

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Tracking CO<sub>2</sub> Migration in Storage Aquifer

---

Luqman Kolawole Abidoye and  
Diganta Bhusan Das

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/intechopen.79296>

---

## Abstract

Monitoring technologies for CO<sub>2</sub> in geological carbon sequestration are based upon the physico-chemical and electromagnetic properties of the CO<sub>2</sub>-water/brine and rock system as well as the induced events such as micro-seismicity. As CO<sub>2</sub> 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 CO<sub>2</sub>, methods like electrical resistivity tomography (ERT), seismicity, capillary pressure and relative permeability as well as geochemical measurements can be reliably employed in monitoring CO<sub>2</sub>. 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:** CO<sub>2</sub>, 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.

CO<sub>2</sub> 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 CO<sub>2</sub> 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]. CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> back to the atmosphere. If this occurs, humans and plants are in danger. In the case of leakage, CO<sub>2</sub> 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 CO<sub>2</sub> above 4%, its inhalation produces fatal results in humans and animals [16]. Thus, there is a need for effective monitoring of CO<sub>2</sub> movement and reactions at the geological sequestration site and the adjoining areas.

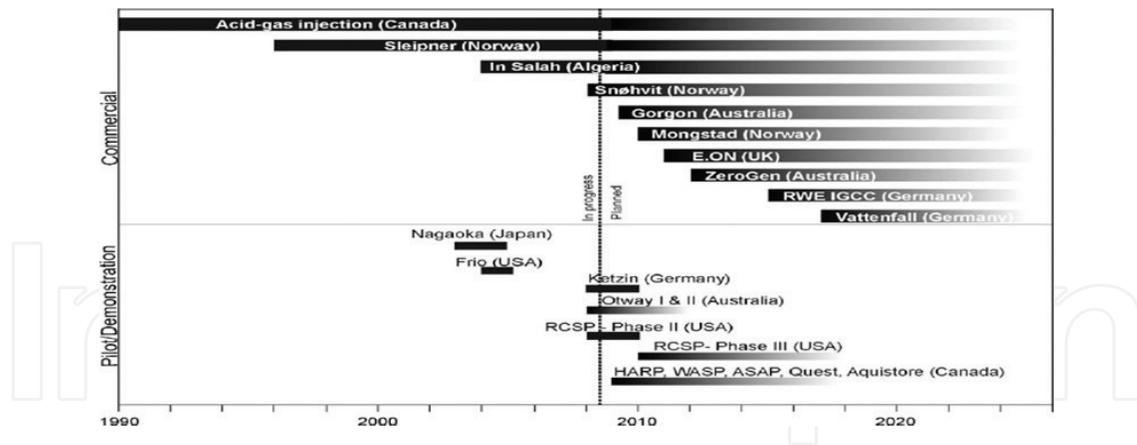


Figure 1. Carbon dioxide sequestration operations at pilot and commercial scales worldwide [15].

Many techniques for monitoring CO<sub>2</sub> in the Earth's surface are available. But, the effective monitoring of CO<sub>2</sub> 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 CO<sub>2</sub> leakage path. For example, if CO<sub>2</sub> 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 CO<sub>2</sub> 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. CO<sub>2</sub> leakage and characteristics

Several mechanisms guide the leakage of CO<sub>2</sub> and its migration through the geological pore networks. For example, gravity override and viscous instability are phenomena that cause the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> applied on the caprock. This pressure arises mainly as a result of difference in density between the formation water and the CO<sub>2</sub>, and the thickness of the carbon dioxide plume accumulation.

Monitoring technologies for CO<sub>2</sub> in geological carbon sequestration are built upon the physico-chemical and electromagnetic properties of the CO<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub> in the aquifer or to understand the displacement of the aquifer brine by the injected CO<sub>2</sub>. 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<sub>2</sub> in water is an exothermic process. As a result, the temperature of the solution is raised as CO<sub>2</sub> dissolves in the brine/water. Also, the change of phase of CO<sub>2</sub> 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<sub>2</sub> presence in water/brine using the temperature signal method. But the dissolution of CO<sub>2</sub> in water is limited. This confines the method to limited time and space because once the water/brine is equilibrated with CO<sub>2</sub>, detecting plume migration or other activities of the CO<sub>2</sub> becomes difficult. Furthermore, CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub>.

Among the monitoring methods described above, electromagnetic techniques like dielectric permittivity ( $\epsilon_r$ ), electrical resistivity ( $\rho$ ) and conductivity ( $\sigma$ ) as well as wave propagation are common in reservoir applications [1, 21, 24]. Also, tracers like SF<sub>6</sub> are applied in the monitoring of fluid movement. To ensure safety in the case of advancing plume of CO<sub>2</sub>, 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 CO<sub>2</sub>. Apart from electrical parameters (e.g.,  $\epsilon$ ,  $\rho$  and  $\sigma$ ), 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. CO<sub>2</sub> 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](http://www.fossil.energy.gov/sequestration/partnerships/index.html)). Multiple monitoring technologies applied in these pilot projects were able to track the CO<sub>2</sub> plume in different subsurface geological environments [20].

S. No.	Classification/application environment	Techniques/parameters
1	Atmospheric CO <sub>2</sub>	Eddy covariance
2	Soil CO <sub>2</sub>	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 CO<sub>2</sub>.

It is conventional to perform monitoring operations in three stages. The first stage is the pre-injection monitoring where background data about the CO<sub>2</sub> level as well as lithological parameters before injection of CO<sub>2</sub> 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<sub>2</sub> is being released. Lastly, post-injection monitoring comes after the stop of the CO<sub>2</sub> injection.

### 3.1. Geophysical techniques

Geophysical monitoring techniques involve the deployment of a variety of electromagnetic and electrical surveying methods to study subsurface CO<sub>2</sub> 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<sub>2</sub>, water and the surrounding geological materials.

To monitor CO<sub>2</sub> sequestration at deep geological layer, electrical resistivity tomography (ERT) is an effective technique. Following injection of CO<sub>2</sub>, 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<sub>2</sub>/brine and subsequent inflow of brine into the near-wellbore area [33].

From the resistivity data, saturation of CO<sub>2</sub> ( $S_{CO_2}$ ) in the reservoir can be evaluated using inverse petrophysical relation [33] by assuming the applicability of Archie's second law:

$$S_{CO_2} = 1 - \left( \frac{\rho_0}{\rho} \right)^{1/n} \quad (1)$$

where  $\rho_0$  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<sub>2</sub> [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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. Also acquired was the CO<sub>2</sub> saturation in the storage reservoir as well as imaging of CO<sub>2</sub> induced resistivity change.

For near-surface measurement of CO<sub>2</sub> activities in shallow aquifers, direct current geoelectric can be employed [20]. As CO<sub>2</sub> 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 CO<sub>2</sub> and its subsurface movement. In pores saturated with water, migrating CO<sub>2</sub> 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 CO<sub>2</sub> was explained in the work of Abidoye and Bello [35]. They stated that for the scenario where the movement of the CO<sub>2</sub> into the pore led to the displacement of the resident pore water, the bulk dielectric permittivity ( $\epsilon_b$ ) of the system decreases. If the pore water was not displaced by the migrating CO<sub>2</sub>, the presence of CO<sub>2</sub> in the system increases the  $\epsilon_b$ . Direct current geoelectric is currently being used at Ressacada Farm, Brazil. The method was used to acquire resistivity changes in the course of CO<sub>2</sub> 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 ( $\epsilon_b$ ) and electrical conductivity ( $\sigma_b$ ) 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  $\epsilon_b$ -S and  $\sigma_b$ -S relationships were investigated for carbonate (limestone) and silicate porous media (both unconsolidated domains) under dynamic and quasi-static supercritical CO<sub>2</sub> (scCO<sub>2</sub>)-brine/water flow. Their results show that the  $\epsilon_b$  in the silica sand sample decreases as the temperature rises in the scCO<sub>2</sub>-water system. For the carbonate porous medium,  $\epsilon_b$  rises only slightly with temperature. The  $\epsilon_b$ -S curve also rises as the domain pressure increases. Furthermore, the bulk electrical conductivity ( $\sigma_b$ ), at any particular saturation for the scCO<sub>2</sub>-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  $\epsilon_b$  and  $\sigma_b$  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.

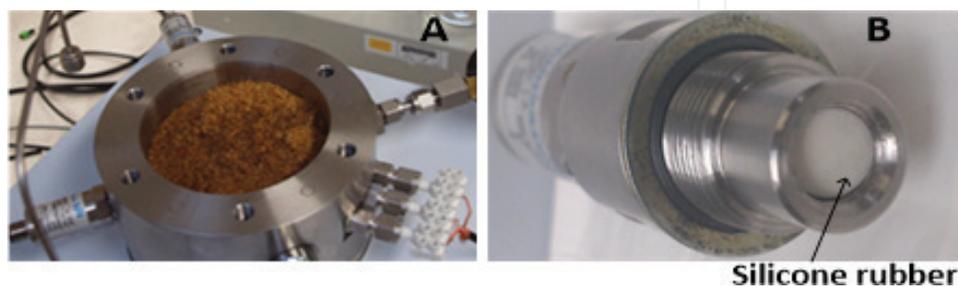
Field demonstrations of geoelectrical monitoring techniques were performed by Lamert et al. [39] as well as Dethlefsen et al. [40]. As in the work of Abidoye and Das [36, 37], time domain reflectometry method was used by Lamert et al. [39]. They installed several copper electrodes at various depths up to 18.5 m below the ground level around the CO<sub>2</sub> injection site in order to monitor the movement of injected CO<sub>2</sub>. They found the suitability of geoelectrical methods for monitoring injected CO<sub>2</sub> 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 CO<sub>2</sub> tracking. However, it has limited depth of penetration as compared to others. However, in the zone of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>.

### 3.2. Membrane-sensor system

Membrane-sensor technique only assesses the presence of subsurface CO<sub>2</sub> without considering its interactions with other elements of the sequestration domain. Selectively, permeable membrane having high selectivity for CO<sub>2</sub> can be utilised. Coupling the membrane with sensor device, the system can accumulate gas like CO<sub>2</sub> in its chamber which can then be quantified with signals from the sensor. Example is shown in **Figure 2** from Abidoeye and Das [44]. Methods of collecting CO<sub>2</sub> into the gas chamber vary and depend on the convenience of the investigators. Abidoeye 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, CO<sub>2</sub> and N<sub>2</sub>. In their results, mass permeation of CO<sub>2</sub> through the membrane was more than 10 times higher than that of N<sub>2</sub>, under similar conditions. It was also found to increase with the geological depths. The gas flux remains higher for CO<sub>2</sub> as compared to N<sub>2</sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> migration or leakage from geological reservoirs. Early detection at depth will allow for more time to prepare and plan for the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> permeation curve through silicone membrane. Other gases will very likely deviate from the pattern.

The abovementioned analysis shows that the CO<sub>2</sub> has unique mass permeation rate that is different from that of N<sub>2</sub> 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 (CO<sub>2</sub>SINK) in Ketzin, Germany. They successfully demonstrated the detection of the CO<sub>2</sub> 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 CO<sub>2</sub> flux rates. Oliva et al. [20] used the technique of gas accumulation chamber to measure CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> flux rate was collected. The authors were able to establish relationship between resistivity changes in injection aquifer to the CO<sub>2</sub> flux rates in the same area.

### 3.4. Geochemical measurement technique

Geochemical monitoring techniques for subsurface  $\text{CO}_2$  activities are aimed at acquiring information about interactions and reactions of  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  contamination of potable water are the changes in the pH and the resultant changes in the electrical conductivity ( $\sigma$ ) of the fluid–fluid-porous media system (i.e.,  $\text{CO}_2$ -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  $\text{CO}_2$ , water, soil/rock and the subsurface gases. Oliva et al. [20] performed geochemical monitoring of  $\text{CO}_2$  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 ( $\text{Fe}^{2+}$ ) and anions bromide ( $\text{Br}^-$ ), chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ) phosphate ( $\text{PO}_4^{3-}$ ), sulphate ( $\text{SO}_4^{2-}$ ) and acetate ( $\text{CH}_3\text{COO}^-$ ) can be obtained from such measurements.

Geochemical activities of  $\text{CO}_2$  can vary based on the chemical characteristics of the domain rock/soil. That was why Abidoye and Das [37] performed geochemical monitoring of  $\text{CO}_2$  activities in silicate and carbonate porous minerals, to investigate the characteristics of the water-saturated porous media contaminated by  $\text{CO}_2$  in the laboratory. They used pH measurements, silicone rubber membrane in the monitoring of  $\text{CO}_2$  diffusion in the porous media and the geoelectrical measurement techniques for the determination of the bulk dielectric constant ( $\epsilon_b$ ) and the bulk electrical conductivity ( $\sigma_b$ ) of the  $\text{CO}_2$ -water-porous media system.

Their results showed three stages in the profile of pH change with time as  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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 ( $\sigma_b$ ) changed in accordance with the fluctuation of the pH values. Since ionic species are formed during the dissolution,  $\sigma_b$  increased accordingly. According to the authors, the rise in  $\sigma_b$  coincided with the initial stage of the change in the pH of the system. The  $\sigma_b$  was higher in limestone than silica sand, and it increased with depth or domain

pressure. Furthermore, the authors provided a mathematical relationship showing that  $\sigma_b$  is dependent on the pH and its initial value,  $\sigma_{bi}$ . 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.  $\sigma_b$  is the bulk electrical conductivity in S/m.  $\sigma_{bi}$  is the value of the  $\sigma_b$  in the domain before the injection of CO<sub>2</sub>.  $\sigma_{br}$  is the ratio of the steady state to the initial values of the  $\sigma_b$  (i.e., value of  $\sigma_{br}$  when the pH is at the steady state, divided by the value of  $\sigma_{br}$  before the injection of CO<sub>2</sub>).  $pH_r$  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 (CO<sub>2</sub>) 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 CO<sub>2</sub>-water (scCO<sub>2</sub>-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 CO<sub>2</sub> is only slightly soluble in brine. The solubility occurs briefly, and afterwards CO<sub>2</sub> continues as separate phase in the porous medium.

Injected CO<sub>2</sub> 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-CO<sub>2</sub> (scCO<sub>2</sub>) 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 CO<sub>2</sub> storage require understanding the capillary behaviour of supercritical CO<sub>2</sub> [62].

However, capillary pressure measurements are influenced by the sand and fluid properties. During injection, the distribution of CO<sub>2</sub> 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 CO<sub>2</sub> injection or relaxation of injection pressure, the displaced brine attempts to reoccupy original position by displacing some of the CO<sub>2</sub>. 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 CO<sub>2</sub> 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{scCO}_2$ -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  $\text{scCO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CO}_2$ -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 CO<sub>2</sub> 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.

## Author details

Luqman Kolawole Abidoye<sup>1\*</sup> and Diganta Bhusan Das<sup>2</sup>

\*Address all correspondence to: [abidoye.luqman@uniosun.edu.ng](mailto:abidoye.luqman@uniosun.edu.ng)

1 Civil Engineering Department, Osun State University, Osogbo, Nigeria

2 Chemical Engineering Department, Loughborough University, Loughborough, Leicestershire, United Kingdom

## References

- [1] Abidoye LK, Das DB, Khudaida K. Geological carbon sequestration in the context of two-phase flow in porous media: A review. *Journal of Critical Reviews in Environmental Science and Technology*. 2015;**45**(11):1105-1147
- [2] Karl TR, Melillo JM, Peterson TC. *Global Climate Change Impacts in the United States*. New York: Cambridge University Press; 2009
- [3] Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, editors. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge: Cambridge University Press; 2007
- [4] DOE. Fossil fuels. 2010. <http://www.energy.gov/energysources/fossilfuels.htm>. [Accessed: 11/14/2010]

- [5] Hansen J, Sato M, Kharecha P, Beerling D, Berner R, Masson-Delmotte V, Pagani M, Raymo M, Royer DL, Zachos JC. Target atmospheric CO<sub>2</sub>: Where should humanity aim? arXiv preprint arXiv:0804.1126; 2008
- [6] Houghton JT, Ding YDJG, Griggs DJ, Noguer M, van der Linden PJ, Dai X, Maskell K, Johnson CA. Climate Change 2001: The Scientific Basis. Cambridge: Cambridge University Press; 2001
- [7] Abu-Khader MM. Recent progress in CO<sub>2</sub> capture/sequestration: A review. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 2006;**28**(14):1261-1279
- [8] Stephens JC. Growing interest in carbon capture and storage (CCS) for climate change mitigation. Sustainability: Science Practice and Policy. 2006;**2**(2):4-13
- [9] Siemons N, Bruining H, Castelijn H, Wolf KH. Pressure dependence of the contact angle in a CO<sub>2</sub>-H<sub>2</sub>O-coal system. Journal of Colloid and Interface Science. 2006;**297**(2):755-761
- [10] White DJ, Burrowes G, Davis T, Hajnal Z, Hirsche K, Hutcheon I, Majer E, Rostron B, Whittaker S. Greenhouse gas sequestration in abandoned oil reservoirs: The international energy agency Weyburn pilot project. GSA Today. 2004;**14**(7):4-11
- [11] Farajzadeh R. Enhanced Transport Phenomena in CO<sub>2</sub> Sequestration and CO<sub>2</sub> EOR [PhD Thesis]. The Netherlands: Technical University Delft; 2009
- [12] Fujii T, Satomi N, Yoshiyuki S, Hiroshi I, Toshiyuki H. Sorption characteristics of CO<sub>2</sub> on rocks and minerals in storing CO<sub>2</sub> processes. Natural Resources. 2010;**1**(1):1-10
- [13] Zahid U, Lim Y, Jung J, Han C. CO<sub>2</sub> geological storage: A review on present and future prospects. Korean Journal of Chemical Engineering. 2011;**28**(3):674-685
- [14] Metz B, Davidson O, de Coninck H, Loos M, Meyer L. IPCC Special Report on Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change. Working Group III. Geneva, Switzerland: Cambridge University Press; 2005
- [15] Michael K, Golab A, Shulakova V, Ennis-King J, Allinson G, Sharma S, Aiken T. Geological storage of CO<sub>2</sub> in saline aquifers. A review of the experience from existing storage operations. International Journal of Greenhouse Gas Control. 2010;**4**(4):659-667
- [16] Bartosik R, Cardoso L, Rodríguez J. Early detection of spoiled grain stored in hermetic plastic bags (silo-bags) using CO<sub>2</sub> monitoring. In: Proceeding of 8th International Conference on Controlled Atmosphere and Fumigation in Stored Products. 2008. pp. 550-554
- [17] Gasda SE. Numerical Models for Evaluating CO<sub>2</sub> Storage in Deep, Saline Aquifers: Leaky Wells and Large-Scale Geological Features. Princeton, NJ, USA: Princeton University; 2008
- [18] Saripalli KP, McGrail BP, White MD. Modeling the sequestration of CO<sub>2</sub> in deep geological formations. In: First National Conference on Carbon Sequestration. 2001. pp. 1-19
- [19] Espinoza DN, Kim SH, Santamarina JC. CO<sub>2</sub> geological storage—Geotechnical implications. KSCE Journal of Civil Engineering. 2011;**15**(4):707-719

- [20] Oliva A, Moreira ACDCA, Chang HK, do Rosário FF, Musse APS, Melo CL, Bressan LW, Ketzer JMM, Contant MJ, Lazzarin HSC, Cavelhão G. A comparison of three methods for monitoring CO<sub>2</sub> migration in soil and shallow subsurface in the Ressacada pilot site, southern Brazil. *Energy Procedia*. 2014;**63**:3992-4002
- [21] Nakatsuka Y, Xue Z, Garcia H, Matsuoka T. Experimental study on CO<sub>2</sub> monitoring and quantification of stored CO<sub>2</sub> in saline formations using resistivity measurements. *International Journal of Greenhouse Gas Control*. 2010;**4**(2):209-216
- [22] Bielinski A, Kopp A, Schütt H, Class H. Monitoring of CO<sub>2</sub> plumes during storage in geological formations using temperature signals: Numerical investigation. *International Journal of Greenhouse Gas Control*. 2008;**2**(3):319-328
- [23] Charpentier F, Bureau B, Troles J, Boussard-Plédel C, Michel-Le Pierrès K, Smektala F, Adam JL. Infrared monitoring of underground CO<sub>2</sub> storage using chalcogenide glass fibers. *Optical Materials*. 2009;**31**(3):496-500
- [24] Abidoye LK, Das DB. Scale-dependent dynamic capillary pressure effect for two-phase flow in porous media. *Advances in Water Resources*. 2014;**74**:212-230. DOI: 10.1016/j.advwatres.2014.09.009
- [25] Mahmood A, Warsi MF, Ashiq MN, Sher M. Improvements in electrical and dielectric properties of substituted multiferroic LaMnO<sub>3</sub> based nanostructures synthesized by coprecipitation method. *Materials Research Bulletin*. 2012;**47**(12):4197-4202
- [26] Plug W-J, Slob E, Bruining J, Moreno Tirado LM. Simultaneous measurement of hysteresis in capillary pressure and electric permittivity for multiphase flow through porous media. *Geophysics*. 2007;**72**(3):A41-A45
- [27] Alnes H, Eiken O, Stenvold T. Monitoring gas production and CO<sub>2</sub> injection at the Sleipner field using time-lapse gravimetry. *Geophysics*. 2008;**73**(6):WA155-WA161
- [28] Leuning R, Etheridge D, Luhan A, Dunse B. Atmospheric monitoring and verification technologies for CO<sub>2</sub> geosequestration. *International Journal of Greenhouse Gas Control*. 2008;**2**(3):401-414
- [29] Wielopolski L, Mitra S. Near-surface soil carbon detection for monitoring CO<sub>2</sub> seepage from a geological reservoir. *Environmental Earth Sciences*. 2010;**60**(2):307-312
- [30] Kikuta K, Hongo S, Tanase D, Ohsumi T. Field test of CO<sub>2</sub> injection in Nagaoka, Japan. In: *Proceedings of the 7th International Conference On Greenhouse Gas Control Technologies*. 2004. pp. 1367-1372
- [31] Hovorka SD, Meckel TA, Tervino RH. Monitoring a large-volume injection at Cranfield, Mississippi—Project design and recommendations. *International Journal of Greenhouse Gas Control*. 2013;**18**:345-360
- [32] Förster A, Norden B, Zinck-Jørgensen K, Frykman P, Kulenkampff J, Spangenberg E, Erzinger J, Zimmer M, Kopp J, Borm G, Juhlin C, Cosma CG, Hurter S. Baseline characterization of the CO<sub>2</sub>SINK geological storagesite at Ketzin, Germany. *Environmental Geosciences*. 2006;**13**:145-161

- [33] Schmidt-Hattenberger C, Bergmann P, Labitzke T, Wagner F. CO<sub>2</sub> migration monitoring by means of electrical resistivity tomography (ERT)—Review on five years of operation of a permanent ERT system at the Ketzin pilot site. *Energy Procedia*. 2014;**63**(2014):4366-4373
- [34] Yang X, Lassen RN, Jensen KH, Looms MC. Monitoring CO<sub>2</sub> migration in a shallow sand aquifer using 3D crosshole electrical resistivity tomography. *International Journal of Greenhouse Gas Control*. 2015;**42**:534-544. DOI: 10.1016/j.ijggc.2015.09.005
- [35] Abidoye LK, Bello AA. Simple dielectric mixing model in the monitoring of CO<sub>2</sub> leakage from geological storage aquifer. *Geophysical Journal International*. 2017;**208**:1787-1795. DOI: 10.1093/gji/ggw495
- [36] Abidoye LK, Das DB. Geoelectrical characterization of carbonate and silicate porous media in the presence of supercritical CO<sub>2</sub>-water flow. *Geophysical Journal International*. 2015;**203**(1):79-91. DOI: 10.1093/gji/ggv283
- [37] Abidoye LK, Das DB. pH, geoelectrical and membrane flux parameters for the monitoring of water-saturated silicate and carbonate porous media contaminated by CO<sub>2</sub>. *Chemical Engineering Journal*. 2015;**262**:1208-1217
- [38] Rabiou KO, Abidoye LK, Das DB. Geo-electrical characterization for CO<sub>2</sub> sequestration in porous media. *Environmental Processes*. 2017;**4**:303-317. DOI: 10.1007/s40710-017-0222-2
- [39] Lamert H, Geistlinger H, Werban U, Schütze C, Peter A, Hornbruch G, Schulz A, Pohlert M, Kalia S, Beyer M, Großmann J, Dahmke A, Dietrich P. Feasibility of geoelectrical monitoring and multiphase modeling for process understanding of gaseous CO<sub>2</sub> injection into a shallow aquifer. *Environmental Earth Sciences*. 2012;**67**(2):447-462
- [40] Dethlefsen F, Köber R, Schäfer D, Al Hagrey SA, Hornbruch G, Ebert M, Beyer M, Großmann J, Dahmke A. Monitoring approaches for detecting and evaluating CO<sub>2</sub> and formation water leakages into near-surface aquifers. *Energy Procedia*. 2013;**37**:4886-4893
- [41] Wraith JM, Or D. Temperature effects on soil bulk dielectric permittivity measured by time domain reflectometry: Experimental evidence and hypothesis development. *Water Resources Research*. 1999;**35**(2):361-369
- [42] Arts RJ, Baradello L, Girard JF, Kirby G, Lombardi S, Williamson P, Zaja A. Results of geophysical monitoring over a “leaking” natural analogue site in Italy. *Energy Procedia*. 2009;**1**(1):2269-2276
- [43] International Energy Agency. World Energy Outlook. 2011. <https://www.iea.org/newsroom/news/2011/november/world-energy-outlook-2011.html>
- [44] Abidoye LK, Das DB. Permeability, selectivity and distinguishing criterion of silicone membrane for supercritical CO<sub>2</sub> and N<sub>2</sub> in the porous media. *Journal Porous Media*. 2018. Article accepted (JPM-25108)
- [45] Zimmer M, Erzinger J, Kujawa C. The gas membrane sensor (GMS): A new method for gas measurements in deep boreholes applied at the CO<sub>2</sub>SINK site. *International Journal of Greenhouse Gas Control*. 2011;**5**(4):995-1001

- [46] Chiodini G, Cioni R, Guidi M, Marini L, Raco B. Soil CO<sub>2</sub> flux measurements in volcanic and geothermal areas. *Applied Geochemistry*. 1988;**13**:543-552
- [47] Aggelopoulos CA, Tsakiroglou CD. The effect of micro-heterogeneity and capillary number on capillary pressure and relative permeability curves of soils. *Geoderma*. 2008;**148**(1):25-34
- [48] Doughty C. Modeling geologic storage of carbon dioxide: Comparison of non-hysteretic and hysteretic characteristic curves. *Energy Conversion and Management*. 2007;**48**(6):1768-1781
- [49] Bottero S, Hassanizadeh SM, Kleingeld PJ. From local measurements to an upscaled capillary pressure–saturation curve. *Transport in Porous Media*. 2011;**88**(2):271-291
- [50] Bottero S, Hassanizadeh SM, Kleingeld PJ, Heimovaara TJ. Nonequilibrium capillarity effects in two-phase flow through porous media at different scales. *Water Resources Research*. 2011;**47**(10):W10505
- [51] Das DB, Gaudie R, Mirzaei M. Dynamic effects for two-phase flow in porous media: Fluid property effects. *AIChE*. 2007;**53**(10):2505-2520
- [52] Goel G, O'Carroll DM. Experimental investigation of nonequilibrium capillarity effects: Fluid viscosity effects. *Water Resources Research*. 2011;**47**(9):W09507
- [53] Hassanizadeh SM, Gray WG. Thermodynamic basis of capillary pressure in porous media. *Water Resources Research*. 1993;**29**(10):3389-3405
- [54] Mirzaei M, Das DB. Dynamic effects in capillary pressure–saturations relationships for two-phase flow in 3D porous media: Implications of micro-heterogeneities. *Chemical Engineering Science*. 2007;**62**(7):1927-1947
- [55] Nordbotten JM, Celia MA, Dahle HK, Hassanizadeh SM. On the definition of macroscale pressure for multiphase flow in porous media. *Water Resources Research*. 2008;**44**(6):1-8
- [56] Anderson W. Wettability literature survey. Part 5: The effects of wettability on relative permeability. *Journal of Petroleum Technology*. 1987;**39**(11):1453-1468
- [57] Bennion B, Bachu S. Drainage and imbibition relative permeability relationships for supercritical CO<sub>2</sub>/brine and H<sub>2</sub>S/brine systems in intergranular sandstone, carbonate, shale, and anhydrite rocks. *SPE Reservoir Evaluation & Engineering*. 2008;**11**(3):487-496
- [58] Lenormand R, Delaplace P, Schmitz P. Can we really measure the relative permeabilities using the micropore membrane method? *Journal of Petroleum Science and Engineering*. 1998;**19**(1-2):93-102
- [59] Water M, Abaci S, Whittaker N. Relative permeability measurements for two phase flow in unconsolidated sands. *Mine Water and the Environment*. 2006;**26**(2):12-26
- [60] Benson SM, Cole DR. CO<sub>2</sub> sequestration in deep sedimentary formations. *Elements*. 2008;**4**(5):325-331
- [61] IPCC. Carbon Dioxide Capture and Storage. In: Metz B, Davidson O, de Coninck H, Loos M, Meyer L, editors. UK: Cambridge University Press; 2005. pp. 431

- [62] Tokunaga TK, Wan J, Jung J-W, Kim TW, Kim Y, Dong W. Capillary pressure and saturation relations for supercritical CO<sub>2</sub> and brine in sand: High-pressure pc(Sw) controller/meter measurements and capillary scaling predictions. *Water Resources Research*. 2013;**49**:4566-4579. DOI: 10.1002/wrcr.20316
- [63] Haines WB. Studies in the physical properties of soil: V. The hysteresis effect in capillary properties, and the modes of moisture distribution associated therewith. *The Journal of Agricultural Science*. 1930;**20**:97-116
- [64] Raeesi B, Morrow NR, Mason G. Capillary pressure hysteresis behavior of three sandstones measured with a multistep outflow–inflow apparatus. *Vadose Zone Journal*. 2014;**13**(3)
- [65] Wang S, Tokunaga TK. Capillary pressure–saturation relations for supercritical CO<sub>2</sub> and brine in limestone/dolomite sands: Implications for geologic carbon sequestration in carbonate reservoirs. *Environmental Science & Technology*. 2015;**49**(12):7208-7217
- [66] Pini R, Krevor SCM, Benson SM. Capillary pressure and heterogeneity for the CO<sub>2</sub>/water system in sandstone rocks at reservoir conditions. *Advances in Water Resources*. 2012;**38**:48-59
- [67] Class H, Mahl L, Ahmed W, Norden B, Kuhn M, Kempka T. Matching pressure measurements and observed CO<sub>2</sub> arrival times with static and dynamic modelling at the Ketzin storage site. *Energy Procedia*. 2015;**76**(2015):623-632