A review of CO₂ storage in geological formations emphasizing modeling, monitoring and capacity estimation approaches

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Abstract

The merits of CO₂ capture and storage to the environmental stability of our world should not be underestimated as emissions of greenhouse gases cause serious problems. It represents the only technology that might rid our atmosphere of the main anthropogenic gas while allowing for the continuous use of the fossil fuels which still power today's world. Underground storage of CO₂ involves the injection of CO₂ into suitable geological formations and the monitoring of the injected plume over time, to ensure containment. Over the last two or three decades, attention has been paid to technology developments of carbon capture and sequestration. Therefore, it is high time to look at the research done so far. In this regard, a high-level review article is required to provide an overview of the status of carbon capture and sequestration research. This article presents a review of CO₂ storage technologies which includes a background of essential concepts in storage, the physical processes involved, modeling procedures and simulators used, capacity estimation, measuring monitoring and verification techniques, risks and challenges involved and field-/pilot-scale projects. It is expected that the present review paper will help the researchers to gain a quick knowledge of CO₂ sequestration for future research in this field.

Keywords CO₂ storage · Geological formation · Modeling for CO₂ storage · Mechanism of CO₂ storage · CO₂ storage projects

1 Introduction

The global warming scourge is threatening to ravage humanity. Rising sea levels, increases in average global air and sea surface temperatures, widespread snow and ice melting are notable effects of global warming (IPCC 2007). The implication of these indicators in the long run on health, nutrition and the economy can be ill-afforded and therefore has been the subject of a great deal of research to date. Numerous strategies have been employed or are under intense scrutiny as a means of tackling climate change, some of which

are greener technologies such as nuclear energy and wind energy which reduce the combustion of fossil fuels associated with emission sources and energy efficiency. The continued need for fossil fuels across the world and the relatively slow pace of renewable energy development suggests that the amount of undesired different gases being emitted into the atmosphere will remain on the increase. It is imperative, therefore, the ways should be developed in which these harmful gases can be expunged from the atmosphere.

Greenhouse gases, a term for the climate-unfriendly gases emitted into the atmosphere, provide a threat to our ecosystem with CO₂ accounting for 82% of greenhouse gases in the atmosphere. Though the global warming potential (GWP) of CO₂ is less than other greenhouse gases (US Environmental Protection Agency 2014), the sheer amount of CO₂ being emitted into the atmosphere makes it the most significant of all greenhouse gases for efficient climate control.

The advent, development and implementation of carbon dioxide capture, utilization and storage (CCUS) technology promises to reduce the amount of greenhouse gases entering the atmosphere. CCUS encompasses the capture of carbon dioxide and its associated compounds from producing

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sources, compression, transportation and the utilization of the captured CO₂ for processes such as injection into deep underground geological formations for permanent storage and injection into existing oil fields for additional recovery of hydrocarbons.

Some previous review articles summarized the different physicochemical methods responsible for suitable CO₂ storage and the difficulties in different aspects (Riaz and Cinar 2014; Belhaj and Bera 2017; Aminu et al. 2017; Thakur et al. 2018). The main motivation of this review paper is to present all aspects of CCUS projects worldwide along with the technologies, modeling issues and physicochemical processes occurred during the CO₂ sequestration within geological formation. This review will serve as a single handbook for understanding CCUS and to provide researchers the facts about CCUS in the oil industry. CO₂ flooding for enhanced oil recovery is one of the effective methods in additional oil recovery. The injected carbon dioxide can be stored in the formation of the reservoir. Therefore, it is important to know the rock capacity and power to store the carbon dioxide for a long time.

Storage of CO₂ has been employed in different parts of the world. The modes of storage can be broadly classified into natural and man-made modes of storage. Natural modes include terrestrial sequestration, while man-made storage includes storage in geologic formations. Several modes for utilizing and storing CO₂ have been explored as follows:

- A. Terrestrial sequestration is the capture of CO₂ from the atmosphere and storing it into soils and vegetation. Removal of CO₂ from the atmosphere through photosynthesis and prevention of the emission of CO₂ from terrestrial sources are the mechanisms for terrestrial storage. It has been postulated to provide an important mechanism for the storage of carbon dioxide (Litynski et al. 2006; Thomson et al. 2008).
- B. Ocean sequestration qualifies as the largest possible sink for carbon dioxide storage with an estimated potential storage of 40,000 gigatonnes (Gt) of CO₂ (Herzog et al. 1997, 2000; Lal 2008) and the possibility of storing over 90% of current CO₂ emissions. It involves the injection and deposition of CO₂ into the water body at depths below 1 km either from moving ships, fixed pipelines or offshore platforms. At this depth, water has a lower density than the injected CO₂ and the latter is expected to dissolve and disperse into the water body (Metz et al. 2005). However, there are huge concerns over the environmental impact of CO₂ on marine life from the acidity of seawater near the injection point (Seibel and Walsh 2001). The scalability of experiments involved in ocean sequestration is also very difficult, thus requiring expensive field experiments (Adams et al. 1998a, b; Auerbach et al. 1997; Herzog et al. 1997; Seibel and Walsh 2003).

The technology is currently at the research stage without any existing pilot tests.

- C. Geological sequestration is the most widely used sequestration technology. In this process, CO₂ is stored in geological underground structures such as saline aquifers, depleted oil and gas reservoirs and unmineable coal beds (IPCC 2007; Kaldi et al. 2009; Metz 2005; Pashin and Dodge 2010). A short description of all storage sites is given below:

1. *Saline aquifer formations*: Saline aquifer formations represent the best salted sink for storage of CO₂ among all geological options due to their enormous storage capacity (Grobe et al. 2009). Recently, estimates of the order of 103 Gt CO₂ have been made for the Alberta deep saline basin by accounting for the solubility trapping mechanism (Bachu and Adams 2003). Another example is the injection of the produced CO₂ into the Utsira aquifer in the North Sea (Korbøl and Kaddour 1995; Torp and Gale 2004). It is required that the aquifer be saline because this already makes it unsuitable for industrial, agricultural and human purposes (Aydin et al. 2010; Metz et al. 2005).

Other storage modes which have been employed for the storage of CO₂ include basalts (Gislason and Oelkers 2014) and mineral carbonation (Oelkers et al. 2008). Among all geologic sequestration mechanisms, deep saline aquifers represent the ones exhibiting highest sequestering capability, as against those provided by depleted oil and gas reservoirs and unmineable coal beds (IPCC 2007; Torp and Gale 2004; Kaldi et al. 2009; Parson and Keith 1998).

2. *Depleted oil and gas reservoirs*: Previously producing oil and gas fields which have been considered uneconomical for further production of hydrocarbons are suitable candidates for geological sequestration. Characteristics required for a storage site are present in such formations and have been employed for geologic sequestration. An important advantage is that they have been adequately characterized previously. Additionally, the safe and secure nature of these formations which have been able to store oil and gas over a long period of time makes them prime candidates. Existing numerical computer models of such formations which have been history-matched provide improved confidence in the formations. Infrastructures and wells used in the development of these fields are also available for CO₂ injection. Storage capacity available in depleted reservoirs is significantly lower due to the need to avoid exceeding pressures that can damage the cap

rock and the significant leakage threat posed by the abandoned wells. (A potential for leaks exists behind well casings.)

3. *Deep unmineable coal beds*: CO₂ has been employed for the recovery of methane from coal seams during the enhanced coal bed methane (ECBM) recovery process (Busch and Gensterblum 2011; Mukherjee and Misra 2018; Pan et al. 2018b). Produced methane from this source can be utilized as an energy source. Coal beds have very large fracture networks through which gas molecules can diffuse into the matrix and desorb tightly adsorbed methane. CO₂ has been proven to raise methane recovery to about 90% from 50% when conventional methods are applied. Injected CO₂ is stored in the formations after methane has been recovered. Storage in coal beds can take place at shallower depths than other formation types and as such relies on CO₂ adsorption on the coal surface. However, the technical feasibility of this storage process strongly depends on the coal's permeability as a result of its depth variation with the influence of effective stress on coal fractures (Metz et al. 2005).

The laboratory and field testing feasibility of commercial CO₂ injection into coal beds and seams has been reported in the San Juan Basin, which is the world's first ECBM project (Reeves 2001). Other enhanced coal bed methane recovery projects reported in the world for laboratory and field testing include the Sydney Basin in Australia (Saghafi et al. 2007) and deep coalbed methane in Alberta Canada (Gunter et al. 1997).

4. *CO₂ storage during enhanced oil recovery*: CO₂ is used for enhanced oil recovery (EOR) from mature fields. CO₂ for EOR operations has been employed in the miscible and immiscible states. When injected into oil, CO₂ has the capability to swell the oil, reduce its viscosity and reduce interfacial tension and in some cases become miscible with the oil allowing for single-phase flow. Of the two miscible states for EOR via CO₂ injection, miscibility of CO₂ in oil usually provides higher recoveries. The ability of CO₂ to become miscible in oil is determined by the minimum miscibility pressure (MMP). At and above this pressure, CO₂ is miscible in oil and below, it is immiscible. Though CO₂ injection in this process is done primarily for EOR, it comes with the added benefit of storage of CO₂ contributing to minimizing the global warming scourge. Over the last decade, CO₂ has been used in over 70 EOR operations around the world with over 40 reported in West Texas (Moritis 2000), Weyburn Field in Canada (Malik and Islam 2000), Shengli Oilfield in

China (Liang et al. 2009) and different parts of the world for simultaneous EOR and storage processes (Ghomian et al. 2008; Gozalpour et al. 2005; Liu et al. 2013; Moritis 2000; Narinesingh et al. 2014).

This integrated review will discuss storage of CO₂ in various geological formations with a focus on saline aquifers. Section 1 contains the introductory part of the review. Section 2 discusses the properties of the gas which favors storage as well as trapping mechanisms and the physical processes involved in the storage process. Section 3 gives a summary of the pilot- and commercial-scale projects which are in the planning phase, in operation or have been abandoned. In Sect. 4, we discuss the modeling strategies for CO₂ which have been applied in the literature. Section 5 covers the estimation methods for storage capacities. In Sect. 6, an overview of the measuring, monitoring and verification tools and challenges is provided. Section 7 reports the risks and challenges that may be present before commercial application of field-scale projects. Finally, conclusions and recommendations are provided in Sect. 8. It is expected that the entire manuscript will provide an overview of CCUS issues of past, present and future challenges for newcomers in this field.

2 CO₂ storage in saline aquifers

2.1 Conditions required for storage sites

The selection of a geological site for storage must be done to meet three main conditions: capacity, injectivity and containment. The requirement of the capacity of a storage site ensures that the selected site possesses adequate pore volumes to store large amounts of CO₂. Typical conditions would mean that the site should contain significant porosity and/or occupy a very large area. Injectivity of CO₂ is assured if the candidate formation possesses high permeability ensuring that lower wellhead pressures can be used to maintain desired injection rates. Competent cap rocks and sealing faults (if present) are necessary to ensure that the injected CO₂ does not escape to the surface or leak into groundwater due to the lower density of the CO₂ gas compared with resident brine. For successful storage of carbon dioxide, it is required that CO₂ be stored in a supercritical phase, the state in which CO₂ exists when it is compressed to higher pressures and temperatures (about 89 °F and 7.4 MPa). In this phase, CO₂ possesses properties of a liquid but flows as a gas. Essentially, CO₂ is required to be stored at this state due to its higher density, reducing the buoyancy differential between CO₂ and in situ fluids (Grobe et al. 2009; Kane and Klein 2002; Koide et al. 1992). Though the density of CO₂ is higher when injected underground, it remains significantly lower than the density of in situ brine which lies in

the region of 1200–2000 kg/m³ depending on the salinity of the brine. The implication of this density differential is the buoyant movement of CO₂ when injected underground and thus demanding the presence of low-permeability cap rocks which overlay the aquifer.

2.2 Trapping mechanisms

The storage capacity, containment and injectivity of CO₂ are dependent on the geological and petrophysical properties of the target formation. The injected supercritical CO₂ is securely trapped underground via two major trapping mechanisms (physical trapping and geochemical trapping) (Fig. 1). The effectiveness of the storage process is governed by a combination of both trapping mechanisms to ensure long-term storage (Coninck et al. 2005).

2.2.1 Physical trapping

Physical trapping is the process where CO₂ maintains its physical nature after injection into an aquifer. It can be subdivided into structural (hydrostratigraphic) and residual (capillary) trapping. Generally, the time period for physical trapping is believed to be less than a century (Juanes et al. 2006).

2.2.1.1 Structural trapping Structural trapping is usually the first form of trapping encountered during geological sequestration, and a similar mechanism has kept oil and gas securely stored underground for millennia. Geological structures such as anticlines covered with cap rocks (an ultra-low-permeability layer), stratigraphic traps with/without sealed faults are employed for the storage of CO₂ as a mobile phase or supercritical fluid. Maximization of this storage mechanism to ensure that CO₂ injected remains

underground in the long term is essential. During the injection process in the targeted formation, viscous forces are the dominant forces for the migration of CO₂. CO₂ is then stored in either the supercritical or the gas phase as a function of depth at the associated pressure and temperature. Once the injection stops, the supercritical CO₂ tends to migrate upward through the porous and permeable rock as a result of the buoyancy effect created by its density difference compared to other reservoir fluids and laterally via preferential pathways until a cap rock, fault or other sealed discontinuity is reached (Han 2008). This will prevent further migration of the CO₂ as shown in Fig. 2. In depleted oil and gas fields, the movement of the CO₂ can also be halted by abandoned wells sealed with solid cement plugs. The risk associated with such trapping is leakages behind casing or through the mentioned plugs. Thus, many studies have been conducted on the leakage of CO₂ through geological structures and existing wells (Ambrose et al. 2017; Eke et al. 2011; Lewicki et al. 2007; Scherer et al. 2015; Shipton et al. 2004, 2006; Temitope and Gupta 2019; Zakrisson et al. 2008).

2.2.1.2 Residual/capillary trapping As supercritical CO₂ percolates through storage formations, reservoir fluids are displaced. The movement of the CO₂ occurs in two directions: upward as a result of density differences and laterally due to viscous forces. Reservoir fluid fills the spots left. However, some of the CO₂ is left behind as disconnected/residual droplets in the pore spaces as displayed in Fig. 3.

Surface tension between CO₂ and brine acts to halt the CO₂ movement, thereby causing higher capillary entry pressure than the average rock pressure as suggested by Saadatpoor et al. (2010). At this point, CO₂ becomes immobilized in the pores at residual gas saturation. It is usually observed in rocks with small-scale capillary heterogeneities. Recent studies have revealed that capillary trapping appears to be

Fig. 1 Different CO₂ trapping mechanisms during the geological storage process

Fig. 2 Physical trapping of injected CO₂ as a result of the formation structure

Fig. 3 Residual trapping of injected CO₂ as a result of the formation pore structure. Arrows in the diagram indicate the movement of the CO₂ plume

a more efficient mechanism to trap CO₂ underground in the short term compared to other short-term trapping mechanisms (Burnside and Naylor 2014; Lamy et al. 2010). Its efficiency is due to exhibition of higher capillary forces to buoyant forces, causing CO₂ to appear as pore-scale bubbles rather than being retained by a somewhat compromised cap rock. Furthermore, it provides an advantage of no risk of major failure associated with structural traps over a short time scale (Jalil et al. 2012).

2.2.2 Geochemical trapping

Geochemical trapping occurs when CO₂ changes its physical and chemical nature by undergoing series of geochemical reactions with the formation brine and the rock and ceases to remain in the mobile or immobile phase. This interaction ensures the disappearance of CO₂ as a separate phase and further increases storage capacity, making this an appropriate feature of long-term storage.

2.2.2.1 Solubility trapping In a similar manner by which sugar dissolves in tea, CO₂ dissolves in other fluids in either the supercritical or gaseous phase. Solubility trapping occurs as a result of the dissolution of the CO₂ in the brine, leading to dense CO₂-saturated brine. At this point, it ceases to remain a separate phase which eliminates any buoyancy effect. Over time, CO₂-saturated brine becomes denser than the surrounding reservoir fluids and falls to the bottom of the formation over time, culminating in more secure CO₂ trapping (Fig. 4).

The dissolution of CO₂ in the aqueous phase leads to the formation of weak carbonic acid which decomposes over time into H⁺ and HCO₃⁻ ions (Eq. 1). It can also react with other cations in the formation brines to form insoluble ionic species as highlighted in Eqs. 1–4. CO₂ solubility in formation water decreases as temperature and salinity increase.

Fig. 4 Pictorial representation of solubility trapping via convective mixing, one of the mechanisms for the dissolution of CO₂ into aquifers

2.2.2.2 Mineral trapping Mineral trapping occurs as a result of the conversion of CO₂ into calcite due to reactions with solid minerals. This trapping is believed to be relatively slow since it occurs during/after solubility trapping and considered as the most permanent form of storage. CO₂ in the aqueous phase forms a weak acid which reacts with rock minerals to form bicarbonate ions with different cations depending on the mineralogy of the formation. An example of such reaction with potassium basic silicate (Eq. 5) and calcium (Eq. 6) is shown below:

Precipitation of carbon dioxide minerals is invariably induced by reactions with the rock formations depending on the mineralogy of these formations. Hence, geochemical

modeling of these reactions is critical to the success of CO₂ sequestration predictions. This trapping mechanism is dependent on the rock minerals, the pressure of the gas, temperature and porosity and has been found to produce significant changes in the rock permeability and porosity (Benson and Cole 2008; Kampman et al. 2014). Perkins et al. (2004) predicted from a simulation study that all the CO₂ injected into the Weyburn Oil Field will be converted to carbon dioxide minerals after 5000 years. They reported greater mineralization capacity for the cap rock and overlying formation rock, which is quite significant for leakage risk assessment. The capacity is estimated based on the amount of minerals available for carbon dioxide precipitation and the quantity of CO₂ used in the reaction processes. The most striking advantage of mineral trapping mechanism over the other mechanisms is that it prevents CO₂ from existing as a separate phase, thus ensuring that its upward movement is halted and also enhances the formation of stable precipitates (Xu et al. 2001, 2003, 2004).

There are multiple mechanisms responsible for the storage operating simultaneously and on different time scales which influence the storage capacity estimate. The interaction between various mechanisms is quite complex, evolves with time and depends highly on local conditions. An example of time scale evolution of different mechanisms at play in a deep saline formation is as shown in Fig. 5.

2.3 Physical processes during CO₂ storage

A number of physical processes are involved in the injection and post-injection phases of carbon dioxide. CO₂ trapping in aquifers is aided by three physical processes buoyancy (gravity), viscous forces and capillary forces (Kong et al. 2013). During the injection period of CO₂ into aquifers, viscous forces are the dominant forces for the vertical and lateral migration of CO₂ due to pressure gradients created by the injection processes. The injected fluid (CO₂) displaces the formation fluid (brine) in a drainage-like process.

In the post-injection phase, a combination of buoyancy and capillary forces are responsible for the trapping of CO₂. Buoyancy forces are usually greater than capillary forces and viscous forces after injection in deep saline aquifers, leading to upward migration of CO₂. Buoyancy results from density differences between the injected CO₂ and the aquifer brine causing the CO₂ to migrate upward after injection displacing water in an imbibition-like process.

The upward migration leads to gravity segregation, and further migration to the surface is prevented by the ultra-low permeable seal at the formation top. Once reaching the top of the formation, the vertical migration is halted, while the lateral migration continues until a sealing fault or formation boundary is reached. Thorough geomechanical analysis has to be made to ensure that leakage of CO₂ does not occur when the buoyant CO₂ reaches the seal. One means of leakage is when the pressure of the CO₂ is high enough to overcome the entry pressure of the seal (Hesse et al. 2006). Others could be due to the cap rock fractures, thermal stresses in the caprock as a result of temperature variation between the injected CO₂ and aquifer and the presence of open faults, fractures and abandoned wells (Chiquet et al. 2007; Goodarzi et al. 2013). Geomechanical considerations involving cap rock integrity are one of the factors that affect the sequestering capacity of the overlying seal.

Fig. 5 Time frame for trapping mechanisms in deep saline formations during and after injection (IPCC 2007; Metz et al. 2005)

The drainage and imbibition-like processes during the injection and post-injection stages of CO₂ storage lead to hysteresis, a process where the capillary pressure and relative permeability curves change pathways. This phenomenon has been described as being very critical to the successful modeling of CO₂ trapping processes (Ghomian et al. 2008; Juanes et al. 2006; Spiteri et al. 2005). This is because as the CO₂ migrates upward after the injection phase, the remaining CO₂ plume gets disconnected due to water displacing CO₂ at the trailing edge and becomes a series of blobs. CO₂ is trapped in these blobs, and the mechanism is termed residual or capillary trapping mechanism, which over time results in the dissolution of the CO₂ in the formation brine.

Heterogeneity and wettability of the aquifer are also key considerations in this mechanism. Heterogeneity has been subdivided into the small and large scales (Gershenson et al. 2014; Lasseter et al. 1986; Li and Benson 2014). Viscous and capillary forces dominate the flow, while gravity forces are generally regarded as unimportant when small-scale heterogeneities are considered. When large-scale heterogeneity is considered, the formation possesses variable pore throat sizes, which are likened to different capillary tubes sizes. As a result, a variable amount of entry capillary pressure is required to displace the formation fluid. This leads to more CO₂ being trapped as the entry pressure is overcome. Wettability and interfacial tension changes have been proven to alter the capillary pressures in a porous medium (Bennion and Bachu, 2006; Chiquet et al. 2007; Jung and Wan 2012; Park et al. 2015; Yang et al. 2005). The basic definition of capillary pressure (Eqs. 7 and 8) and Young–Laplace equation (9) can be shown as follows in terms of mathematical forms:

$$P_c = P_{nw} - P_w \quad (7)$$

$$P_c = \frac{4\sigma\gamma_w}{d\gamma_w} = \frac{4\sigma}{d} \quad (8)$$

$$P_c = P_{CO_2} - P_w = \frac{2\sigma_{w,CO_2} \cos \theta}{R} \quad (9)$$

where d is diameter; R is the pore throat radius; P_c is defined as the capillary pressure; P_{nw} and P_w are the pressures of the non-wetting and wetting phases, respectively; P_{CO_2} is the pressure of CO₂; γ_w is the water surface tension; σ is the interfacial tension; σ_{w,CO_2} is the interfacial tension between water and CO₂, and θ is the contact angle between the wetting medium and the rock surface.

In a typical CO₂–water system, CO₂ is usually described as the non-wetting phase, while water is the wetting phase; however, it has been proven that during the CO₂ upward migration, this wetting state can be changed (Broseta et al. 2012; Chiquet et al. 2007; Marckmann et al. 2003; Siemons et al. 2006; Yang et al. 2005). Equation 9 shows that the capillary pressure is dependent on the pore throat radius, R , the

interfacial tensions (σ) and the contact angles (θ) between the wetting medium and the rock surface. Therefore, the interfacial tensions and wettability have a significant impact on the sequestration capabilities of aquifer rocks.

During the residence time of trapped CO_2 in the blobs and ganglia, CO_2 dissolves into brine and this dissolution has been proven to occur by three principal mechanisms. They are (a) diffusion of CO_2 within the aqueous phase, (b) reactions with the host minerals (classified as mineral trapping) and (c) convective mixing driven by slight density differences between the water saturated with CO_2 and the unsaturated water (Ennis-King and Paterson 2003; Hassanzadeh et al. 2007). Ennis-King and Paterson (2003) stated that the dominant mechanism for long-term dissolution of CO_2 in the formation brine is convective mixing rather than pure diffusion as it is in orders of magnitude faster than diffusion and chemical reaction with the host mineral.

The disproportionate dissolution of CO_2 in brine leads to gravitational instabilities which could further aid in solubility trapping. Several researchers have worked on trying to determine the onset time of convective mixing and the influencing factors (Bestehorn and Firoozabadi 2012; Ennis-King and Paterson 2003; Hassanzadeh et al. 2007; Rasmusson et al. 2015; Riaz et al. 2006; Xu et al. 2006b). Ennis-King and Paterson (2003) used a linear stability analysis technique to provide an estimate of the time required for convective instability to begin. They predicted the time to be typically up to tens of years, and this method has been used by several other researchers (Hassanzadeh et al. 2006; Hesse et al. 2006; Riaz et al. 2006). Riaz et al. (2006) determined the critical time and wavelength or the onset of convective mixing using the method of linear stability. It was determined that the critical time varies between 2000 years and 10 days and the critical wavelength varies between 200 and 0.3 m for a permeability variation of 1–3000 mD. Rasmusson et al. (2015) applied the Rayleigh number (Ra) in determining the onset of gravity-driven instabilities. They predicted that a prerequisite for Ra , which must be greater than a critical Ra , is required for the onset of density-driven instabilities. Finally, as CO_2 remains dissolved in the brine, it forms weak acids which react with the host minerals to form precipitates (Gunter et al. 2000; Kumar et al. 2005; Xu et al. 2001).

3 Field-scale projects on CO_2 storage

CO_2 sequestration projects are currently ongoing or in the planning stage across the world. Notable among these are the Sleipner project in Norway, the Weyburn Project in Canada and the In Salah Project in Algeria. Tables 1, 2, 3 and 4 present the lists of most of the projects. These field-scale injections of CO_2 into candidate formations have provided more insight into the physics of the processes involved in geologic

storage and on the effective monitoring tools which could be used for large-scale injections. These projects can be broadly classified according to the storage location of the different projects (saline, EOR, depleted gas reservoirs, ECBM), based on the mode of capture of the carbon dioxide (power plants CCS projects and non-power plant CCS projects) and based on the current status of the projects (planned, ongoing and completed CCS projects).

The Sleipner project in Norway is the first case of large-scale commercial CO_2 storage in the world (Torp and Gale 2004). The project began in 1996 and injected about a million tons of CO_2 into the sands of the Utsira Formation which is about 900 m below the bottom of the North Sea. The major incentive behind the commencement of the Sleipner project was the need for minimization of taxes placed on the direct emission of CO_2 into the atmosphere (Christiansen 2001; Global CCS 2017; Kongsjorden et al. 1998). The companies involved were faced with the options of paying heavy taxes for atmospheric emissions or injecting the CO_2 into saline aquifers. Injection of CO_2 into saline aquifers provided a beneficial means for cost reduction by the parties involved. Policies such as carbon dioxide pricing which would coerce companies with high CO_2 emissions into considering the need for CO_2 storage are major ways to ensure emissions into the atmosphere are significantly reduced. Another incentive for CO_2 storage is the low cost of capturing; this has especially been noticed in the current field-scale projects where CO_2 injected was obtained from the separation of CO_2 from produced gases, thus reducing the need for capturing from coal plants which have not undergone separation and would cost more to capture from such plants. The high cost of capturing CO_2 from combustion processes has triggered the idea of carbon dioxide capture utilization and storage (CCUS) where the CO_2 could also be used for enhanced oil recovery and revenue derived from the produced oil could be used to offset the cost of capturing and injecting into formations. The success of the Sleipner project elicited the increased field deployments on CO_2 storage.

Several pilot-scale projects have also been implemented across the world. These projects typically inject small amounts of CO_2 into identified formations for a small period of time. These projects provide answers to questions of interest to the investigators. The first pilot-scale project in the USA was the Frio Project where about 1600 tons of CO_2 was injected at a depth of about 1500 m below the surface for a period of 10 days (Hovorka et al. 2006). The Frio Project provided information about the movement of CO_2 plume and was able to validate numerical models developed to analyze subsurface CO_2 migration. Other notable pilot-scale projects are the Cranfield Project (Hosseini et al. 2013; Hovorka et al. 2013), Decatur Project (Finley 2014; Senel et al. 2014), Ketzin site in Germany (Kempka and Kuhn 2013; Martens et al.

Table 1 Storage projects across the world: saline aquifer projects

Project name	Country	Company operators	Total planned storage	Capture mode	CO ₂ fate	Status of project	References
Captain	UK	Captain Clean Energy Limited (CCEL) owned by Summit Power and CO ₂ Deep Store	3.8 Mt/year	Power	Pipeline to offshore deep saline formations	Planning	James (2013)
Don Valley	UK	2Co Energy Ltd, Samsung Construction & Trading, BOC	4.9 Mt/year	Power	Pipeline for sequestration in offshore deep saline formations	Planning	
Killing Holme	UK	C-GEN NV and National Grid	2.5 Mt/year	Power	Offshore pipeline for storage in deep saline aquifers	Planning	
Korea CCS	Korea	Korea Carbon Capture and Sequestration R&D Center (KCRC)	1 Mt/year	Power	Ulleung deep saline formation or the Gorae gas reservoir	Planning	Lee et al. 2012
Lianyungang	China	Summit Power, National Grid, CO ₂ Deep Store	1 Mt/year	Power	Binhai for saline aquifers or North Jiangsu oilfields for EOR	Planning	Pang et al. (2012) and Qiao et al. (2012)
Longyearbyen	Norway	UNIS CO ₂ Lab-AS	Not available	Power	Onshore storage in a saline aquifer	Planning	Braathen et al. (2012)
White Rose	UK	Capture Power Limited, the consortium of Alstom UK Limited, Drax Power Limited and National Grid plc	2 Mt/year	Power	Pipeline to offshore storage in a saline aquifer	Planning	Verdon (2014)
Cranfield	USA	SECARB	1–1.5 Mt/year	Non-power	Saline reservoir, Tuscaloosa Sandstone Formation, down dip of the mature Cranfield Oil Field	In operation since 2009	Lu et al. (2012)
Citronelle	USA	SECARB, Denbury, Southern Energy	0.25 Mt/year	Non-power	The southern flank of the Citronelle dome	In operation since 2011	Haghighat et al. (2013)
Decatur	USA	Archer Daniels Midland, MGSC (Led by Illinois State Geological Survey), Schlumberger Carbon Services and Richland Community College	1 Mt/year	Non-power	Sequestration in Mount Simon sandstone	In operation since 2011	Zhou et al. (2010)
Kevin Dome	USA	Big Sky Partnership, Schlumberger Carbon Services, Vecta Oil & Gas Ltd, Lawrence Berkeley National Lab, Los Alamos National Lab	0.125 Mt/year	Non-power	The Duperow Formation (3900 ft)	Planning	Riding and Rochelle (2005)

Table 1 (continued)

Project name	Country	Company operators	Total planned storage	Capture mode	CO ₂ fate	Status of project	References
Wasatch Plateau	USA	South West Partnership (SWP), New Mexico Institute of Mining and Technology, University of Utah, Schlumberger and Los Alamos National Laboratory	1 Mt/year	Non-power	The Jurassic Entrada Formation and Navajo sandstone	Planning	Parry et al. (2007)
Fort Nelson	Canada	Plains CO ₂ Reduction Partnership (PCOR), Spectra Energy, British Columbia Ministry of Energy, Mines and Petroleum Resources	2.2 Mt/year	Non-power	Middle Devonian carbonate rock	Planning	
Quest	Canada	Athabasca Oil Sands Project; Shell Canada, Chevron Canada, and Marathon Oil Sands	1.1 Mt/year	Non-power	Injection into the Cambrian Basal Sands	Launched in November 2015	Brydie et al. (2014)
Sleipner	Norway	StatOil	0.9 Mt/year	Non-power	Utsira Formation	In operation since 1996	Chadwick et al. (2004)
Ketzin	Germany	GFZ German Research Centre for Geosciences and Ketzin partners	0.06 Mt/year	Non-power	Stuttgart sandstone reservoir	In operation since 2008	Schilling et al. (2009)
Snohvit	Norway	Statoil ASA, Petoro AS (Norwegian state direct interest), Total E&P Norge AS, GDF Suez E&P Norge AS, Norsk Hydro, Hess Norge	0.7 Mt/year	Non-power	Saline Tubaan sandstone formation reservoirs	In operation since 2007	Hansen et al. (2013)
ULCOS Florange	France	ArcelorMittal and ULCOS (Ultra-Low-CO ₂ -Steel)	0.7–1.2 Mt/year	Non-power	Onshore deep saline formations	On hold	Global CCS (2017)
Ordos	China	Shenhua Group	1 Mt/year	Non-power	EOR/saline aquifer	In operation since 2010	Li et al. (2016)
Gorgon	Australia	Gorgon Joint Venture (Chevron Australia, ExxonMobil, Shell, Tokyo Gas, Osaka Gas and Chubu Electric)	3.4–4.0 Mt/year	Non-power	Dupuy Formation 2.5 km below Barrow Island	Under construction	Flett et al. (2009)
Yulin	China	Shenhua Group, Dow Chemicals	2–3 Mt/year	Non-power	Onshore deep saline aquifers	Planning	Li-ping et al. (2015)
Minami-Nagaka	Japan	EnCana, IEA	0.015 Mt/year	Non-power	Haizume Formation	In operation since 2002	Zwingmann et al. (2005)
Frio	USA	Bureau of Economic Geology of the University of Texas	177 t/day	Non-power	Frio Formation	In operation since 2004	Hovorka et al. (2006)
Teapot Dome	USA	Rocky Mountain Oilfield Testing Center (RMOTC)	170 t/day	Non-power	Tensleep and Red Peak Formation	In operation since 2006	Friedmann and Stamp (2006)

Table 2 Storage projects across the world: CO₂ EOR/storage projects

Project name	Country	Company operators	Total planned storage	Capture mode	CO ₂ fate	Status of project	References
Santos Basin	Brazil	Petrobras, BG E&P Brasil Ltda, Petrogal Brasil	1 Mt/year	Non-power	Lula and Sapinhoá oil fields	In operation since 2013	Saini (2017)
Boundary Dam	Canada	SaskPower	1 Mt/year	Power	EOR in Weyburn field, excess to be used at the Aqistore project	October 2014–date	Stéphenne (2014)
Bow City	Canada	Bow City Power, Cansolv (Subsidiary of Shell), Lusscar, Fluor	1 Mt/year	Power	Pipeline for EOR	Planning	Global CCS (2017)
Pembina	Canada	Penn West	50 t/day	Non-power	Cardium Formation	In operation since 2005	
Weyburn-Midale	Canada	Genovus Energy, Apache Canada, PTRC (Petroleum Technology Research Center)	1 Mt/year	Non-power	EOR in 2 carbonate fields: Weyburn field (6500 t/day) and Midale field (1200 t/day)	In operation since 2000	White (2009)
Zama	Canada	PCOR, Apache Canada Ltd	0.067 Mt/year	Non-power	EOR in Zama Keg River oil field	In operation since 2006	Smith et al. (2009)
Alberta Carbon Trunk Line	Canada	Enhance Energy Inc.	14.7 Mt/year	Non-power	Injection into the Clive oil reservoir	Planning	Cole and Itani (2013)
Daqing	China	Alstom and China Datang Corporation	1 Mt/year	Power	EOR in nearby fields	Planning	Xiuzhang (2014)
Dongguan	China	Dongguan Taiyangzhou Power Corporation, Xinxing Group, Nanjing Harbin Turbine Co, KBR, Southern Company,	1 Mt/year	Power	EOR in Shandong Province	Planning	Liu et al. (2016)
GreenGen Shengli	China	GreenGen	2 Mt/year	Power	Onshore EOR	Planning	Haszeldine (2009)
	China	Sinopec	1 Mt/year	Power	EOR in Shangdong Province	Planning	Liang et al. (2009)
Uthmaniyah	Saudi Arabia	Saudi Aramco	0.8 Mt/year.	Power	Pipeline for onshore EOR	In operation	Liu et al. (2012)
Uthmaniyah	Saudi Arabia	Saudi Aramco	0.8 Mt/year.	Non-power	Pipeline for onshore EOR	In operation since 2015	Liu et al. (2012)
ESI CCS Project	United Arab Emirates (UAE)	Abu Dhabi Future Energy Company (Masdar) and Abu Dhabi National Oil Company (ADNOC)	0.8 Mt/year	Non-power	EOR, Rumaitha Zone-B, and Bab Zone-B	Started in 2017	Temitope et al. (2016)

Table 2 (continued)

Project name	Country	Company operators	Total planned storage	Capture mode	CO ₂ fate	Status of project	References
Taweelah	United Arab Emirates (UAE)	Abu Dhabi Future Energy Company (Masdar) and Taweelah Asia Power Company (TAPCO) and Emirates Aluminium (EMAL)	2 Mt/year	Power	Injection for EOR	Planning	
Bell Creek	USA	PCOR, Denbury	1 Mt/year	Non-power	EOR at Bell Creek oil field, Montana	Planning	Gorecki et al. (2012)
Hydrogen Energy California Project (HECA)	USA	SCS Energy	3 Mt of CO ₂ captured annually	Power	Pipeline to onshore EOR in Occidental's Elk Hills oil field	Planning	Global CCS (2017)
Kemper County	USA	Mississippi Power, Southern Energy, KBR	3.5 Mt of CO ₂ annually	Power	Pipeline for onshore EOR	In construction	Global CCS (2017)
Port Arthur	USA	Air Products and Chemicals, Denbury Onshore LLC, University of Texas Bureau of Economic Geology and Valero Energy Corporation	1 Mt/year	Non-power	EOR in West Hasting's and Oyster Bayou oil fields, Texas	In operation since 2013	Global CCS (2017)
Texas Clean Energy Project (TCEP)	USA	Summit Power Group Inc, Siemens, Fluor, Linde, R. W. Beck, Blue Source and Texas Bureau of Economic Geology	2–3 Mt/year captured	Power	EOR in the Permian Basin	Planning	Global CCS (2017)
WA arish Petra Nova	USA	Petra Nova Holdings: a 50/50 partnership between NRG Energy and JX Nippon Oil & Gas Exploration Corp.	1.4 Mt of CO ₂ captured annually	Power	Pipeline for onshore EOR in the West Ranch Oil Field in Jackson County, Texas	In construction	Global CCS (2017)

Table 3 Storage projects across the world: depleted reservoir projects

Project name	Country	Company operators	Total planned storage	Capture mode	CO ₂ fate	Status of project	References
In Salah	Algeria	BP, Sontrach, and Statoil	1.2 Mt/year	Non-power	The Krechba Formation	2004–2011 suspended	Ringrose et al. (2009)
Otway	Australia	CO ₂ CRC (Cooperative Research Center for Greenhouse Gas Technologies)	0.065 Mt/year	Non-power	The Waarre Formation	In operation since 2008	Underschultz et al. (2011)
*ROAD (Rotterdam Opslag en Afvang Demonstrate project)	Netherlands	E.ON Benelux, Electrabel, GDF Suez and Alstom	1.1 Mt/year	Power	Pipeline for storage in depleted reservoirs	Planning	Global CCS (2017)
K12B	Netherlands	Gaz de France	0.365 Mt/year	Non-power	Rotleigendes	In operation since 2004	van der Meer et al. (2006)
Peterhead	UK	Scottish and Southern Energy (SSE) and Shell	1 Mt/year	Power	Pipeline to off-shore depleted Goldeneye gas reservoir	Planning	
Northern Reef Trend	USA	Midwest Regional Carbon Sequestration Partnership (MRCSP). DTE Energy, Core Energy and Batelle	0.365 Mt/year	Non-power	Depleted oil field in the Northern Reef Trend (carbonate reservoir)	In operation since 2013	

Table 4 Storage projects across the world: CO₂ ECBM projects

Project name	Country	Company operators	Total planned storage	Capture mode	CO ₂ fate	Status of project	References
Fenn Big Valley	Canada	Alberta Research Council	50 t/day	Non-power	Mannville group	In operation since 1998	Gunter et al. (2005)
CSEMP	Canada	Suncor Energy	50 t/day	Non-power	Ardley Formation	In operation since 2005	Shi and Durucan (2005)
Qinshui Basin	China	Alberta Research Council	30 t/day	Non-power	Shanxi Formation	In operation since 2003	Wong et al. (2007)
Yubari	Japan	Japanese Ministry of Economy, Trade and Industry	0.004 Mt/year	Non-power	Yubari Formation	In operation since 2004	Shi et al. (2008)
Recopol	Poland	TNO-NITG (Netherlands)	1 t/day	Non-power	Silesian Basin	In operation since 2003	van Bergen et al. (2003)

2013) and the Otway Project in Australia (Etheridge et al. 2011; Underschultz et al. 2011).

Even though carbon dioxide capture is outside the scope of this review, it is obvious that the deployment of many carbon dioxide storage projects would be dependent on the cost and success of carbon capture processes. Celia et al.

(2015) noted that the embryonic stage of technology on CO₂ capture would mean high costs of capture from power plants for early movers. Early movers need to be encouraged by governments through subsidies. Successful cases of subsidies by the government can be seen in the Boundary Dam Project by SaskPower and the Quest Project by Shell both in Canada.

4 Modeling strategies employed for CO₂ storage

Numerical modeling is typically carried out before the commencement of injection projects. They are used for predictions and optimizations. The flow path of the injected CO₂ needs to be predicted prior to injection. Furthermore, the optimization of well location needs to be properly assessed during the planning phase. Several authors have attempted to model the plume movement of injected CO₂ in saline formations. Modeling of CO₂ storage in saline aquifers is usually performed using either analytical or numerical models. The choice of modeling technique employed is dependent on the aims of the researchers, the nature of the problem and the data available. Analytical models have the advantage of providing a quick insight into the suitability of a formation for storage. Zhou et al. (2008) employed an analytical model to determine the storage capacity in saline aquifers and expected pressure buildup during storage operations. Mathias et al. (2009a) developed approximate solutions for pressure buildup in aquifers assuming vertical pressure equilibrium and accounting for the Forchheimer flow of CO₂ and brine. Solutions from the study were subsequently applied in the screening of potential CO₂ storage sites (Mathias et al. 2009b). Analytical models have been used for plume migration studies. Nordbotten et al. (2005a) also developed approximate solutions for the prediction of the plume migration path in a CO₂ storage site. The model was validated with the commercial simulator ECLIPSE with very good accuracy. The underlying assumptions of analytical models are, however, too simplistic and cannot account for reservoir property and model geometry heterogeneities. More so, the complex geochemical reactions expected in CO₂ storage cannot be reliably captured by analytical models. Streamline simulations, vertical equilibrium models and regular, conventional grid-based numerical models are forms of numerical modeling techniques which have been applied for the modeling of CO₂ storage (Cavanagh and Haszeldine 2014; Gasda 2010; Jiang 2011; Li et al. 2012; Obi and Blunt 2006; Pruess 2008; Saadawi et al. 2011; Wheeler et al. 2008). Streamline simulations work by splitting the simulation domain into small grid sizes and determining the pressure in each grid block using a finite difference technique. The resulting pressure field is applied in tracing the streamlines which determine the expected flow fields. As opposed to other forms of numerical modeling, streamline simulations are faster and computationally efficient as flow equations are reduced to one-dimensional equations along the streamlines. Obi and Blunt (2006) and Qi et al. (2009) have applied streamline simulations in the modeling of CO₂ storage. In their model, Obi and Blunt (2006) coupled transport and flow equations and

solved the equations using the streamlined methodology. Though their model was able to solve the pressure-driven flow in complex flow fields, it was limited by the assumptions of a simple geochemical model and incompressible flow. Qi et al. (2009) used the model developed by Obi and Blunt (2006) to postulate a design strategy for injection of CO₂ which would render a large percentage of the CO₂ immobile on the pore scale. As their work was focused on maximizing the gas trapped via the residual gas trapping mechanism, they modified the existing model by assigning relative permeabilities on a block by block basis. All in all, these papers have been able to demonstrate the feasibility of modeling storage of CO₂ in saline aquifers by employing the streamlined methodology. Streamline simulations are, however, best suited to processes where limited pressure changes are expected to occur. Given that only injection is usually modeled in CO₂ storage in saline aquifers thus leading to significant pressure changes, streamline simulations have found limited applications in CO₂ storage modeling. Vertical equilibrium models work by discretizing the simulation domain only in the horizontal direction leaving one layer in the vertical direction. Two forms of the vertical equilibrium model exist: vertically integrated numerical models which include capillary forces and analytical models including a sharp interface where the capillary pressure zone is thin with homogeneous formation parameters. The technique capitalizes on the strong density differential between supercritical CO₂ and the in situ brine which leads to a marked upward increase in the CO₂. Particularly, on short time scales, the density differential could lead to a strong buoyancy segregation of the two fluids. The idea behind this technique is to derive a better understanding of the lateral plume spread and the segregation between the different fluid phases. Its limitation is in its inability to model heterogeneity in the vertical direction. The technique has, however, been applied (Gasda et al. 2009, 2011) in modeling of CO₂ storage. Another modeling technique which has been applied to the simulation of CO₂ in aquifers is the inversion percolation technique. In this approach, viscous forces are ignored; therefore, the only forces that dominate the flow are the capillary and gravity forces. Consequently, this technique is most suitable in systems with low fluxes. Inversion percolation is employed when the capillary number (ratio of viscous forces to capillary force) is less than 0.0001. High-resolution inversion percolation models are noted for their simplicity and the speed of their numerical solutions. Limitations of this approach are, however, found when flow rates are high and capillary heterogeneity is not pronounced. Notably, this approach has been employed in the modeling of the In Salah Field Project and the Sleipner storage with a high degree of accuracy (Cavanagh and Ringrose 2011; Cavanagh and Haszeldine 2014). Conventional 3D simulations making use of highly

developed numerical discretization techniques have been used to overcome the shortcomings of the other techniques by incorporating all relevant physics such as expected pressure increases and heterogeneities in both the vertical and horizontal directions. Typically, they employ finite difference/element/volume techniques to solve transport and flow equations. In addition, they are able to couple other related physical phenomena such as geochemistry, geomechanics and thermal changes. As a result of the detailed modeling of inherent physics, the regular 3D grid-based numerical modeling techniques are more computationally costly than the other techniques. Most commercial simulators which have been employed for modeling of CO₂ storage issues have full modeling capabilities (Class et al. 2009; Nghiem et al. 2009).

Modeling of CO₂ storage is a multi-component, multi-phase process with the two fluid phases as the brine and a CO₂-rich phase and the components like CO₂, H₂O, dissolved salts in the brine and rock minerals. It should be noted that the number of components modeled can be different depending on the problem to which it is applied. The fundamental equations used in CO₂ storage modeling are basically the same as equations that describe the flow of oil, gas and water in porous media. These equations are the conservation of mass, momentum and energy. Constitutive relations are used to formulate solutions for these equations. Other physics which could be coupled with the basic equations are equations that predict geomechanical effects and geochemical reactions among others (Temitope and Gupta 2019).

The conservation of mass equation for components can be written as the summation of the advection, diffusive terms and the time rate of change of mass which equal a source or sink term.

$$\frac{\partial}{\partial t} \left[\phi \sum_{\alpha} (\rho_{\alpha} s_{\alpha} X_i^{\alpha}) \right] + \sum_{\alpha} \nabla \cdot (\rho_{\alpha} q_{\alpha} X_i^{\alpha}) - \sum_{\alpha} \nabla \cdot (\phi \tau_{\alpha} \rho_{\alpha} D_{\alpha} \nabla X_i^{\alpha}) = S_i \quad (10)$$

Darcy's law for a single-phase flow can be written as

$$\mathbf{v}_{\alpha} = \frac{\mathbf{q}_{\alpha}}{\phi} = -\frac{k k_{\alpha}}{\mu_{\alpha} \phi} (\nabla p_{\alpha} + \rho_{\alpha} g \nabla z) \quad (11)$$

where t represents the time, ϕ represents the porosity, ρ is the density, $\mathbf{q}$ is the Darcy flux, $\mathbf{k}$ is the permeability tensor, k is the relative permeability, D is the diffusivity, X is the mole fraction, s_{α} is the saturation term, τ is the tortuosity, S_i denotes the source/sink term, $\mathbf{v}$ is the velocity vector, μ is the dynamic viscosity, p is the pressure, g is the acceleration due to gravity, and z represents the depth. Subscripts α and i are the phase and index, respectively.

The permeability tensor can be written fully as

$$\mathbf{k} = \begin{pmatrix} k_{xx} & k_{xy} & k_{xz} \\ k_{yx} & k_{yy} & k_{yz} \\ k_{zx} & k_{zy} & k_{zz} \end{pmatrix} \quad (12)$$

Conservation of energy can also be solved for by equating the summation of the time rate of change of the energy term, advection and conduction terms to the source term as shown below:

$$\frac{\partial}{\partial t} \left[\phi \sum_{\alpha} (\rho_{\alpha} s_{\alpha} U^{\alpha}) + (1 - \phi) \rho_s C_s T \right] + \sum_{\alpha} \nabla \cdot (\rho_{\alpha} \mathbf{q}_{\alpha} H^{\alpha}) - \nabla \cdot (\lambda \nabla T) = S_H \quad (13)$$

where U represents the specific internal energy, H is the specific enthalpy, T is the temperature, C is the specific heat capacity, and all other symbols have definitions as described earlier. Subscript s represents the solid phase.

These equations (Eqs. 10, 11 and 13) represent the fundamental equations for the modeling of storage of CO₂ in porous media (DePaolo et al. 2019; Nghiem et al. 2004; Pan et al. 2018a). These equations could be coupled with geochemical reactions, geomechanical modules and other relevant physical phenomena. The solution of these equations requires either a sequential, simultaneous or fully coupled approach.

Over the years, researchers have made numerous attempts to describe underground CO₂ migration and trapping mechanisms using numerical analysis. Weir et al. (1996) developed a two-dimensional model to evaluate CO₂ quantities that migrated beyond a cap rock after CO₂ injection for 10 years into a 3-km-deep aquifer at a mass transfer rate of 100 kg/s. They varied the confining layer's permeability in order to determine the amount of CO₂ that could pass through the layer. They concluded that a low-permeability seal should overlay any target formation as this would mean that higher capillary pressures would be required for the CO₂ to penetrate the seal. Another CO₂ storage study conducted by researchers at the Alberta Research Council (Gunter et al. 1993; Law and Bachu 1996) for the Upper Manville Group where the modeled formation was a Cretaceous glauconitic sandstone aquifer 1.46 km in depth. The formation top of the aquifer was overlain by several regional-scale aquitards (low-permeability shale layers) that inhibited upward migration of the injected CO₂. The unevenness of the formation permeability was modeled based on drill-stem tests performed during exploration. The study showed no CO₂ leakage during the modeled time scale.

Nghiem et al. (2004) developed a fully coupled EOS compositional simulator for modeling CO₂ storage in aquifers. The module consisted of geochemical reactions such as

gas dissolution in the aqueous phase, chemical equilibrium reactions, mineral dissolution, and precipitation. The highly coupled sets of nonlinear equations were solved simultaneously using the Newton approach. The geochemistry module of the simulator was validated with the Geochemist Workbench® (GWB) developed at the University of Illinois with high accuracies. The resulting codes were applied on two numerical grids: a 2D reservoir used to analyze the impact of mineral trapping and a 3D grid used to study the evolution of the CO₂ plume. Rutqvist et al. (2010) coupled a geomechanical simulator (FLAC3D) and a multi-phase flow simulator (TOUGH2) to study the ground deformations which would occur at the In Salah storage site in Algeria. Surface deformation results derived from monitoring using interferometry synthetic aperture radar (InSAR) were employed in this study to validate the numerical models and displayed good agreements with obtained results. A summary of the workflow for most of the reservoir simulators for CO₂ storage issue is provided in Fig. 6.

Many researchers exploring CO₂ storage issues have focused more on simulations for large-scale analysis with most experiments carried out aimed at better understanding the physics of the processes that occur during the injection and post-injection phases. Thus, due to the complex nature of storage of CO₂ and the time period taken for carbon dioxide to be stored underground, the only effective way to understand the storage capacity of an aquifer before injection commences is through modeling and simulations. This explains why there exists a myriad of simulators which have the capacity to model CO₂ storage in aquifers; among them includes CMG (Computer Modelling Group) GEM-GHG Module (Nghiem et al. 2004, 2009), ECLIPSE 100 and 300 (Schlumberger), CO2STORE Module (Pickup et al. 2011, 2012; Sifuentes et al. 2009), Automatic Differentiation

General Purpose Reservoir Simulator (AD_GPRS) by Stanford University (Benson et al. 2013; Fan 2006; Iskhakov 2013), MUFTE-UG (Multiphase Flow Transport and Energy Model on Unstructured Grids) developed by a joint effort of the University of Stuttgart and the University of Heidelberg (Ebigbo et al. 2006), IPARS-CO2 (Integrated Parallel Accurate Reservoir Simulator) developed by the University of Texas at Austin (Kong 2014; Wheeler et al. 2008); also existing are several simulators by the National Laboratories in the USA including TOUGH and TOUGH2 usually used in collaboration with ECON2 (Hovorka et al. 2006; Pruess et al. 2002), STOMP Subsurface Transport over Multiphase Processes (Bonneville et al. 2013) [see Table 5 for full list]. The difference between most of these simulators lies in the numerical methods and discretization technique used, the inclusion or non-inclusion of certain physics and the coupling methods of the physics.

Numerical simulations have been applied to assess the feasibility of commercial storage in aquifers. In a recent study, Temitope et al. (2016) employed the Computer Modelling Group (CMG) simulator with an advanced geochemical modeling module to evaluate the possibility of commercial injection in the Shuaiba aquifer of the Falaha syncline in the United Arab Emirates (UAE). Simulation results were able to provide the possible migration path of injected CO₂ into the aquifer. In modeling the impact of thermal factors on the injection of CO₂ into the FutureGen 2.0 Site in Illinois in the USA, Nguyen et al. (2016) made use of the simulators STOMP-CO₂ coupled with the ABAQUS finite element simulator. Results suggested that in the range of temperatures in which injection would take place, fracturing would be unlikely to happen due to thermal factors. Basirat et al. (2016) employed the TOUGH2 simulation codes to model the injection of CO₂ into an experimental site in

Fig. 6 Workflow for CO₂ storage modeling

Table 5 List of simulators and codes for CO₂ storage

Simulators	Full names	Description	Developers	Relevant literature
ABAQUS-FEA	ABAQUS-FEA	Geomechanical, single- and two-phase flow	SIMULIA	Gemmer et al. (2011) and Le Gallo et al. (2006)
AD_GPRS	Automatic Differentiation—General Purpose Reservoir Simulator	Generalized multiple phase compositional/thermal model for unstructured grids	Stanford University	Huo and Gong (2010) and Li et al. (2012)
CO ₂ —PENS	CO ₂ —Predicting Engineered Natural Systems	System-level modeling of the long-term fate of CO ₂ in sequestration sites	Los Alamos National Laboratory (LANL)	Pawar et al. (2006) and Stauffer et al. (2006)
CO ₂ Toolkit Permedia™	Permedia	High-resolution petroleum migration simulator for multi-phase flow behavior in porous, faulted and fractured media	Landmark	Cavanagh and Ringrose (2010, 2011)
COMET3	COMET#	Black oil production, hydrocarbon dioxide recovery from desorption-controlled reservoirs	Advanced Resources International	Mingjun et al. (2010) and Schepers et al. (2009)
COMSOL Multiphysics	COMSOL	General partial differential equation solver with finite element solver	COMSOL	Farajzadeh et al. (2009) and Houdou et al. (2008)
COORES	CO ₂ Reservoir Environmental Simulator	Multi-component, three-phase and 3D fluid flow in heterogeneous porous media	Insititut français du pétrole	Estublier and Lackner (2009) and Le Gallo et al. (2006)
CrunchFlow	Crunch Flow	3D, multi-phase transport with equilibrium and kinetic mineral–gas–water reactions	Lawrence Livermore National Laboratory I	Siirila et al. (2012) and Steefel and Lasaga (1994)
RetrasoCodeBright	Retraso (REactive TRAnsport of SOlutes) CodeBright (COupled DEformation of BRIne Gas and Heat Transport)	A solution of the flow, heat and geomechanical model equations	Technical University of Catalonia (UPC), Barcelona, Spain	Kvamme and Liu (2009) and Olivella et al. (1996)
DuMux	DUNE for Multi-(Phase, Component, Scale, Physics)	Multi-scale, multi-physics toolbox for the simulation of flow and transport processes in porous media	University of Stuttgart	Class et al. (2009) and Flemisch et al. (2007)
ECLIPSE	ECLIPSE	Non-isothermal multi-phase flow in porous media	Schlumberger	Juanes et al. (2006), Martens et al. (2012) and Sifuentes et al. (2009)
ELSA	Estimating Leakage Semi-Analytically	Provides quantitative estimates of fluid distribution and leakage rates in systems involving a sedimentary succession of multiple aquifers and aquitards	Princeton University	Nordbotten et al. (2005b, 2009)
FEFLOW	FEFLOW	Solving the groundwater flow equation with mass and heat transfer, including multi-component chemical kinetics	DHI-WASY	Melikadze et al. (2013)

Table 5 (continued)

Simulators	Full names	Description	Developers	Relevant literature
FEHM	Finite Element Heat and Mass Transfer Simulator	Non-isothermal, multi-phase flow (including phase-change) in unfractionated and fractured media with reactive geochemistry & geochemical coupling	Los Alamos National Laboratory	Pawar et al. (2005) and Robinson et al. (2006)
GASMOD/GCOMP	GASMOD/GCOMP	Multi-phase reservoir simulator	PHH Engineering Software Limited	Palmer and Mansoori (1996)
GEM-GHG	Generalized Equation of State Model—Greenhouse Gases	Non-isothermal multi-phase flow in porous media	Computer Modelling Group (Canada)	Kumar et al. (2005) and Nghiem et al. (2009)
GMI-SFIB	Geomechanics International—Stress and Failure of Inclined Boreholes	Three-dimensional stress modeling for compressional (wellbore breakout) and tensional (tensile wall fractures) stress failure, fracture modeling	Geomechanics International	Fang (2011) and Fang and Khaksar (2012)
GWB	The Geochemist's Workbench	Chemical reactions, pathways, kinetics	University of Illinois	Bethke and Yeakel (2009) and Lu et al. (2011)
IPARS-CO2	Integrated Parallel Accurate Reservoir Simulator	Non-isothermal compositional EOS coupled with geochemical reactions	University of Texas at Austin	Delshad et al. (2011) and Kong et al. (2015)
MASTER	Miscible Applied Simulation Techniques for Energy Recovery	Black oil simulator, compositional multi-phase flow	National Energy Technology Laboratory	Amner and Brummert (1991)
METSIM 2	METSIM 2	A non-isothermal multi-component coalbed gas simulator	Imperial College	Durucan et al. (2004) and Law et al. (2004)
MODFLOW	MODFLOW	Solving groundwater flow equation to simulate the flow through aquifers	US Geological Survey (USGS)	Nicot et al. (2009)
MoRes	Modular Reservoir Simulator	A modular object-oriented design for black-oil, equation-of-state (EOS) and K-value compositional simulations	Shell	Class et al. (2009) and Wei and Saaf (2009)
ACCRET	Athena Carbon Dioxide Capture and Storage Geochemistry Module	Thermal multi-phase 3D reactive transport numerical code	University of Bergen	Hellevang and Kvamme (2006, 2007)
MUFTE-UG	Multiphase Flow Transport and Energy Model on Unstructured Grids	Isothermal and non-isothermal multiphase-multi-component flow and transport processes in porous and fractured porous media	University of Stuttgart	Assteerawatt et al. (2005) and Ebigo et al. (2006)
NEFFLOW-FRACGEN	Fracture Network Generator Flow Simulator	Two-phase, multi-component flow in fractured media	National Energy Technology Laboratory	Myshakin et al. (2015) and Schwartz (2006)
NUFT	Non-isothermal Unsaturated-saturated Flow and Transport model	Non-isothermal multi-phase flow and chemical reactions in porous media	Lawrence Livermore National Laboratory	Hao et al. (2012)
OGS: [Couples GEM, BRNS, PHREEQC, ChemApp, Rockflow]	OpenGeoSys	Porous and fractured media THMC simulation	Helmholtz Centre for Environmental Research (UFZ)	Graupner et al. (2011) and Li et al. (2014)

Table 5 (continued)

Simulators	Full names	Description	Developers	Relevant literature
PFLOTRAN	Parallel Reactive Flow and Transport	Non-isothermal multi-phase, multi-component, chemically reactive flows in porous media	Los Alamos National Laboratory	Lu and Lichtner (2005, 2007)
PHAST	PHAST	Multi-component, 3-D transport with equilibrium and kinetic mineral–gas–water reactions	US Geological Survey (USGS)	Parkhurst et al. (2004)
PHREEQC	PHREEQC	The low-temperature aqueous geochemical simulator	US Geological Survey (USGS)	Parkhurst and Appelo (2013) and van Pham et al. (2012)
PSU- COALCOMP	Pennsylvania State University- COALCOMP	Three-dimensional, two-phase, dual porosity, sorption, fully implicit, compositional coalbed methane reservoir simulator	Pennsylvania State University/ National Energy Technology Laboratory	Bromhal et al. (2005) and Manik et al. (2000)
ROCKFLOW	Rock Flow	Multi-phase flow and solute transport processes in porous and fractured media, as well as thermal–hydraulically–mechanical (THM) coupled processes	Bundesanstalt für Geowissenschaften und Rohstoffe and University of Hannover	Kolditz et al. (2003)
SOLVEQ/CHILLER	CHILLER	Multi-component multi-phase equilibrium geochemical calculation software based on minimum free-energy	Department of Geological Sciences, University of Oregon	Palandri and Kharaka (2005) and Reed and Spycher (2006)
RTAFF2	Reactive Transport and Fluid Flow	Non-isothermal multi-phase and a multi-component flow simulator	French Geological Survey (BRGM)	
SIMED II	SIMED II	Two-phase three-dimensional multi-component coalbed gas simulator	The Netherlands/Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia	Stevenson and Pinczewski (1995) and van Bergen et al. (2002)
STOMP	Subsurface Transport over Multiphase Processes	Non-isothermal multi-phase flow in porous media, coupled with reactive transport.	Pacific North-West National Laboratory	Bonneville et al. (2013) and White et al. (2012)
TOUGH/TOUGH2	Transport of Unsaturated Groundwater and Heat	Non-isothermal multi-phase flow in unfractured and fractured media	Lawrence Berkeley National Laboratory	Pruess et al. (2002) and Pruess and Spycher (2007)
TOUGH-FLAC	Transport of Unsaturated Groundwater and Heat	Non-isothermal multi-phase flow in unfractured and fractured media with geomechanical coupling	Lawrence Berkeley National Laboratory	Rutqvist (2012) and Rutqvist and Tsang (2003)
TOUGHREACT	Transport of Unsaturated Groundwater and Heat Reactive Transport	Non-isothermal multi-phase flow in unfractured and fractured media with reactive geochemistry	Lawrence Berkeley National Laboratory	Xu et al. (2006a)
VESA	Vertical Equilibrium with Subsurface Analytical	Vertically averaged numerical model for large-scale flow coupled with an embedded analytical model for wellbore flow	Princeton University	Gasda et al. (2009)

Maguelone, France. Geophysical monitoring tools were used in their field experiments to gain useful information about the site and also to monitor the movement of the gas. They highlighted the importance of accounting for geological heterogeneity in modeling procedures. In addition, the study was able to provide information on the usefulness of geophysical monitoring tools in analyzing plume migration in storage sites.

Benchmark studies have thus been performed to understand the capabilities of different softwares used for carbon dioxide storage. Pruess et al. (2002) performed a critical comparison on the performance of different commercial reservoir simulator codes for accurate prediction of CO₂ storage processes (that is TOUGH2, Geoquest's ECLIPSE, CMG's GEM, etc.). They concluded that all softwares could be used to simulate the essential flow and transport processes that would accompany geologic storage. However, the hydromechanical process would only be solved by one code TOUGH-FLAC. Law et al. (2004) analyzed the results of five simulators to a benchmark problem for CO₂ storage issues in coalbed formations. Class et al. (2009) also performed a benchmark study with the use of different simulators to address the problems related to CO₂ storage in geologic formations. The outcome of such benchmark studies illustrates that the results of the simulation of any storage problem would depend on the simulator used and are highly dependent on the numerical methods used and the physics of processes implemented. It is suggested that the choice of the simulator to be used would depend on the physical processes being focused on for best results.

Simulation of CO₂ storage is generally a little more difficult than conventional simulations due to the interplay between phase change, composition and reservoir heterogeneity which require highly efficient computational algorithms (Jiang 2011). The striking difference between CO₂ storage issues and conventional porous media modeling is the large temporal and spatial scale differences. A multi-scale methodology which incorporates advanced numerical schemes may be the best way to approach such scale differences in such a way as to capture the complex multi-phase, multi-component species, and physics in heterogeneous systems and also save computational cost. Such multi-scale, multi-physics approach has been implemented in the development of certain simulators (Flemisch et al. 2007).

5 Capacity estimation for CO₂ storage projects

An initial estimate of the storage capacity of a formation is required for successful implementation of CCS projects. Such estimates assist in project planning and in potential risk

analysis expected from commercial injection into the formation. Different methods exist for the calculation of storage volumes and can be broadly classified into static and dynamic estimation methods. As the names would suggest, static estimation methods do not change with time and only require basic rock and fluid properties. They are typically determined using volumetric and compressibility parameters. Conversely, dynamic estimation methods vary with time and are determined using reservoir simulations and some analytical methods which incorporate time-dependent variables in their derivations. Estimation of CO₂ storage capacity in geological media is at best an approximation due to the many uncertainties present both in the formation (heterogeneity) and in the physics of the processes. The level of uncertainty also varies with the method being used to determine the storage capacity and the amount of available data. The methodology to be used for the determination of the capacity is dependent on the formation type, that is coal seams, depleted oil and gas reservoirs or saline aquifers. In addition, the extent of the storage medium may determine the approach to be used in storage capacity determination. Open boundaries where the extent of the media is assumed to be infinite, closed where the extent of the media is assumed to have a finite end and semi-closed are all different forms available in the literature for storage capacity determination.

Because candidate storage sites are usually not fully characterized before estimates are made, they are usually reported as a low- and high-capacity estimate of storage (DOE 2007) with Monte Carlo simulations employed to account for uncertainties. Two primary methodologies are being used; they include the methodology by the Department of Energy (DOE) of the USA (DOE 2007) and the Carbon Dioxide Sequestration Leadership Forum (CSLF) (Bachu et al. 2007b) and the formulas used by the two bodies for storage determination are summarized in the next subsections.

5.1 Coal seams

The formulas for calculating the storage capacity of coal seams by the DOE and CSLF methods are as follows:DOE:

$$M = Ah_g C \rho E \quad (14)$$

CSLF:

$$M_{CO_2} = Ah(1 - f_a - f_m) \rho_{CO_2} n_c G_c \quad (15)$$

$$G_{cs} = V_L * \frac{P}{P + P_L} \quad (16)$$

where A represents the area, h is the thickness, h_g is the gross thickness, C is the concentration of CO₂ standard volume per unit of coal volume, f_a and f_m are the ash and moisture

weight fraction of coal, M is the mass storage, E is the CO_2 storage efficiency factor that reflects a fraction of the total coal bulk volume that is contacted by CO_2 , ρ is the density, n_c is the bulk coal density, G_c is the gas coal content, G_{cs} is the gas content at saturation, V_L and P_L are the Langmuir volume and pressure, respectively, and P represents the pressure. The Langmuir volume is the maximum adsorption capacity of the gas for a particular coal at a defined temperature and infinite pressure. Its unit is usually given in scf/ton (volume of gas per mass of unit coal). The Langmuir pressure (also known as the critical desorption pressure) is the pressure at which one half of the Langmuir volume can be adsorbed/stored.

In the CSLF method, the storage capacity available in coal seams for CO_2 is determined in a manner akin to the determination of initial gas in place in coalbed methane reservoirs as shown in Eq. 15. The ability of the coal gas to adsorb the injected CO_2 is dependent on pressure, temperature and coal characteristics of the formation. The gas content at saturation is determined by Eq. 16. The two equations assume that the CO_2 contacts all the available coal and that the coal adsorbs CO_2 to full capacity. In reality, however, this may not be practicable; hence, a correction factor is introduced to account for the non-ideality as given in Eq. 17:

$$M_e = M_{\text{CO}_2} * C * R_f \quad (17)$$

where M_e is the effective storage capacity, C is the completion factor, and R_f is the recovery factor. The product of completion and recovery factor is together known as the gas deliverability. The completion factor C is an estimate of that part of the net cumulative coal thickness within the drilled coal zone that will contribute to gas production or storage; it is dependent on the individual thickness of the separate coal seams and on the distance between them and is lower for thin coal seams than for thick ones (Bachu et al. 2007a). Monte Carlo uncertainty analysis can be employed to account for uncertainties in the determination of unknown parameters.

5.2 Oil and gas reservoirs

Estimation of available storage capacity in depleted oil and gas reservoirs is not as complicated as with coal seams and saline aquifers as these reservoirs have been adequately characterized during the production stages of the reservoir. The basic assumption in the formulation of storage capacities is the availability of all the pore spaces vacated by hydrocarbon fluids. In other words, it is assumed that the formation fluids have not been replaced by water from any supporting aquifer around the region of the field. The storage capacity by the CSLF and DOE methods are as stated below.

DOE:

$$M = Ah_n \phi_e \rho (1 - S_w) B_f E \quad (18)$$

CSLF:

$$\text{Gas fields : } M_{\text{CO}_2} = \rho_{\text{CO}_2} R_f (1 - F_{\text{IG}}) \text{OGIP} \left[\frac{(P_s Z_r T_r)}{(P_r Z_s T_s)} \right] \quad (19)$$

$$\text{Oil fields : } M_{\text{CO}_2} = \rho_{\text{CO}_2} \left[\frac{R_f \text{OOIP}}{B_f} - V_{\text{iw}} + V_{\text{pw}} \right] \quad (20)$$

where A represents the area, h_n is the net thickness, ϕ_e is the effective porosity, M is the mass storage, E is the CO_2 storage efficiency factor that reflects a fraction of the total pore volume from which oil and/or gas has been produced and that can be filled by CO_2 , ρ is the density, B_f is the formation volume factor, S_w is the average water saturation, P represents the pressure, Z and T are the compressibility factors, respectively, R_f is the recovery factor, OOIP and OGIP stand for the original oil and gas in place, respectively, F_{IG} is the fraction of injected gas, and V_{iw} and V_{pw} are the volumes of injected and produced water, respectively.

5.3 Saline aquifers

Bachu et al. (2007a) as part of research conducted by the Carbon Sequestration Leadership Forum (CSLF) expressed the effective storage capacity available in structural traps in terms of volume and mass of CO_2 as in Eqs. 21 and 22, respectively. The boundaries of the aquifer are considered to be open.

$$V_{\text{CO}_2} = Ah \phi (1 - S_{w_{\text{irr}}}) C_c \quad (21)$$

$$M_{\text{CO}_2} = Ah \phi (1 - S_{w_{\text{irr}}}) \rho_{\text{CO}_2} C_c \quad (22)$$

where the spatial variation of the formation is known; the volumes can be expressed as

$$V_{\text{CO}_2} = \iiint \phi (1 - S_{w_{\text{irr}}}) dx dy dz * C_c \quad (23)$$

where A is the area, h is the thickness, $S_{w_{\text{irr}}}$ is the irreducible water saturation, ρ_{CO_2} is the density of CO_2 , and C_c is the capacity coefficient which is dependent on the trap heterogeneity, buoyancy and sweep efficiency.

The capacity coefficient is usually site-specific and is best determined through numerical simulations or detailed field work. It incorporates effects such as the heterogeneity of the aquifer, buoyancy effect and sweep efficiency. The International Energy Agency Greenhouse Gas R&D Programme (IEAGHG 2009) in their study evaluated the capacity coefficient as a function of lithology based on extensive numerical studies. The values derived for carbonate formations based on the 10th, 50th and 90th percentiles were 1.41%, 2.04% and 3.27%, respectively. The formula for capacity estimates derived by the US Department of Energy (DOE-NETL 2015) is similar to that of the CSLF. The only difference lies

in the capacity coefficient given for the carbonate formations with the DOE estimating the 10th, 50th and 90th percentiles as 0.51%, 2.0% and 5.5%, respectively.

The storage volume available by residual trapping can be determined using the correlation below:

$$V_{\text{CO}_2t} = \Delta V_{\text{trap}} \phi S_{\text{CO}_2t} \quad (24)$$

where S_{CO_2t} (saturation of CO_2) is dependent on the hysteresis effects of the relative permeabilities and the CO_2 saturations during reversal flow.

As highlighted earlier, the dissolution of CO_2 in brine is a continuous and slow process that is dependent on the convection, diffusion and dispersion. The storage capacity on a basin and regional scale, as determined by Bachu et al. (2007a) for solubility trapping, is given below

$$M_{\text{CO}_2t} = \iiint \phi (\rho_s X_s^{\text{CO}_2} - \rho_o X_o^{\text{CO}_2}) dx dy dz \quad (25)$$

where ϕ is the porosity, ρ is the density, X stands for mass fraction, M denotes the mass, and subscripts s and o denote the carbon dioxide content at the saturation and initial stages, respectively. The time frame required for mineral trapping to occur makes it difficult to provide correlations for the determination of the mineral trapping capacity.

Zhou et al. (2008) devised a simple method for determining the storage capacity in closed and semi-closed aquifers. The main idea lies in the premise that injected CO_2 will lead to a pressure increase in the formation. This will, in turn, lead to a displacement of native brine which can either be stored in the expanded pore space due to compression of the rocks (closed systems) or the pore space in the seals overlying the formation (semi-closed systems).

Zhou et al. (2008) showed the derivations for closed systems by using the given in Eqs. 26 and 27 below.

$$V_{\text{CO}_2} = (\beta_p + \beta_w) V_{\text{pore}} \Delta P_{\text{max}} \quad (26)$$

$$M_{\text{CO}_2} = (\beta_p + \beta_w) V_{\text{pore}} \Delta P_{\text{max}} \rho_{\text{CO}_2} \quad (27)$$

For semi-closed systems the following equation is suggested:

$$\begin{aligned} V_{\text{CO}_2}(t_1) = & (\beta_p + \beta_w) \Delta P_{\text{max}}(t_{\text{max}}) V_{\text{pore}} \\ & + 0.5(\beta_{ps} + \beta_w) \Delta P_{\text{max}}(t_{\text{max}}) V_s \\ & + \int_0^{t_{\text{max}}} \frac{2Ak_s \Delta P_{\text{max}}(t)}{\mu_w B_s} dt \end{aligned} \quad (28)$$

where β is the compressibility, A is the area, k is the permeability, subscripts s , p , w refer to the seal, pore and water, respectively, β_{ps} refers to the compressibility of the rock from pore to seals, V is the volume, μ is the water viscosity, B_s stands for thickness of the top and bottom seals, t

is the time, and ΔP_{max} is the maximum allowable pressure increase.

Dynamic simulations still represent the best method for the determination of storage capacities of geological formations selected for storage as they contain detailed information regarding the petrophysical properties of the formation. Coupled with this, numerical simulators nowadays have embedded in their simulators the ability to calculate the storage capacity provided by the different storage mechanisms over an extended period. Analytical determination methods such as fractional flow theory (Moghanloo et al. 2015) and relative permeability curve analysis method (Zhu et al. 2017) for the determination of storage volumes can also be found in the literature.

The aforementioned described techniques have been employed mainly in the determination of storage capacities across the world. Lindeberg et al. (2009) used both analytical and reservoir simulations to estimate the available storage capacity in the Utsira Formation of Norway. Their reservoir simulations were done in such a way to model elevated pressures in the aquifer. In addition, a CO_2 breakthrough from production wells was also monitored in estimate determination. In China, Liu et al. (2005) estimated the storage capacities in gas fields and coalbeds present in the country. Similarly, Suekane et al. (2008) determined the residual and solubility capacities available in Japanese aquifers. By improving on the flaws of the conventional analytical techniques for storage estimation, Ding et al. (2018) proposed new analytical methodologies for the determination of solubility and mineral trapping in aquifers and depleted oil reservoirs. Their model was applied to the HB oil field in China, and estimates were compared to a similar methodology by Xu et al. (2004) with slight discrepancies observed. They, however, argued that their model would be superior as, in addition to the model's ability to determine storage capacity by solubility trapping, the model could also determine the annual storage capacities by mineral trapping.

6 Measurement, monitoring and verification techniques during CO_2 storage

Monitoring the movement of the plume for leakages is critical in the post-injection phase of storage. Containment of the CO_2 is achieved if proper monitoring is performed as leakages could be detected early, thus ensuring that the environment and groundwater are not at risk from released gases. Furthermore, monitoring could be employed in the validation of simulation predictions by tracking the pressure buildup in the formation (Bourne et al. 2014). Mass balance verifications are also an important reason for carrying out monitoring studies. Injected CO_2 volumes must be tracked to ensure they are stored in identified zones and in

line with emission quotas specified before the commencement of such projects. Successful verification of simulations via monitoring would provide researchers with greater confidence in the use of simulation tools. Consequently, a lot of effort is continuously made to develop accurate monitoring tools. As with the modeling approach, monitoring of CO₂ can either be classified on a spatial or temporal basis. On a spatial basis, it is monitored based on the area which the CO₂ affects. On this basis, it can be classified into atmospheric monitoring, near-surface monitoring and subsurface monitoring (which involves the faults, wells, reservoir and seals) (Brown et al. 2009). On a temporal basis, monitoring can be grouped as during the injection phase and post-injection phase. For further discussion, we limit ourselves to discussing monitoring on a spatial basis.

6.1 Atmospheric monitoring tools

As the name implies, these tools ensure that the CO₂ injected into the formations does not leak into the atmosphere above it. This monitoring strategy is important due to the concerns about leaked CO₂. Atmospheric monitoring tools are typically required to be very sensitive as leakage of CO₂ from the formation could be quickly dispersed in the atmosphere, thus making it difficult for other forms of monitoring tools to recognize the gas immediately. Atmospheric monitoring tools are placed at the potential leakage sources so as to increase their detection capability and are especially required to provide confidence in carbon dioxide storage and for carbon accounting verification. The tools used to detect CO₂ leakage in the atmosphere are optical sensors, atmospheric tracers and eddy covariance (Brown et al. 2009). Other systems which can be used in monitoring the atmospheric levels of CO₂ include CO₂ detectors, advanced leak detection system, laser systems and LIDAR. As the quantity of safe CO₂ required to exist in the atmosphere must not exceed certain limits, CO₂ detectors can be applied to sense the existence of excess CO₂ in the atmosphere. Application of CO₂ detectors might, however, prove to be impractical due to the enormous number of detectors that would be required to effectively detect the gas. Eddy covariance also known as eddy flux is an important atmospheric monitoring tool used to quantify the fluxes of gases between the surface of the earth and the atmosphere. It has the advantage of being able to cover kilometers of space, thereby providing quick monitoring and having a low to moderate cost. Atmospheric tracers are artificial substances injected into the formation along with the CO₂ in order to observe the leakage of CO₂ early on. They are also used to monitor the flow direction of the CO₂ in the formation. Conventional tracers which have been employed for monitoring studies are the perfluorocarbons (PFCs) and sulfur hexafluoride (SF₆). Perfluorocarbons (PFCs) are, however, preferred to sulfur hexafluoride (SF₆) because

they can easily be detected even at low concentrations, are highly soluble in CO₂, are non-toxic and are non-radioactive. A notable CO₂ injection project which has made use of the tracer technique for monitoring is the Frio Project (Nance et al. 2005). Their monitoring design made use of PFCs as the chemical tracer to monitor leakages. Fibrous elements such as capillary absorbent tubes (CATs) were placed on surface installations in order to adsorb the PFCs. The CATs were removed on a periodic basis to ascertain the amount of PFCs which had sorbed on the surface of the CATs using thermal desorption and gas chromatograph techniques. Laser systems are remote sensing technologies that make use of either optical absorption, breakdown spectroscopy or non-linear optics to monitor gas leakages. A laser application for CO₂ detection, however, only makes use of the optical absorption technique. In this technique, the laser beams a light which has been tuned to the wavelength of the CO₂ on the gas. The scattered light which emanates from the gas after absorption is examined. An issue with this technique is the accurate determination of the wavelength of CO₂ as the absorption wavelengths of CO₂ must be carefully determined without infringing on the absorption wavelengths of water vapor.

6.2 Near-surface monitoring tools

Usually, the flow of CO₂ at the near-surface consists of bubbles which emanate from faults or near an abandoned wellbore. Monitoring of CO₂ at the near-surface is important as it serves as a link between the subsurface and the atmosphere. Therefore, it can provide information on leaks in the subsurface while preventing leaks to the atmosphere if detected in time, monitoring in this area has been proven to be less expensive than atmospheric and subsurface monitoring. Some techniques which can be used for near-surface monitoring could also be used for subsurface monitoring. Such techniques which could be used for this monitoring have been summarized in the next subsection. Such techniques include interferometric synthetic aperture radar (InSAR), tiltmeters, time-lapse seismic among others.

6.3 Subsurface monitoring tools

The objectives of subsurface monitoring are to track the movement of an injected CO₂ plume in a deep geologic formation; to define the lateral extent and boundaries of the plume; to track associated pressure changes in the reservoir; and to demonstrate long-term stability of the CO₂ plume (Brown et al. 2009). Numerous monitoring techniques can be employed for the monitoring of CO₂ plume in the subsurface. The choice of monitoring techniques to be used for subsurface monitoring is dependent on the information

required, costs of monitoring technique and time frame to achieve information.

Seismic methods have been employed to evaluate the distribution of faults and the subsurface structures using 3D techniques. In a 4D mode that includes time-lapse data, seismic methods can also be used to track the movement of the injected plume and gas leakages. Multi-component 3D surface seismic provides better information when the geology of the formation is non-uniform. Together with time-lapse, multi-component seismic profiling provides valuable information on the migration of the injected gas. If cost considerations are taken into account, 2D time-lapse seismic monitoring could be used to provide data on the injected plume. The downside of the 2D methods is in their inability to track plume movement in formations with complex geometries. 2D seismic techniques would be more useful where observation wells are available and cross-well seismic technology could be employed. Vertical seismic profile (VSP) has been employed to provide information on the leakages and the migration path of CO₂ (El-Kaseeh et al. 2017). Most of the conventional seismic methods have been used to determine leakages and migration path of the CO₂. In order to quantify the injected gas, seismic methods have been employed by combining the measurement of the velocity with Gassmann modeling. This method requires that the density of CO₂ at reservoir conditions is known. Determination of this density is not an easy process, and therefore, seismic monitoring tools have been combined with gravimetry. Gravimetry basically involves using gravity to monitor the in situ changes in the density of the injected gas. Results from gravimetric monitoring could provide reliable inputs for flow simulations. Gravimetric methods, however, possess low sensitivity and require a sizeable amount of CO₂ injected into the formation before responses can be picked up.

Electromagnetic and electric methods have found important use as monitoring tools. They make use of electrical and electromagnetic responses from the subsurface to determine the changes in saturation. These techniques involve measuring important electric parameters such as conductivity, resistivity and employing correlations such as the Archie expression to relate these parameters to saturations. Different methods that use these concepts are the magnetotelluric sounding, electromagnetic resistivity, electrical resistivity tomography (ERT), electromagnetic induction tomography (EMIT) among others.

Geophysical logs have also been employed for the monitoring of subsurface-injected plumes. They provide useful information on well properties and reservoir fluids. Examples of geophysical logging tools which could be employed include sonic logs, neutron logs and density logs. Coupled with their ability to map saturation, geophysical logging tools could also provide information on the onset of corrosion in the casings of wellbores. Tiltmeters can be used

to observe the extent of geomechanical deformation in the subsurface. They are particularly useful in the monitoring of cap rock deformations. InSAR has been applied for the monitoring of surface deformations. It achieves its objectives by making use of two synthetic aperture radars to generate maps. This technique is sensitive to changes in deformations and has been used to measure millimeter changes in surface deformation. Different forms of the InSAR techniques include corner reflector Interferometric synthetic aperture radar (CR-InSAR), permanent scatterer interferometric synthetic aperture radar (PS-InSAR) and differential interferometric synthetic aperture radar (D-InSAR). The technique has been applied for the monitoring of natural occurrences such as volcanoes and earthquakes. The ability of the InSAR technique to monitor surface deformations has been applied in storage sites for tracking fluid pressure alterations, thus determining leakages. Recently, it was pioneered as a monitoring tool at the In Salah storage site in Algeria.

The choice of monitoring tool to be employed on any specific storage site is dependent on the nature of the site. For example, geophysical monitoring from the surface is dependent on the extent of overburden on the aquifer. Therefore, in geologically complex scenarios, monitoring of the injected plume via this technique would be more cumbersome. In the same vein, information available on a particular storage site could influence the monitoring technique chosen. Depleted oil and gas reservoirs which have been adequately characterized and have been proven to have assured seal integrity would make for easier monitoring of the injected CO₂ plume.

Established commercially known CCS projects have employed different monitoring tools. Torp and Gale (2004) provided useful information on the monitoring tools used at the Sleipner project in Norway. Repeated seismic data were among the many tools used for monitoring (Fig. 7). The monitoring procedures confirmed some of the estimates from reservoir simulation. The injected CO₂ moved upward due to buoyancy after the injection and accumulated under the cap rock overlying the formation. Also, it was observed that solubility trapping would occur faster than mineral trapping. The simulation model for the Sleipner project was then history-matched with the seismic data results to provide accurate predictions for the future. However, seismic monitoring is costly and other monitoring tools such as pressure monitoring and observation wells could provide viable alternatives.

Ringrose et al. (2013) analyzed the lessons learned from the In Salah Project in Algeria. Among these were the need for characterization of the overburden and the reservoir prior to injection, constant risk assessments of the identified storage sites and the significance of flexibility in the design of capture, compression and injection systems. The interferometric synthetic aperture radar (InSAR) method for

Fig. 7 Seismic survey results for the Sleipner project (Torp and Gale 2004)

storage monitoring was pioneered in this project. InSAR was able to provide information on millimeter changes in ground surface elevation; it was also able to give insights into the geomechanical response to CO₂ injection. Arts et al. (2004) made use of time-lapse seismic studies to monitor plume movement in the Utsira Formation. Notably, they were able to demonstrate that the impact of the movement of CO₂ on seismic measurements was considerable and thus seismic could be used as a suitable monitoring tool during the life-cycle of a storage project. A summary of monitoring tools used at select CCS projects is provided in Table 6.

On a broader scale, monitoring is usually quantified as monitoring, verification and accounting (MVA) to include mass balance verifications and accounting for operators. Interested readers are referred to Plasynski et al. (2011) for details on MVA strategies for different projects.

7 Risks and challenges in CO₂ storage

The high dependency of world energy on coal-fired power plants makes carbon capture and storage a very important technology for the mitigation of global warming. Therefore, it represents the only viable option in the short term to limit global warming effects and must be pursued vigorously. However, just as with most technologies, carbon dioxide storage comes with its own risks and challenges which must be properly catered for before venturing into it. Questions

such as failure modes (risk evaluation), likelihood and consequences of failure must be answered when performing risk assessments for projects. Risks and challenges involved in CO₂ storage are highlighted below.

7.1 Leakage

The primary and most important risk factor is leakage. Most modeling and monitoring studies conducted in the development, implementation and monitoring phases of carbon dioxide storage are done primarily to avoid leakage of the gas into the atmosphere, groundwater aquifers, shallow soil zones and overlying resource bearing strata and to ensure secure containment of gas. The leakage of carbon dioxide could be as a result of the following:

1. **Aquifer over-pressurization:** Aquifer over-pressurization could lead to cracks in the cap rock overlying it and in the reactivation of faults and thus should be avoided. The risk of aquifer over-pressurization is much less in depleted hydrocarbon dioxide reservoirs due to reduced pressure before the injection started. Saline aquifers pose more risk from aquifer over-pressurization because the pressure of the aquifer begins from the initial pressure, thereby leading to quick buildup of pressure when injection commences. Vilarrasa et al. (2010) performed numerical simulations to ascertain the risk of over-pressure during injection. The authors employed an axisymmetric horizontal aquifer–cap rock system cou-

Table 6 Monitoring techniques used in field-scale projects

Field project	Category	Monitoring techniques	Select literature
Sleipner	Saline aquifer	Time-lapse gravity; micro-seismic; time-lapse seismic	Arts et al. (2004) and Cavanagh (2013)
Ketzin	Saline aquifer	Pulsed-neutron gamma logs; 4D seismic; 3D repeat seismic survey; electrical resistivity tomography (ERT); cross-well seismic; geophysical monitoring	Ivanova et al. (2012) and Kiessling et al. (2010)
Weyburn	EOR	Passive seismic; 4D time-lapse; vertical seismic profile (VSP); tracer injection; geochemical sampling analysis; production data analysis; cross-well seismic	Bellefleur et al. (2003), Preston et al. (2005) and White (2011)
Otway	Depleted gas field	Hydrodynamic sampling; high-resolution travel time, flask sampling; 3D surface seismic; head-space gas sampling; logging pressure/temperature; flux tower; surface soil gas; downhole fluid sampling; CO ₂ sniffers; VSP; micro-seismic; borehole seismic; groundwater chemistry	Boreham et al. (2011), Etheridge et al. (2011) and Urosevic et al. (2011)
Cranfield	Saline aquifer	Cross-well seismic tomography; 4D seismic, electrical resistance tomographic monitoring; vertical seismic profile; above zone monitoring interval; tracers	Ajo-Franklin et al. (2013), Alfi et al. (2015), Carrigan et al. (2013) and Kim and Hosseini (2014)
In Salah	Depleted gas field	Well log data; 3D seismic baseline survey; 4D seismic monitoring; groundwater monitoring wells; micro-seismic monitoring; satellite InSAR monitoring; tracers in CO ₂ injection wells; core analysis (storage unit); soil and surface gas sampling; core analysis (cap rock unit)	Mathieson et al. (2010), Onuma and Ohkawa (2009) and Ringrose et al. (2009)
Rumaitha Zone-B, Abu Dhabi	EOR	Cross-well seismic; DTS (distributed temperature sensing in observation well, 41 meters from injector; permanent multi-phase flow meter (MPFM), logging tools, sponge coring near injector well; production data analysis	Al-Hajeri et al. (2010) and Figuera et al. (2014, 2016)

pled with hydromechanics. Their results showed that the highest risk of over-pressures and fault reactivation were at the beginning of injection where fluid pressures rise. Lindeberg et al. (2009) also noted the importance of the consideration of injection pressures in the prevention of leakages through the cap rock. An engineering strategy has been proposed by Eke et al. (2011) to minimize the leakage of CO₂. In their paper, they argued that surface mixing of CO₂ with brine prior to injection could enhance the dissolution trapping mechanism. Subsequently, this would lead to a denser CO₂ which is saturated with brine being injected into the reservoir. By implication, the strong buoyancy drive, typically experienced in aquifers, is minimized and the risk of CO₂ leaking via prolonged contact of the CO₂ with the seal is curtailed. It is therefore important before commencing any storage activity to perform a geomechanical analysis in order to understand the fracturing pressure of the cap rock and thus avoid over-pressurization of the aquifer. Large areal extents of a proposed aquifer could also mean that pressure propagates much faster, ensuring that it takes a significant amount of time before the seal

of the aquifer encounters pressures capable of breaking the seal.

2. Abandoned wells: Another significant leakage pathway is abandoned wells; this leakage pathway is more plausible in a depleted hydrocarbon reservoir which has been used previously for the commercial production of hydrocarbon dioxides than in saline aquifers. This is because depleted hydrocarbon dioxide reservoirs possess wells whose structural integrity might have degraded over time. Degradation of wells could be as a result of casing corrosion and reactions of the minerals with plug-in materials or reservoir fluids which compromise integrity. Human errors in the design of wells such as loose plugs could also create pathways for leakage of gases. Several studies have been conducted to assess the impact of leakages through wells (Carey 2018; Kopp et al. 2010).
3. Faults and fractures: It is essential while performing site selection and characterization to ensure that there are no transmissive faults and fractures in the identified formation. Additionally, during the injection of CO₂, care must be taken to ensure that inactive faults are not activated due to the high aquifer pressures. Fractures could also

be developed in the cap rock if the temperature of the injected CO₂ is much lower than the in situ temperature in the aquifer. In the Abu Dhabi Rumaitha Zone-B project, the CO₂ is heated at the surface prior to injection, to ensure thermal induced fractures are not created in the reservoir.

7.2 Induced seismicity

Another postulated risk associated with CO₂ storage is that of induced seismicity. The risk, however, has been proven to be negligible in field-scale projects that have been carried out due to the relatively small size of the projects and low injection rates. Nicol et al. (2011) noted that induced seismicity could lead to earthquakes that exceed magnitudes of M6 and have the potential to impact on the containment, infrastructure and public perceptions of safety at CO₂ storage sites. The possibility of the occurrence of a seismic event would be higher if faults are present. This reiterates the need for proper site characterization and identification of faults and fractures to avoid their reactivation and the possible consequences of this reactivation (Oldenburg 2014).

7.3 Economic considerations

Carbon dioxide capture and carbon dioxide storage are two technologies that go hand-in-hand, hence the popular acronym CCS. The success of one process is dependent to a large extent on the success of the other. As such, it is necessary to state that the deployment of carbon dioxide storage projects would be greatly enhanced if carbon dioxide capture processes are also successful. The key economic issue associated with carbon dioxide capture processes is the high cost of the capture of CO₂ from stationary power plants. In fact, most successful commercial deployment of carbon dioxide storage projects has pursued the option of separating CO₂ from produced gas rather than capturing CO₂ from coal plants. This represents a cheaper option for the companies involved. As with most burgeoning technology, there is always a higher cost for companies which make the first step toward developing the technology before the technology improves and costs are reduced. For this reason, there is a reticence among companies to avoid making the first move. This disposition can be quelled by government action in subsidizing the costs involved for the early movers, thereby encouraging more participation.

Lewicki et al. (2007) made use of leakages of CO₂ from natural and industrial formations to analyze the features, events and processes (FEPs) of the leakages from both natural and man-made sources. A total of 12 natural and 4 industrial analogues were looked into in their comparisons. They concluded at 5 FEPs which could lead to the release of stored CO₂ in aquifers: (1) accumulation of CO₂ beneath

primary and secondary entrapments, (2) seismic activities which could lead to the natural release of CO₂ into the atmosphere, (3) fractures and faults which could lead to the rapid release of CO₂, (4) abandoned and structurally weak wells which possess the ability to release large amounts of CO₂ back to the atmosphere and (5) release of CO₂ that rarely occurs through eruptive processes.

8 Conclusions

The risk of global warming is no longer hearsay. Several countries have accepted that our world is facing the risk of an endangered atmosphere and this must be addressed. The problem is not just a scientific one but also affects other spheres of human endeavor. In this review, we provide the reader with the state of the art on carbon dioxide storage science and technology. From a scientific viewpoint, the understanding of the processes involved in the process has been greatly enhanced over the years with concrete information available on the fate of the injected CO₂ before, during and after the injection phases. However, there are certain issues which we believe still need to be addressed before the science can be considered full-fledged. The modeling procedures involved in carbon dioxide storage is multi-scale in both the temporal and spatial scales; we believe that for the physics of the different level scales to be effectively understood, the problem needs to be approached using multi-scale formulations. This would require the development of advanced numerical algorithms which are very robust and computationally efficient for best results. Improvements in monitoring tools used at commercial CCS sites would also go a long way toward validating scientific models and simulation predictions. An improvement in the capability of monitoring and modeling tools implies that the risk of the leakage of CO₂ is greatly reduced. It is obvious that these could not be accomplished if the number of commercial CCS sites does not greatly increase. Governments would need to establish and enforce policies such as carbon dioxide pricing and taxation which would compel companies that would otherwise have considered the cheaper option of the emission of CO₂ directly into the atmosphere into considering CCS.

In summary, a successful carbon dioxide storage project would involve accurate site selection, characterization (storage capacity estimation, plume modeling) and monitoring to avoid the risks of leakages through seals, faults and abandoned wells. The site characterization would be successful through the use of modeling and simulation tools whose accuracy would be greatly enhanced through measurement, monitoring and verification during the post-injection phase. Carbon dioxide storage is a technology that has come to stay with the advantage of allowing the continued use of fossil

fuels while still saving our environment from the risks of global warming and therefore must be embraced by all.

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