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Tracking CO₂ Migration in Storage Aquifer

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Abstract

Monitoring technologies for CO₂ in geological carbon sequestration are based upon the physico-chemical and electromagnetic properties of the CO₂-water/brine and rock system as well as the induced events such as micro-seismicity. As CO₂ migrates in the subsurface, its interactions with elements like rock, water/brine can be used to track its presence and direction. For deep subsurface storage of CO₂, methods like electrical resistivity tomography (ERT), seismicity, capillary pressure and relative permeability as well as geochemical measurements can be reliably employed in monitoring CO₂. Other methods like membrane-sensor technique and gas accumulation chamber are mainly suitable for shallow geological sequestration. However, prior to the full-scale deployment, it is necessary to understand the principles of operations and limitations of the adopted technologies as well as obtain experimental and practical information from them. In the field application, pre-injection baseline assessment is necessary followed by critical assessments during the storage process and post-injection period. Accuracy in leakage quantification and identification of sinks are also important. Factors that can influence the results of these technologies include fluctuations of pressure, temperature, initial salinity level, initial pH level, porosity, fluid properties, porosity, tortuosity, pore size distribution, wettability, reservoir mineralogy and surface chemistry.

Keywords: CO₂, sequestration, leakage, two-phase flow, geophysical technologies
membrane

1. Introduction

Climate change and the accompanying global warming are of concerns to science, engineering and political stakeholders. Particularly, the effects of climate change on the living and non-living species and the possible future impacts have led to global efforts at curtailing

the emission of greenhouse gases. The current problem of global warming emanated from anthropogenic activities, mainly from excessive use of fossil fuel for energy as well as the degradation of natural carbon sinks, especially by deforestation [1, 2]. Emissions from fossil energy source have been shown to aggravate the climate change by forming a blanket of gases which accumulate at the lower part of the atmosphere, trapping the reflected radiation from the earth, thereby raising the surface temperature [2, 3]. According to DOE [4], 90% of world's primary sources of energy still come from fossil fuel. As a result, the readiness to cut the reliance on this source of energy presents a daunting challenge. Continuous dependence of man on fossil fuel is based on the desire for an improvement in the standard of living, education, health care, and so on. These goals are directly related to energy consumption.

CO₂ concentration in the atmosphere should be reduced to the maximum of 350 ppm in order to restore the planet to the similar level obtainable in the pre-industrial revolution era (200 to ~385 ppm) [5, 6]. To mitigate the problems of climate change, efforts are being made by scientists and many technologies are under investigations and implementations to curtail the emissions of greenhouse gases into the atmosphere. To reduce human dependence on fossil fuels, energy sources from wind and sun are being considered globally. However, carbon emissions will realistically persist till the near or foreseeable future owing to the derivations of many industrial and household products from crude oil. As a result, carbon capture and storage (CCS) is a viable route to check accumulation of greenhouse gases in the atmosphere.

CCS is providing methods and procedure to deal with the CO₂ emitted from various emission sources. Advanced capture technologies have emerged from the development and discovery of novel solvents together with optimised capture procedures like pre and post-combustion capture techniques [7, 8]. CO₂ can be stored in several natural media. These storage media include ocean and saline aquifers, unminable coal seams and depleted oil reservoirs [9, 10]. Storage of CO₂ can also be made economical through its use to recover remnant oil in depleted oil reservoir [11]. Among the possible storage sites, geological carbon sequestration in saline aquifers is considered as the most viable option as it seems to have the largest carbon storage potential [12, 13]. The reasons for this include the stability and capacity of these geological media. Stable sedimentary basins are essential for dependable sequestration activities, and such basins are found in most continents [14] with estimated capacities of around 1000–100,000 gigatonnes of carbon dioxide [13]. Across the globe, **Figure 1** shows the carbon sequestration projects that are either ongoing or completed.

The current issues in the practice of geological carbon sequestration are those of safety of the process. There are concerns about the possible leakage of the CO₂ back to the atmosphere. If this occurs, humans and plants are in danger. In the case of leakage, CO₂ migrating through the subsurface may encounter potable water, with which it forms acid that can affect the plant and animal lives. In case the leakage gets into the atmosphere, at a concentration of CO₂ above 4%, its inhalation produces fatal results in humans and animals [16]. Thus, there is a need for effective monitoring of CO₂ movement and reactions at the geological sequestration site and the adjoining areas.

Figure 1. Carbon dioxide sequestration operations at pilot and commercial scales worldwide [15].

Many techniques for monitoring CO₂ in the Earth's surface are available. But, the effective monitoring of CO₂ in the subsurface is still posing challenges. Meanwhile, it is important that we develop effective subsurface monitoring techniques in order to avert dangers to humans, animals and plants on the Earth, animals in the ocean as well as the potable water aquifers in the subsurface that might lie along the CO₂ leakage path. For example, if CO₂ leaks from the geological sequestration site as a result of fault in the cap rock or seismic effects, subsurface monitoring measures should be efficient enough to alert the monitoring team immediately in order to possibly curtail the movement of the plume before it contaminates the subsurface potable water aquifers or before it reaches the surface. In this scenario, humans and animals can be moved away from the leakage site on time. Effective monitoring will also provide the possibility of preparing for the plume before reaching the surface by making provisions for its containment.

This chapter examines the existing monitoring techniques for the CO₂ activities in the geological carbon sequestration. The challenges inherent in these techniques are identified, and the implications of these challenges are discussed under different conditions and in different porous media.

2. CO₂ leakage and characteristics

Several mechanisms guide the leakage of CO₂ and its migration through the geological pore networks. For example, gravity override and viscous instability are phenomena that cause the CO₂ to move to the top of the injection layer bypassing large quantities of brine [14, 17, 18]. Also, if the caprock has fault line that is permeable enough for the plume, this can cause favourable pathways via which CO₂ could escape, thereby compromising the intention of the sequestration process. Also, gravity override together with viscous instability can create the vertical buoyant pressure, which the CO₂ applied on the caprock. This pressure arises mainly as a result of difference in density between the formation water and the CO₂, and the thickness of the carbon dioxide plume accumulation.

Monitoring technologies for CO_2 in geological carbon sequestration are built upon the physico-chemical and electromagnetic properties of the CO_2 -water/brine and rock system or the identification of the reaction by-products and/or the coupled process effects such as micro-seismicity [19]. Monitoring can provide vital information for verification, accounting and risk assessment at storage site, and is fundamental to ensure that the effective containment of the gas has actually taken place. Monitoring also contributes to building public acceptance of the geologic storage as a viable method for mitigating greenhouse gas emissions [20]. Existing monitoring techniques include electromagnetic techniques [21], temperature signals [22] and infrared monitoring [23]. Some of these techniques have been widely demonstrated both in the laboratory and pilot applications. Electromagnetic techniques make use of the wide difference between the electrical/dielectric characteristics of CO_2 and water/brine as well as those of other geological elements to create contrasts among the phases, which can then be used to monitor the migration of the CO_2 in the aquifer or to understand the displacement of the aquifer brine by the injected CO_2 . Traditionally, this electromagnetic method is often employed in the monitoring and control of two-phase flow in porous media [1, 24–26].

For the temperature signal technique, the principle employed in its use includes the fact that the dissolution of CO_2 in water is an exothermic process. As a result, the temperature of the solution is raised as CO_2 dissolves in the brine/water. Also, the change of phase of CO_2 from, for example, supercritical state to liquid or gas is accompanied by change in enthalpy. These effects are utilised in non-isothermal detection of CO_2 presence in water/brine using the temperature signal method. But the dissolution of CO_2 in water is limited. This confines the method to limited time and space because once the water/brine is equilibrated with CO_2 , detecting plume migration or other activities of the CO_2 becomes difficult. Furthermore, CO_2 is known to have characteristic infrared wave absorption property. This is harnessed in the infrared monitoring technique. How well these methods can be utilised in the subsurface and large-quantity monitoring of the gas in the subsurface still poses questions.

Monitoring the region around the storage aquifers should be coupled with near-surface and surface monitoring [1]. These regions of monitoring are important because migration or leakage of CO_2 can extend to the atmospheric space. Near-surface monitoring techniques are well developed and are essential in the detection and monitoring of the gas emanating from different emission sources and even leakage from geological sequestration sites. Near-surface monitoring techniques involve the analysis of near-surface water, air and soil samples on a regular basis as CO_2 leaks can acidify the water and create conspicuous contrast between the original and current soil and air compositions [19]. Also, on the surface, gravity method [27] can be employed based on the fact that CO_2 is heavier than air and lighter than water. Thus, increase in air density and/or reduction in density of water may signify the presence of CO_2 . Remote sensing of air composition [28] and surface analysis of carbon content by inelastic neutron scattering (INS) [29] are techniques also known for the surface monitoring of CO_2 .

Among the monitoring methods described above, electromagnetic techniques like dielectric permittivity (ϵ_r), electrical resistivity (ρ) and conductivity (σ) as well as wave propagation are common in reservoir applications [1, 21, 24]. Also, tracers like SF₆ are applied in the monitoring of fluid movement. To ensure safety in the case of advancing plume of CO₂, the monitoring methods should extend several hundred metres beyond the injection region. This has the potential of protecting the potable water aquifers that lie in the possible path of migrating CO₂. Apart from electrical parameters (e.g., ϵ , ρ and σ), capillary parameters are commonly employed in the study of two-phase flow, for example, oil and water, gas and water, and so on, and can as well be included in the monitoring techniques. This chapter is primarily concerned with the safety of the geological carbon sequestration and the techniques to ensure it. These techniques are expatiated in the following subsection.

3. CO₂ monitoring techniques

Monitoring techniques can be classified according to the different mechanisms of operations and the principles as well as the environment of applications. The following classes are popular in the literature.

With the exception of the (3) in **Table 1**, most of the techniques are mainly suitable for shallow injection layer or atmosphere. Worldwide, monitoring technologies have been in operations at many pilot sites like in Nagaoka (Japan) [30], Frio (USA) [31] and Ketzin [32]. Several other projects under the USDOE were involved in the trial of the technologies (www.fossil.energy.gov/sequestration/partnerships/index.html). Multiple monitoring technologies applied in these pilot projects were able to track the CO₂ plume in different subsurface geological environments [20].

S. No.	Classification/application environment	Techniques/parameters
1	Atmospheric CO ₂	Eddy covariance
2	Soil CO ₂	Soil accumulation chambers
3	Geophysical monitoring	Geoelectrical, seismic, ground penetrating radar, etc.
4	Biological stress	Multispectral image analysis of plants and microorganisms
5	Geochemical analysis	Monitoring water quality changes
6	Satellite-borne Interferometric Synthetic Aperture Radar (InSAR)	Detection of ground deformation or surface movement
7	Capillary-based parameters	Capillary pressure-saturation-relative permeability relationship

Table 1. Monitoring techniques for CO₂.

It is conventional to perform monitoring operations in three stages. The first stage is the pre-injection monitoring where background data about the CO_2 level as well as lithological parameters before injection of CO_2 can be obtained. This gives the baseline data. The injection stage monitoring follows, where ongoing changes in the soil, water and surrounding space are recorded as CO_2 is being released. Lastly, post-injection monitoring comes after the stop of the CO_2 injection.

3.1. Geophysical techniques

Geophysical monitoring techniques involve the deployment of a variety of electromagnetic and electrical surveying methods to study subsurface CO_2 activities and its interactions with the rock/soil, water/brine and other gases. These methods include geoelectrical, seismic, ground penetrating radar, gravity and electromagnetic assessment. These techniques make use of the electrical behaviours of the CO_2 , water and the surrounding geological materials.

To monitor CO_2 sequestration at deep geological layer, electrical resistivity tomography (ERT) is an effective technique. Following injection of CO_2 , increase will occur in the resistivity level of the bulk reservoir domain owing to the non-conductive nature of the gas. The resistivity profile may remain stagnant following steadiness in injection operation or after the stop of injection. In addition, after the stop of injection, there may occur a dip in the resistivity profile from the repeal of the contact surface of CO_2 /brine and subsequent inflow of brine into the near-wellbore area [33].

From the resistivity data, saturation of CO_2 (S_{CO_2}) in the reservoir can be evaluated using inverse petrophysical relation [33] by assuming the applicability of Archie's second law:

$$S_{\text{CO}_2} = 1 - \left(\frac{\rho_o}{\rho} \right)^{1/n} \quad (1)$$

where ρ_o is the baseline resistivity and n is the saturation exponent.

ERT works effectively if properly calibrated and is well suitable to track dissolved and gaseous CO_2 [34]. Application of electrical resistivity tomography (ERT) has been demonstrated at various pilot sites (see, e.g., [33, 34]) for detecting and tracking the CO_2 and brine distribution and their migrations in the subsurface. ERT has the advantage of imaging the injection reservoir and the migration activities of the fluids. It consists of the array of borehole electrodes which can be arranged to serve as a permanent reservoir monitoring tool. It possesses the ability to map quantitative CO_2 saturation in the subsurface. ERT has been found suitable for deep geological layer survey. Example of this technique in field application is found at Ketzin pilot site, Germany. The method was used to acquire data on resistivity changes with the injection of CO_2 . Also acquired was the CO_2 saturation in the storage reservoir as well as imaging of CO_2 induced resistivity change.

For near-surface measurement of CO_2 activities in shallow aquifers, direct current geoelectric can be employed [20]. As CO_2 passes through the water-filled and wetted pores, owing to dissolution and ionisation, carbonic acid is formed. This process activates the electrical characteristics of the system. The formation of acid promotes dissolution of minerals in the aqueous media which

further enhances the electrical characteristics of the system. Thus, the determination of changes in resistivity of the domain will be of immense advantage in monitoring the presence and impact of CO₂ and its subsurface movement. In pores saturated with water, migrating CO₂ can displace part of the resident water to replace its position with the gas. In this case, resistivity will increase. This phenomenon of changing electrical characteristics which occurs with the displacement and replacement of water by CO₂ was explained in the work of Abidoye and Bello [35]. They stated that for the scenario where the movement of the CO₂ into the pore led to the displacement of the resident pore water, the bulk dielectric permittivity (ϵ_b) of the system decreases. If the pore water was not displaced by the migrating CO₂, the presence of CO₂ in the system increases the ϵ_b . Direct current geoelectric is currently being used at Ressacada Farm, Brazil. The method was used to acquire resistivity changes in the course of CO₂ injection. The changes in resistivity are compared to the baseline values. At the Ressacada Farm, the resistivity value in the vicinity of the injection well increased by 50% in comparison with the baseline value. However, 8 days after the injection stopped, the resistivity change dropped to less than 14% [20].

Laboratory demonstrations and mathematical simulations of geoelectrical monitoring system were well demonstrated in the works of Abidoye and Das [36, 37], Abidoye and Bello [35], Rabiou et al. [38], Lamert et al. [39] and Dethlefsen et al. [40]. Abidoye and Das [36, 37] and Rabiou et al. [38] used unconsolidated porous media of silicate and carbonate soil samples in a sample holder of 10 cm diameter and 4 cm height. They performed simultaneous measurements of bulk relative permittivity (ϵ_b) and electrical conductivity (σ_b) measurements using three-pin time domain reflectometry probes (TDR probes), which was connected to the wave generator, TDR100 reflectometer (Campbell Scientific Ltd., Shepshed, UK). Using this system, the effects of pressure, temperature and salt concentration on bulk ϵ_b -S and σ_b -S relationships were investigated for carbonate (limestone) and silicate porous media (both unconsolidated domains) under dynamic and quasi-static supercritical CO₂ (scCO₂)-brine/water flow. Their results show that the ϵ_b in the silica sand sample decreases as the temperature rises in the scCO₂-water system. For the carbonate porous medium, ϵ_b rises only slightly with temperature. The ϵ_b -S curve also rises as the domain pressure increases. Furthermore, the bulk electrical conductivity (σ_b), at any particular saturation for the scCO₂-brine system rises as the temperature increases with a more significant increase found around full water saturation. These findings were corroborated by the work of Wraith and Or [41] where ϵ_b and σ_b values were found to be greater in the limestone than silica sand porous samples for similar porosity values. From their results, it can be inferred that the geoelectrical techniques are highly dependent on water saturation. Furthermore, Rabiou et al. [38] performed similar investigations with the inclusion of basalt as porous medium. Similar findings were recorded.

Field demonstrations of geoelectrical monitoring techniques were performed by Lamert et al. [39] as well as Dethlefsen et al. [40]. As in the work of Abidoye and Das [36, 37], time domain reflectometry method was used by Lamert et al. [39]. They installed several copper electrodes at various depths up to 18.5 m below the ground level around the CO₂ injection site in order to monitor the movement of injected CO₂. They found the suitability of geoelectrical methods for monitoring injected CO₂ and geochemically altered groundwater. Similar to the conclusion of Abidoye and Das [36, 37], they also found that the site-specific conditions influence the electrical characteristics.

Apart from the abovementioned methods, other geophysical tools exist with varying capacity to monitor subsurface gas activities. For example, ground penetrating radar (GPR) is another well-established tool that can be used in subsurface CO₂ tracking. However, it has limited depth of penetration as compared to others. However, in the zone of CO₂ leakage, it can give a deeper signal penetration [42]. GPR and other technologies like magnetic resonance sounding (MRS) have depth of penetration of <60 cm [43]. Logging tools like sonic, neutron and pulsed neutron techniques also offer some effectiveness in CO₂ monitoring.

The abovementioned discussions show that myriads of geophysical monitoring techniques are in existence. But the parameters of measurements can be affected by operational conditions as well as the porous media characteristics. Monitoring strategies should, therefore, take these factors into consideration to minimise deviations of the results from the realities. This can be achieved by taking notes of site-specific characteristics that are key to effective prediction of the fate of CO₂.

3.2. Membrane-sensor system

Membrane-sensor technique only assesses the presence of subsurface CO₂ without considering its interactions with other elements of the sequestration domain. Selectively, permeable membrane having high selectivity for CO₂ can be utilised. Coupling the membrane with sensor device, the system can accumulate gas like CO₂ in its chamber which can then be quantified with signals from the sensor. Example is shown in **Figure 2** from Abidoye and Das [44]. Methods of collecting CO₂ into the gas chamber vary and depend on the convenience of the investigators. Abidoye and Das [44] demonstrated membrane-sensor technique in a laboratory experiment using a high-pressure experimental rig. The chapter shows how silicone membrane-sensor system can be employed in the monitoring of subsurface gases, especially in the leakage scenario. In their work, mass permeation, membrane resistance to gas permeation and the gas flux across the membrane are reported for two gases, namely, CO₂ and N₂. In their results, mass permeation of CO₂ through the membrane was more than 10 times higher than that of N₂, under similar conditions. It was also found to increase with the geological depths. The gas flux remains higher for CO₂ as compared to N₂. The authors established a simple criterion for distinguishing the presence of the different gases at various geological depths based on the rate at which the mass permeation of gas through the membrane occurs.

Figure 2. Photographs of (A) the sample holder showing silica sand and pressure transducer (B) the pressure transducer and the silicone rubber sheet (metal cap not shown). Sample holder size: internal diameter=10cm, sample height=4cm [44].

Silicone was used by the authors due to its favourable selectivity for CO₂ permeation. Other suitable membrane can, as well, be used. Silicone membrane is a non-porous flat sheet material. Gas permeates the membrane by diffusion under the influence of the driving force, for example, the pressure difference across the membrane. This membrane-sensor method is useful in the early detection of CO₂ migration or leakage from geological reservoirs. Early detection at depth will allow for more time to prepare and plan for the CO₂ plume before its arrival in shallow groundwater or the earth's surface [45]. In application, alarm system can be triggered to signify the presence of CO₂ if the mass permeation rate follows the power law model provided in Eq. (2). This equation can be used to program the membrane-sensor system.

$$y = 10^{-8} x^{1.0652} \quad (2)$$

where y is the rate of mass permeation into the membrane-sensor chamber in kg/h and x is the geological depth in metre (m). The equation conforms to the profile of CO₂ permeation curve through silicone membrane. Other gases will very likely deviate from the pattern.

The abovementioned analysis shows that the CO₂ has unique mass permeation rate that is different from that of N₂ and conceivably other gases found in the porous media. With the relation of the mass permeation rate to geological depth, using Eq. (2), the authors showed that the membrane-sensor system can be used to monitor gas leakage under different geological conditions. Thus, at any depth, the system can be applied to give unique indication of gas present. Membrane coupled with miniaturised sensor can be installed at depth to perform the monitoring operations.

Field applications of similar monitoring method were performed by Zimmer et al. [45]. They demonstrated the applicability of silicone rubber as a membrane in the detection of gases present in the underground and boreholes. Investigations by Zimmer et al. [45] were connected to the geological carbon sequestration project (CO₂SINK) in Ketzin, Germany. They successfully demonstrated the detection of the CO₂ front at observation wells, located at different distances to the injection well, using the gas membrane sensor that includes the silicone rubber. However, the analyses of the gases through the device rely on the mass spectrometer located on the ground surface.

3.3. Gas accumulation chamber

Measuring subsurface gas and monitoring its movement can be used for the delineation of fault zones and for the characterisation of migration process dynamics [20]. According to Chiodini et al. [46], such measurements have been used for environmental research in geothermal and volcanic areas to determine CO₂ flux rates. Oliva et al. [20] used the technique of gas accumulation chamber to measure CO₂ emissions, soil temperature and moisture on PVC collars arranged in a square grid with 1 m spacing centred on the injection well. They performed the measurements before CO₂ injection, during the whole injection period and 7 days after the injection stopped. Field application of this method was demonstrated at the Ressacada Farm, Brazil, where parameter like CO₂ flux rate was collected. The authors were able to establish relationship between resistivity changes in injection aquifer to the CO₂ flux rates in the same area.

3.4. Geochemical measurement technique

Geochemical monitoring techniques for subsurface CO_2 activities are aimed at acquiring information about interactions and reactions of CO_2 with rock, soil, water and other gases in the subsurface. Products of such interactions and reactions are often the main targets in the monitoring and measurements. Following dissolution of CO_2 in the aquifer water, carbonic acid is produced, which makes the solution acidic and lowers the pH. Furthermore, increase in acid level may lead to the dissolution of rock minerals, thus, raising the concentration of major and trace minerals in the solution. Dethlefsen et al. [40] stated that the most significant geochemical processes, which occur during the CO_2 contamination of potable water are the changes in the pH and the resultant changes in the electrical conductivity (σ) of the fluid–fluid-porous media system (i.e., CO_2 -water-porous media system). Popular mineral dissolution that occurs includes carbonates, sulphides, iron oxy-hydroxide minerals and surface reactions such as adsorption/desorption and ion exchange [20].

Geochemical monitoring techniques involve the use of chemical parameters and their appropriate sensors to detect the interactions of CO_2 , water, soil/rock and the subsurface gases. Oliva et al. [20] performed geochemical monitoring of CO_2 activities in shallow well by sampling multilevel wells installed in the vicinity of the injection well. From such observatory wells, groundwater samples can be collected before, during and after the injection periods at intermittent schedules. Measurements of temperature, pH, electrical conductivity, oxidation–reduction, salinity and dissolved oxygen can be performed in-situ. Indicator parameters like alkalinity, acidity, ferrous iron (Fe^{2+}) and anions bromide (Br^-), chloride (Cl^-), nitrate (NO_3^-), nitrite (NO_2^-) phosphate (PO_4^{3-}), sulphate (SO_4^{2-}) and acetate (CH_3COO^-) can be obtained from such measurements.

Geochemical activities of CO_2 can vary based on the chemical characteristics of the domain rock/soil. That was why Abidoye and Das [37] performed geochemical monitoring of CO_2 activities in silicate and carbonate porous minerals, to investigate the characteristics of the water-saturated porous media contaminated by CO_2 in the laboratory. They used pH measurements, silicone rubber membrane in the monitoring of CO_2 diffusion in the porous media and the geoelectrical measurement techniques for the determination of the bulk dielectric constant (ϵ_b) and the bulk electrical conductivity (σ_b) of the CO_2 -water-porous media system.

Their results showed three stages in the profile of pH change with time as CO_2 dissolved and diffused in water-saturated silica sand. The initial stage was characterised by quick fall in the pH value from the start of the experiment. This behaviour was connected with quick dissolution of CO_2 and the formation of carbonic acid along with bicarbonate. At the second stage, there was a short rise in pH value. This was explained to be owing to the reverse reaction, which resulted into the formation of aqueous and gaseous CO_2 and water. At the last stage, static equilibrium has been attained in the system which was marked by constant pH value, which remained unchanged till the end of the experiment. During these stages, the bulk electrical conductivity (σ_b) changed in accordance with the fluctuation of the pH values. Since ionic species are formed during the dissolution, σ_b increased accordingly. According to the authors, the rise in σ_b coincided with the initial stage of the change in the pH of the system. The σ_b was higher in limestone than silica sand, and it increased with depth or domain

pressure. Furthermore, the authors provided a mathematical relationship showing that σ_b is dependent on the pH and its initial value, σ_{bi} . This is shown in Eq. (3):

$$\sigma_{br} = 3.87 \sigma_{bi}^{0.42} pH_r^{-0.4} \quad (3)$$

The equation has a regression value of 0.997 and SSE of 0.0023. σ_b is the bulk electrical conductivity in S/m. σ_{bi} is the value of the σ_b in the domain before the injection of CO₂. σ_{br} is the ratio of the steady state to the initial values of the σ_b (i.e., value of σ_{br} when the pH is at the steady state, divided by the value of σ_{bi} before the injection of CO₂). pH_r is the ratio of the steady-state value to the initial value of the pH.

3.5. Capillarity-based monitoring technique

Capillary pressure (P^c) and relative permeability (K_r) for wetting (water) and non-wetting phases (CO₂) are parameters of key importance in modelling the two-phase flow processes encountered during transport of immiscible phases in the underground [47] and they constitute critical parameters used to history match and design field-scale injection projects using reservoir simulators [48]. On two-phase flow, several publications exist concerning capillary pressure-saturation relationship (P^c -S) [49–55] while several others are based on the K_r -S relationship [56–59].

In the context of geological carbon sequestration, flow of supercritical CO₂-water (scCO₂-water) can be considered as a two-phase system. Characterisation of such flow can be performed with capillary pressure-saturation-relative permeability relationships (P^c -S- K_r) [1]. This is because CO₂ is only slightly soluble in brine. The solubility occurs briefly, and afterwards CO₂ continues as separate phase in the porous medium.

Injected CO₂ moves through permeable pore networks of the storage reservoir. This movement determines its distribution and stability within reservoirs used for carbon sequestration (Tokunaga and Wan 2013), and this process is dependent on capillary interactions with the displaced brine [60, 61]. Multiphase flow models are powerful tools to understand and predict the capillary activity and trapping of supercritical-CO₂ (scCO₂) in deep saline geologic formations. The constitutive relationship between capillary pressure (P^c) and saturation (S_w) is the essential input parameter into these multiphase models. Reliable predictions of CO₂ storage require understanding the capillary behaviour of supercritical CO₂ [62].

However, capillary pressure measurements are influenced by the sand and fluid properties. During injection, the distribution of CO₂ and brine in the pore space varies with distances from the well, and is controlled by the drainage P^c - S_w relation of the reservoir. After the stop of CO₂ injection or relaxation of injection pressure, the displaced brine attempts to reoccupy original position by displacing some of the CO₂. This is referred to as imbibition and is also described by reverse cycle of P^c - S_w curve. The incomplete rewetting or incomplete displacement of the CO₂ by the imbibing brine will lead to major storage mechanism- capillary trapping, which relies on the path- and history-dependent saturation characteristics to control distributions of multiphase fluid flow in pore spaces [63–65].

Routine measurements of P^c - S_w relationship include by porous plate, mercury injection or centrifuge methods. Plug et al. [26] measured drainage and imbibition relations in quartz sand packs of different grain sizes using CO_2 and water with the porous plate technique. They determined the drainage and imbibition cycles of the P^c - S_w relationship and were able to determine residual trapped CO_2 saturation ($s_{\text{nwr},\text{CO}_2}$). The parameter, $s_{\text{nwr},\text{CO}_2}$, is key to determining the success of the storage process because it indicates the amount of the CO_2 that is permanently immobilised. Tokunaga et al. [62] also used drainage and imbibition processes to determine P^c - S_w relationship on quartz sand for scCO_2 -brine at pressures of 8.5 and 12.0 MPa (45°C). They also determined $s_{\text{nwr},\text{CO}_2}$. Their results show that scCO_2 will easily enter silica-rich reservoirs and be stored through capillary trapping at fairly high $s_{\text{nwr},\text{CO}_2}$.

In relation to field applications of P^c - S_w technique, the work of Pini et al. [66] report P^c - S_w relationship for consolidated media, namely, the Berea and Arqov sandstone samples. Discussing the relation in reference to temperature, the curves for the Berea sandstone showed that capillary pressure decreases as temperature reduces, and this behaviour was attributed to an increase in CO_2 dissolution as the temperature decreases reducing the interfacial tension. Thus, P^c - S_w relationship curve can be influenced by subsurface conditions, reservoir characteristics and fluid properties. Complex dependence of P^c - S_w behaviour on fluid properties, porosity, pore geometry and tortuosity, pore size distribution, wettability, reservoir mineralogy, geochemistry, and surface chemistry make the relationship difficult to predict [65].

Field applications of these techniques involve coring of rock samples from the injection reservoir. On these samples, core-flooding operations are performed often in the laboratory. Capillary pressure, relative permeability and residual gas saturations are often the targeted parameters for measurement. The techniques have been used to assess safety and performances of geological carbon sequestration in the UK and Australia [66] and at Ketzin pilot site in Germany [67].

4. Conclusion

Myriads of techniques are currently in existence to detect and monitor CO_2 interactions with water/brine, rock/soil and other gases as well as its migration through complex pore networks. These techniques utilise the physico-chemical and electromagnetic properties of the CO_2 -water/brine and rock/soil system as well as the induced events such as micro-seismicity. However, prior to the full-scale deployment of the monitoring technologies, it is necessary to understand the principles of operations and limitations of the adopted technologies as well as obtain experimental and practical information from them. Some of them are suitable for deep geological layer while many are appropriate at the shallow aquifers.

Among the monitoring technologies, geophysical tools have gained more grounds in monitoring pilot sequestration projects across the globe. Techniques like seismic method, electrical resistivity tomography (ERT) offered good promise, especially at deeper levels in the scale of hundred metres to kilometres, while the likes of direct current geoelectric and ground penetration radar (GPR) are only good for monitoring at near-surface or shallow storage

reservoirs. However, in order to effectively assess the potential effects of CO₂ leakage for any of the methods, a pre-injection baseline is critical followed by critical assessments during the storage process and post-injection period.

Among the challenges in the majority of the field applications are the accuracy in leakage quantification and the myriads of factors that can influence the outputs of the measurement techniques, making them non-unique. Accuracy in leakage quantification is often due to the offset in background natural variability and the detection limits of the techniques currently available. Factors that can influence the results of these technologies include pressure, temperature, initial salinity level, initial pH level, porosity, fluid properties, porosity, pore geometry and tortuosity, pore size distribution, wettability, reservoir mineralogy, geochemistry and surface chemistry.

Finally, it is encouraging that important instruments and tools for laboratory and shallow aquifer monitoring techniques are readily available and may be affordable by intended users. However, the cost of the deployment of full-scale monitoring technique for deep geological layer sequestration remains a challenge. Thus, focus should be on bringing down the cost by encouraging price competition among potential manufactures while governments should also make necessary fund available.

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