N₂O is used as the EGS working fluid, only thermal extraction is considered, and the combined
effects of carbon emission reduction, and thermal energy extraction have not been comprehensively considered.

**CO₂ solubility in different P–T–m systems**

After hydraulic stimulation, some water will remain in the HDR thermal reservoir (dedicated fresh water, brackish or geothermal brine) (Hirschberg et al. 2014). During the CO₂-EGS process, the injected CO₂ is dissolved to form a CO₂–H₂O or CO₂–H₂O–NaCl fluid system. Therefore, it is necessary to study the solubility of CO₂ at a wide range of pressures, temperatures, and ionic strengths (P–T–m) to estimate the CO₂ storage.

In recent two decades, many predictions of CO₂ solubility have been made for a wide range of P–T–m systems. Duan and Sun (2003) extended the temperature, pressure and ionic strength ranges for the thermodynamic model for CO₂ solubility prediction to 273–533 K, 0–2000 bar, and 0–4.3 mol/kg, respectively. The calculated results were close to the experimental results with an error of 7%. In addition, they indicated that ions with the same charge have approximately the same interaction parameters, and the interaction parameters of divalent cations were twice those of monovalent cations. They also extended their model to other complex aqueous systems using this method. Mao et al. (2013) proposed an improved model to increase the solubility temperature range of CO₂ in NaCl solution to 723 K, but the calculation results were unreasonable when the pressure exceeded 1500 bar. The average absolute deviation of the calculated CO₂ solubility compared to the reliable experimental data was 4.62%. However, the deviation will
exceed 10% near the supercritical region. Figure 8 shows the CO₂ solubility calculated by the model.

CO₂ dissolution decreases the pH of the fluid system in the EGS reservoir, causing dissolution of feldspar (alkali feldspar, plagioclase) and precipitation of carbonate. Duan and Li (2008) added solid-phase CaCO₃ to the original H₂O–CO₂–NaCl ternary system and developed a computational model for the coupling phase and ion solution equilibrium (273–525 K, 1–1000 bar, NaCl concentration reached the saturated concentration of rock salt). Changes in temperature, pressure, and NaCl concentration affect the solubility of CO₂, and the dissolved CO₂ content affects the solubility of plagioclase. In turn, the dissolution of plagioclase changes the ion balance of the solution system, which in turn leads to changes in the solubility of CO₂. Spycher and Pruess (2010) suggested that both the solubility of CO₂ in water and the solubility of water in CO₂, which also affects the reaction of CO₂ with the surrounding rock mass, should be considered in CO₂-EGS systems. They improved and expanded the previously established mutual solubility model (temperature range 288–373 K, pressure < 600 bar) for CO₂ and water. The expanded model has the NaCl concentration of 6 mol/kg and the temperature of 673 K. 

As the temperature increases, the effect of dissolved salt on the solubility of water in CO₂ is less than that of CO₂ in water. For the CO₂–H₂O system, Zhao et al. (2015) compared the experimental values of the solubility of CO₂ at temperatures of 323.15 K, 373.15 K, and 423.15 K with the calculated values of the established model. The pressure range of 1–1000 bar was divided into three regions: 1–163.1 bar (region I), 163.1–466.2 bar (region II), and 466.2–1000 bar (region III). When the pressure was less than 163.1 bar, the solubility of CO₂ in the aqueous phase decreased as temperature increased. When the pressure reached 163.1 bar, the CO₂ solubility reached 1.051 mol/kg at both 373.15 K and 423.15 K. In the region of 163.1–466.2 bar, when the pressure was increased to 256.9 bar, the solubility of CO₂ reached 1.370 mol/kg at both 323.15 K and 423.15 K. Similar results occurred at 466.2 bar (323.15 and 373.15 K). When the pressure was greater than 466.2 bar, the solubility of CO₂ increased as temperature increased. The findings for region I and region II were consistent with the findings of Guo et al. (2014)
Effect of stimulation and CO₂ injection on reservoirs

With the development of the EGS pilot project, some related scientific problems have gradually emerged, including resource exploration, reservoir stimulation, micro-seismic monitoring, multi-field coupling (thermal–hydrologic–mechanical–chemical processes) of a deep high-temperature rock mass, energy conversion efficiency, efficient use of power generation systems (Lu and Wang 2015). Geothermal reservoir reconstruction methods mainly include hydraulic stimulation, chemical stimulation, and thermal stimulation. The first two are commonly used in EGS (Wang et al. 2012a; Brehme et al. 2017; Breede et al. 2013). The initial development of EGS by hydraulic stimulation and chemical stimulation will cause the pores and fractures of the reservoir to fill with water, so the CO₂-EGS system operates with CO₂ replacement water.

Effect of stimulation on reservoirs

Hydraulic stimulation

Hydraulic stimulation involves two mechanisms: hydraulic fracturing and hydraulic shearing. Hydraulic fracturing causes the initiation and extension of tensile fractures. Hydraulic shearing causes pre-existing defects in the reservoir to be reactivated by irreversible shear expansion, and the sliding of the rock along the fractures can increase the permeability by up to 2–3 orders of magnitude. Hydraulic shearing is the primary mechanism for increasing permeability and occurs at least tens of meters from the point of injection. However, the occurrence and propagation of hydraulic fracturing may be an important way for the near-field wellbore to connect the reservoir to the original fracture network within the reservoir (Amann et al. 2018; Hu et al. 2017). Enhancing permeability through shear sliding is a common means of EGS, and the shear stimulation of reservoirs by CO₂ is better than stimulation by water (Deng et al. 2018).

Chemical stimulation

Acid treatment was initially applied in the petroleum industry to increase the productivity of oil and gas wells, and geothermal extraction was only used to remove minerals deposited in the well. Then, acid treatment was applied to the fracture network in the vicinity of the enhanced well and was successfully implemented in granite geothermal reservoirs such as Fjäll-backa in Sweden and Beowawe in the United States. In recent years, the reliability of acidified sandstone intervals has significantly improved. In the United States, about 90% of geothermal wells have increased fluid production by 2–4 times (Portier et al. 2009). The acids injected include hydrochloric acid (HCl), common mud acid (HCl–HF), and organic clay acid (C₆H₈O₇–HF–HBF₄–NH₄Cl). Acid stimulation improves the hydraulic permeability of production and injection wells to various degrees. The efficiency of chemical stimulation can be improved by developing directional stimulation techniques for selected areas (Nami et al. 2008). In addition, the injection of high pH chelating agent solutions into the reservoir can result in the dissolution of calcite and plagioclase, prevent the precipitation of calcite at high temperatures, and
increase the reservoir’s porosity and permeability, especially near the injection well (Rose et al. 2010).

**Effect of CO\(_2\) injection**

Spycher and Pruess (2010) developed a phase separation correlation model for brine (aqueous NaCl solution) and CO\(_2\), and used this model to simulate the production flow during the CO\(_2\)-EGS reservoir flooding two-phase flow process. Their simulation showed that water productivity declined, while the CO\(_2\) content of the liquid produced continued to increase, and the water productivity was zero after 4 years. At this point, about 6% by weight of water remained in the resulting single phase CO\(_2\) stream. In the above process, the CO\(_2\) dissolved in the formation fluid had the following reaction equations (Thomas et al. 2016):

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\text{Dissociation of carbonic acid into active hydrogen ions and bicarbonate ions [Eq. (3)] may trigger complex reactions with geological fluids and formation rocks, immobilizing the CO}_2\text{ in the aqueous and mineral phases. The reactions involving the reaction of SCCO}_2\text{ and carbonic acid with formation fluids and rocks, i.e., CO}_2\text{–fluid–rock interactions, vary depending on the chemical compositions of the fluid and the mineral. The EGS reservoir with granite as the host rock layer has relatively large feldspar content, but few calcite (Xu et al. 2006). CO}_2\text{–fluid–rock interactions may cause calcite, oligoclase (Na-feldspar, Ca-feldspar), and K-feldspar to dissolve, and eventually, to regenerate carbonate, which can fix CO}_2\text{ into solid minerals (mineral trapping}}
\]
storage) and may be accompanied by the precipitation of aluminosilicates such as kaolinite and muscovite (Rosenbauer et al. 2005; Ueda et al. 2005; Na et al. 2015; Liu et al. 2003). The reactions for this process are as follows:

\[
\text{CaCO}_3(\text{calcite}) + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-
\]  

(5)

\[
\text{CaAl}_2\text{Si}_2\text{O}_8(\text{Ca-feldspar}) + \text{H}^+ + \text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{CaCO}_3(\text{calcite}) + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{kaolinite})
\]  

(6)

Kaieda et al. (2009) conducted field experiments to test the CO$_2$–fluid–rock interactions in water injected with dissolved CO$_2$ in ~210 °C boreholes. When river water was injected into the borehole, the Ca concentration reached a maximum of 7 mg/L at 22 h (Fig. 10a). After injecting water containing 3 wt% CO$_2$, the Ca concentration reached a maximum of 85.2 mg/L at 1 h (Fig. 10b), and then, it gradually decreased, indicating that the injection of CO$_2$ caused the rapid dissolution of Ca-containing minerals, followed by calcite precipitation. The dissolution effect of CO$_2$ injection is stronger than that of water.

The Ca required for the mineralization of CO$_2$ is mainly derived from the Ca-feldspar and aragonite in granite, and the initially dissolved calcite may be derived from the alteration of granite. Ré et al. (2014) determined the relationship between the geochemistry and mineralogy of water–granite (epidote) ± SCCO$_2$ systems (250 °C, 25–45 MPa) based on five experiments. The metastable precipitation of clay minerals, e.g., illite and montmorillonite, can occur in granite or feldspar hosted formations; the former can be found in the H$_2$O-EGS system, while the latter can be found in the CO$_2$-EGS system. The formation of these clay minerals has an impact on the porosity and permeability of the reservoir.

During operation, the CO$_2$-EGS reservoir can be divided into a single supercritical CO$_2$ zone, a two-phase water–CO$_2$ mixture zone, and a single aqueous phase with dissolved CO$_2$ zone. The dissolution and precipitation of minerals mainly occur in the peripheral regions of the reservoir system, which can reduce the permeability and affect the growth and lifetime of the reservoir (Xu et al. 2014). Pan et al. (2017) studied the CO$_2$–fluid–rock interactions in a reservoir at 200 °C and 20 MPa using a three-dimensional numerical model. This study suggested that more aqueous CO$_2$ solution accumulates in the upper and lower layers than in the injection/production layer, which lowers the pH and promotes the dissolution and precipitation of the upper and lower minerals in the system. Compared with water, SCCO$_2$ has a larger magnitude rate of oligoclase dissolution, and there are significant differences in the distribution of the dissolved morphologies in the profile.

The incidental effect of mineral precipitation on CO$_2$ trapping in EGS can affect the reservoir’s thermal recovery. Injecting CO$_2$ into a saltwater-filled EGS reservoir system reveals that different degrees of salting-out (NaCl) plugging occurred in the production wells and injection wells of the low salinity and high salinity reservoir systems. In the low salinity systems, the CO$_2$-EGS heat extraction rate was not significantly affected by plugging. However, in the high salinity systems, the CO$_2$-EGS had a lower heat extraction rate (Borgia et al. 2012). In addition, according to the study of Yarushina and Bercovici (2013), CO$_2$ storage in rocks decreased the seismic risk of seismic activity since mineral
precipitation increased the contact area between the solid particles (reducing the effective fluid pressure), dispersed the off-stress load, and increased the frictional contact. Therefore, mineralization storage has the potential to reduce the risk of seismic activity when the fluid pumping rate does not exceed a critical value.

**Storage potential of CO₂ in EGS**

**CO₂ storage evaluation from engineering**

An EGS reservoir is pressurized during the thermal production process, and the higher pressure forces the fluid through the fractures and pores, resulting in the fluid diffusing into the surrounding rock mass. Typically, this fluid loss is unrecoverable unless the reservoir is subjected to negative pressure for extended periods of time. After SCCO₂ injection, dissolved CO₂ causes mineral dissolution and precipitation in the outermost aqueous phase zone, resulting in CO₂ dissolution and mineralization storage (Xu et al. 2014). Therefore, the use of SCCO₂ as a working fluid enables permanent storage of partial CO₂ in the EGS. At Habanero geothermal field in the Cooper Basin of South Australia, 94,500 t of CO₂ can be stored annually under doublet production conditions assuming 5% (may be over-estimated) fluid loss in production. The CO₂ loss rate here may be mainly a large amount of solubility trapping storage and a small amount of mineral storage, and the latter has very high stability. For EGS reservoirs with a burial depth of more than 3 km, due to the limitation of reservoir fracturing range, it is impossible for dissolved CO₂ to completely migrate out of crystalline rock mass. Even if there is, there may be only a very small amount. Besides, the sedimentary rocks overlying the EGS reservoir have small permeability, which can also ensure the stability of CO₂ storage. When using the six-spot well layout in the next phase, the storage capacity will increase to 572,000 t of CO₂ per year (Xu et al. 2016a).

Under high temperatures and high pressures, the CO₂ storage rate of an EGS reservoir is higher than that of a general oil/gas reservoir. According to the water loss data
obtained by the Fenton Hill EGS project for long-term flow observation, Pruess (2006) estimated that CO2 loss could reach 1 t/s per 1000 MW electric capacity during the CO2-EGS operation, i.e., CO2-EGS with an installed capacity of 1000 MW can store all of the CO2 generated by a coal-fired power plant with 3000 MW electricity. Taking the first industrial-scale geological CO2 storage project in the Sleipner Vest gas field in the Norwegian North Sea as an example, about 1 Mt of CO2 (31.7 kg/s of the injection rate) has been injected into the saline aquifer every year for more than 10 years (Audigane et al. 2007). Spycher and Pruess (2010) estimated that the CO2 storage of the Sleipner field could be achieved by CO2-EGS with an installed capacity of 30–35 MW.

CO2 storage analysis from experiment

A high-temperature/high-pressure triaxial seepage experiment system (as shown in Fig. 11) was used to conduct the SCCO2 flooding water heat extraction experiment, the operation process of the experimental system can refer to the previous work (Li et al. 2019). The water samples in the rock sample fractures were collected after each alternating cycle injection, and the mineral dissolution/precipitation caused by SCCO2 injection was analyzed. In order to overcome the limitation of the experimental period and the size of the rock sample, water alternating SCCO2 cycle injection was adopted, and each cycle lasted 72 h. The axial pressure and confining pressure were 35 MPa and 30 MPa, respectively.

Table 2 Fluid injection parameters and changes of water sample pH in each alternating cycle

<table>
<thead>
<tr>
<th>Number of alternating cycles</th>
<th>Experimental temperature (°C)</th>
<th>Injection parameter of SCCO2</th>
<th>Injection parameter of water</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Injection pressure (MPa)</td>
<td>Injection temperature (°C)</td>
<td>Average injection rate (mL/min)</td>
</tr>
<tr>
<td>0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>19.8</td>
</tr>
<tr>
<td>1</td>
<td>200±0.4</td>
<td>7.5±0.1</td>
<td>40±0.3</td>
<td>17.9</td>
</tr>
<tr>
<td>2</td>
<td>201±0.3</td>
<td>7.5±0.06</td>
<td>39±0.6</td>
<td>19.5</td>
</tr>
<tr>
<td>3</td>
<td>200±0.2</td>
<td>7.5±0.1</td>
<td>40±0.4</td>
<td>20.3</td>
</tr>
<tr>
<td>4</td>
<td>200±0.3</td>
<td>7.5±0.08</td>
<td>40±0.3</td>
<td>19.7</td>
</tr>
<tr>
<td>5</td>
<td>200±0.2</td>
<td>7.5±0.13</td>
<td>40±0.2</td>
<td>20.6</td>
</tr>
<tr>
<td>6</td>
<td>200±0.4</td>
<td>7.5±0.05</td>
<td>40±0.5</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from the table that after 0–1 injection cycles, the pH of the water sample is reduced from 6.5 to 4.1, which indicates that the reaction Eqs. (1) to (4) involved in this process proceed to the right. As a result, more CO2 is dissolved, and the content of H+ and CO3^2− in the water sample gradually increases. At this time, the pressure dissolution of the rock sample was enhanced. The high H+ concentration promoted the mineral dissolution process, and carbonate mineral precipitation was easily generated.

During the subsequent injection cycles, the pH of the water sample increased slightly, but it was always between 4 and 5. This shows that as the dissolution of CO2, mineral dissolution and precipitation continue to occur on the fracture surface, such as reaction...
Eqs. (5) and (6), $H^+$ is constantly in the dynamic process of consumption and generation. However, the specific chemical reaction process in each cycle can be analyzed by the change of anion and cation content in water samples.

Figure 12 shows the anion and cation content after each cycle of injection ($K^+$ is the left vertical axis, and the rest is the right vertical axis). Due to experimental conditions, $CO_3^{2−}$ and $HCO_3^{−}$ can not be measured. Observing the anions first, it can be seen that as the number of cyclic injections increased, the content of $Cl^{−}$, $NO_3^{−}$ and $SO_4^{2−}$ did not change significantly. According to the conservation of solution charge, other anions (such as $CO_3^{2−}$, $HCO_3^{−}$, and $OH^{−}$) content changed accompanied with that of cation content.

The minerals of the granite used in this experiment mainly contain quartz, potash feldspar, albite, anorthite, biotite and calcite. It was observed that during 0–2 cycles of injection, the content of $Na^+$ increased rapidly, and the content of $Ca^{2+}$ also increased slightly, indicating that albite and anorthite produced dissolution and released corresponding cations. During the 0–1 cycles of injection, the contents of $Mg^{2+}$ and $K^+$ increased slightly. It may be speculated that biotite was dissolved in high-temperature/pressure acidic environment to release the corresponding $Mg^{2+}$ and $K^+$.

During the 1–3 cycles of injection, the content of $Mg^{2+}$ increased slightly, while the content of $K^+$ increased significantly. This indicates that potash feldspar was dissolved during the dissolution of the biotite, and a large amount of $K^+$ was released. During the 2–3 cycles of injection, the $Ca^{2+}$ content gradually decreased, and it was speculated that calcite precipitated. During the 3–5 cycles of injection, the $Ca^{2+}$ content was still slowly decreasing, while the $Mg^{2+}$ content began to decrease significantly, and then increased slightly. This indicates that Ca/Mg carbonate mineral precipitation occurred during this process, and it was speculated that dolomite [$CaMg(CO_3)_2$] was formed. During the subsequent 5–6 cycles of injection, the contents of $Ca^{2+}$ and $Mg^{2+}$ increased slightly. This is because with the consumption of the corresponding ions, the dissolution reaction of anorthite and biotite is promoted.

![Fig. 12 Ion content changes in each alternating cycle](image-url)
It can be seen that during the 3–4 cycles of injection, when the K\(^+\) content decreases, the Na\(^+\) content gradually increases. This indicates that the water sample is rich in potassium, so that the feldspar is dissolved and illite is formed, while Na\(^+\) is released. As the Na\(^+\) content continues to increase, it is speculated that during the 4th to 5th cycles injection phase, Na-containing cancrinite is formed. In the 5th to 6th cycles injection phase, due to the decrease of the Na\(^+\) content, the albite is dissolved and K\(^+\) in the solution is consumed. As a result, Na\(^+\) is released while illite is generated.

According to the above results, after the water alternating SCCO\(_2\) cycle injection, the feldspar minerals on the granite fracture surface were dissolved, and the carbonate minerals were formed. Rock sample of same location was scanned by computerized tomography before and after the experiment (as shown in Fig. 13), it was found that mineral
precipitation was prone to occur at the intersection of the main fracture and the micro-fracture, blocking the micro-fracture and reducing its aperture. In the meandering convex part of the main fracture, mineral dissolution was prone to occur, which increased the fracture aperture here. When there was a bridge between the main fracture and the micro-fracture, both mineral dissolution and mineral precipitation occurred here.

Therefore, after hydraulic fracturing, the porosity of granite thermal reservoir can be divided into large-scale main fractures and small-scale micro-fractures, as shown in Fig. 14. In large-scale main fractures, due to the fast fluid velocity, the mineral dissolution effect is greater than the mineral precipitation. In small-scale micro-fractures, capillary effect and mineral precipitation promote CO₂ storage.

Conclusions and outlook
The current global carbon emission situation and the challenges faced by existing CO₂ emission reduction technologies were reviewed, and the potential of coupled carbon storage and EGS geothermal extraction using CO₂ as the working fluid was investigated from the perspectives of the fluid’s thermophysical and thermodynamic properties and the thermal-flow alteration of EGS reservoirs. At present, there is common consensus that CO₂-EGS is a promising alternative. However, the current CO₂ storage using this technology is mostly estimated based on the fluid loss rate of H₂O-EGS. The CO₂–fluid–rock interactions at various experimental and numerical simulation scales also use CO₂ in industrial applications of CO₂-EGS technology, and the amount of CO₂ storage was estimated. However, in numerical simulations, some of the simplifying assumptions may result in the overestimation of the above amount of CO₂ stored.

In addition, the mineral dissolution and precipitation that form CO₂ mineralization and storage may have a negative effect on the CO₂-EGS heat extraction efficiency. If the resulting mineral precipitation plugs the reservoir’s fractures, it will reduce the reservoir’s permeability and hot CO₂ productivity. One view is that the EGS reservoir is a porous medium with pores and fractures. If effective technical means, e.g., reservoir stimulation, CO₂ injection rate, injection pressure, and injection temperature, are adopted, it is possible to ensure that mineral precipitation mainly occurs in the pores of the matrix and more mineral dissolution occurs on the surface of the reservoir’s fractures. This not only ensures the storage of CO₂, it also increases the porosity of the reservoir and ensures a high geothermal recovery rate.

Over time periods of a decade or more, the high-temperature CO₂ produced in the production well may dissolve a certain amount of water. Therefore, in addition to considering the impact of this problem on reservoir remodeling, the impact on the design of the surface thermal energy conversion system should also be considered. The advantage of the carbon storage potential of the CO₂-EGS is that it compensates for the cost of the geological storage of CO₂ by producing electricity, which is a decisive factor in the application of this technology. Therefore, the commercial value and environmental impact of this technology should be evaluated based on its CO₂ storage capacity, the power generation of the EGS, and the cost of the heat extraction system and the energy conversion system.
Abbreviations
CCS: Carbon capture and storage; EGS: Enhanced geothermal system; HDR: Hot dry rock; CA: Carbonic anhydrases (EC 4.2.1.1); CCUS: Carbon (CO2) capture, utilization, and storage; SCCO2: Supercritical CO2; ECBM: Enhanced coal bed methane recovery; EOR: Enhanced oil recovery; EGR: Enhanced gas recovery.

Symbols
$P$ [bar] or [MPa]: Pressure; $T$ [K] or [°C]: Temperature; $m$ [mol/kg]: Molarity of the solutes or ions in the solution.

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Authors’ contributions
PL conducted literature analysis and drafted the manuscript, YW guided the interpretation of the corresponding results, edited and improved the manuscript. Both authors read and approved the final manuscript.

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Availability of data and materials
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Competing interests
The authors declare no competing financial interests.

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