Geoelectrical characterisation of CO$_2$–water systems in porous media: application to carbon sequestration

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Abstract
Carbon sequestration is a promising method for the reduction of carbon dioxide (CO$_2$) emissions as it permits the storage of compressed CO$_2$ in the subsurface. The carbon sequestration sites must be monitored to detect potential leaks; one possible method involves the monitoring of geoelectrical properties such as electrical conductivity ($\sigma_b$) and dielectric constant ($\varepsilon_b$). This investigation focuses on using a time domain reflectometry (TDR) sensor to determine the influence of different factors on the measurements of the electrical conductivity ($\sigma_b$) and dielectric constant ($\varepsilon_b$) of a porous rock reservoir in relation to the soil water saturation ($S_w$). The factors investigated were presence of surfactant, salt concentration, pH and rock type which are unique to a given storage site. A number of dynamic two-phase flow experiments were performed using gaseous CO$_2$. It was found that salt concentration, rock type and presence of a surfactant had a notable effect on the $\sigma_b$–$S_w$ and $\varepsilon_b$–$S_w$ relationships. Higher salt concentrations were found to give higher values for $\sigma_b$ and $\varepsilon_b$ for given $S_w$ values. Limestone was found to result in the highest values of both $\sigma_b$ and $\varepsilon_b$ for any given $S_w$, followed by silica and basalt samples. The presence of a surfactant resulted in higher values for $\sigma_b$ at higher $S_w$ values and lower values for $\sigma_b$ at lower $S_w$ values compared to the case when no surfactant was present. Surfactant presence also resulted in lower values for $\varepsilon_b$ at given $S_w$ values. Initial pH values (with silica sand) were found to have no significant effect on the $\sigma_b$–$S_w$ and $\varepsilon_b$–$S_w$ relationships. The measurements of $\sigma_b$ and $\varepsilon_b$ indicate that the use of TDR presents a viable monitoring option. Furthermore, statistical analysis using non-linear regression was carried out on the experimental results and the model shows a good reliability in the prediction of the monitoring process in geological carbon sequestration.

Keywords Time domain reflectometry · Water saturation · Carbon sequestration · Geoelectrical monitoring · Salt concentration · pH · Anionic surfactant

Introduction

Global warming due to anthropogenic greenhouse gas production is widely regarded as one of the major issues threatening the planet (Solomon et al. 2009). One method for reducing excessive atmospheric CO$_2$ emission is carbon capture and sequestration (CCS); a general term for the capture, transport and storage of carbon dioxide from the atmosphere or large emission sources. An effective form of sequestration is geological sequestration, whereby carbon dioxide in gaseous, liquid, supercritical or dissolved form is injected underground into porous rock formations typically at depths larger than 1 km for long-term storage (Ansolabehere et al. 2007). The supercritical conditions of CO$_2$ exist above temperatures of 31.1 °C and pressure of 73.9 bar. Under these conditions, CO$_2$ exhibits properties of both liquid phase and gaseous phase. For example, CO$_2$ will occupy a container like a gas but with liquid density (Petrik and Mabee 2011; Metz et al. 2005).

Notably, suitable formations for CO$_2$ storage include deep saline aquifers, basalts, hydrocarbon reservoirs and unmineable coal seams located at a depth of 800 m or above, where pressures and temperatures of the reservoirs keep the CO$_2$ in liquid or supercritical condition (Franceschina et al. 2015; Metz et al. 2005). If all the sedimentary basins worldwide are considered for CCS, the storage capacity for CO$_2$ in geological formations would be enormous; however, the
acceptability of any specific storage site depends on many features such as proximity to CO2 sources, possibility for leakages and other specific factors such as permeability and porosity (Folger 2009).

It is important to know that for CCS to become a successful climate change mitigation option, it must be possible to securely store CO2 underground for millennia without leakage into the atmosphere; and to ensure that the CO2 is successfully trapped, the reservoir sites must be monitored (Khudaïda and Das 2014; Benson and Cole 2008). Geological CO2 storage can occur through four main trapping mechanisms: physical barriers, capillary forces, solubility trapping, and mineralisation (Ansolabehere et al. 2007; Abidoye et al. 2015; Khudaïda and Das 2014). Although carbon sequestration is an economically and ecologically viable method, the carbon must be effectively trapped to avoid leakages back into the atmosphere or undesirable migration to shallow aquifers via fractures, permeable pathways and nearby penetrable wells, whereby potable water could become contaminated (Abidoye and Das 2015b).

Monitoring techniques can also minimize the risks of CO2 leakage, because it gives early warning of CO2 storage problem, in other words, it quantifies the amount of CO2 storage (Hartai 2012). Many geophysical techniques exist to monitor carbon sequestration (Kiessling et al. 2010; Hovorka et al. 2011).

Geoelectrical characterization of the carbon sequestration presents a simple and non-invasive monitoring method as it can relate the electrical properties of the rock formation to its water saturation (White et al. 2003; Abidoye et al. 2015), which is directly related to the CO2 content of the reservoir. Two main electrical properties exist: the electrical conductivity, σ (a metric for the current induced upon application of an electric field or ability of an aqueous solution to carry electric current) and the dielectric constant, ε (a metric for the electrical polarization induced upon application of an electric field) (Keller 1966; Han 2011). These are suitable parameters for monitoring because of their sensitivity to changes in saturation of the water-CO2 phase (Abidoye and Das 2015a). A time domain reflectometry (TDR) sensor, which is inexpensive and presents a reliable and simple technique to measure both σ and ε, is a potential sensor for the measurement of these parameters as it can be incorporated underground around the area of storage.

It is observed in the literature that seismic method also provides an effective monitoring technique to assess CO2 plume. A repeated seismic survey is important for ensuring both containment and conformance monitoring. Seismic method has been shown to be an excellent monitoring method to quantify small amount of CO2 saturations in the reservoir, but it has been less successful in determining the increase in CO2 saturation (Furrea et al. 2017; Alfia et al. 2019). Electromagnetic and electric methods are also important tools for monitoring CO2. They utilise the electrical and electromagnetic responses from the subsurface to determine the changes in CO2 or water saturations. The methods involve the quantification of electric parameters such as resistivity and conductivity and, determining the correlations such as the Archie expression to relate these parameters to saturations. Methods that use these concepts are the electrical resistivity tomography (ERT), electromagnetic resistivity (ER), electromagnetic induction tomography (EMIT) among others (Ajayi et al. 2019). Dafflon et al. (2012) explained the importance of electrical resistance tomography (ERT) in monitoring the migration of groundwater with dissolved CO2. As the electrical response of rocks is highly independent of the mechanical response, electrical and seismic quantifications provide complementary estimates of CO2 saturation (Daley 2019).

To date, most CO2 sequestration projects involve injecting CO2 in supercritical phase (Metz et al. 2005; Hosa et al. 2010; Abidoye and Das 2015a). Although the storage of CO2 in supercritical form can be safer and more effective, it is important to consider the high cost of compression from gaseous to supercritical phase (Petrik and Mabee, 2011). In addition, the implication of injecting ScCO2 under high pressure during the injection process can cause natural disasters such as earthquakes (Bachu 2000; Metz et al. 2005).

Therefore, this work focused on using both the gaseous and supercritical CO2. Research has shown that gaseous CO2 has been used as an alternative to supercritical CO2 (see, e.g., U.S Department of Energy 2008). Nonetheless, commercial scale of CO2 storage in gaseous form is very unlikely because of its unfavourable risk assessment. This study is also important, because CO2 stored in supercritical condition may leak due to faulty caprock and form a gaseous phase. Therefore, if monitoring sensors are situated at lower depth of the reservoir (i.e., 200–400 m), the sensor can detect the gaseous CO2 when there is leakage. A wide range of geo-electrical monitoring methods have been developed to monitor the movement and storage of injected supercritical CO2 (Rabiu et al. 2017; Abidoye and Das 2015a), yet there is an outstanding need to find out whether this robust tool can track gaseous CO2 efficiently and effectively.

Characteristics of some of the geological rock formations currently used for carbon sequestration have been

| Parameter | Values |
|-----------|--------|
| Porosity  | 0.18–0.30 |
| Depth (km) | 0.6–2.7 |
| T (°C)    | 35–98 |
| P (bar)   | 70–285 |
| Salt conc. w/w % | 5–20 |
| pH        | 5.4–8.1 |

Table 1 - Typical characteristics of deep saline aquifers used for carbon sequestration (Ranganathan et al. 2011; Rempel et al. 2011; De Silva et al. 2015; Metz et al. 2005)
summarised in Table 1. The rock types being investigated are silica, limestone and basalt; with silica and limestone being the most ubiquitous rock types in deep saline aquifers (Bentham and Kirby 2005; De Silva et al. 2015). Basalt is also investigated as it offers the possibility of improving carbon mineralisation and thus provides permanent CO2 storage (Matter and Kelemen 2009; Adam et al. 2011; Rabiu et al. 2017). Therefore, to effectively relate the geoelectrical characteristics to the water saturation, the factors influencing these electrical properties must be properly understood. Previous studies have shown that $\sigma_b$ and $\varepsilon_b$ are influenced by temperature, pressure, rock type, salt concentration, surfactants, permeability, mineralogy and clay content (Rabiu et al. 2017; Abidoye and Das 2015a, b; Han 2011; Magill 2009; Carcione et al. 2012) when injecting liquid or supercritical CO2 into a bed of sand particles. The purpose of this study is to understand how these factors affect the measurements, for which there is currently little data and significant uncertainty as to the extent to which these factors affect these parameters.

The work of Rabiu et al. (2017) characterised CO2 sequestration in silicate, limestone and basalt using geoelectrical properties. But their investigation was limited on liquid and ScCO2 phases. Earlier, the works of Kaszuba et al. (2003) as well as Abidoye and Das (2015a) investigated supercritical CO2 trapping in porous materials. Therefore, it can be concluded that most of the existing publications focus on injecting liquid and supercritical CO2 in porous media. However, the important question concerning whether gaseous CO2 and scCO2 have the same effect on geoelectrical properties remains unanswered. This work explores this gap in knowledge by investigating geoelectrical characterisation of CO2 sequestration during the injection of gaseous CO2.

**Experimental**

**Solutions**

All artificial brine solutions were created with analytical grade sodium chloride (NaCl) salt acquired from Fisher Scientific (Loughborough, UK) and distilled water. For the experiments using surfactant, the brine solution was created using 0.2 g of Plantacare 1200 UP (BASF SE, Ludwigshafen, Germany) to create a 0.02% w/w surfactant solution. Before each experiment, the pH of the saturated sand sample was measured with a pH meter (Fisher Scientific, Loughborough). The first pH measurement of silica sand after saturated with brine water is 6.1 ± 0.2. For the experiments at pH 8.1, the pH of the saturated sand sample was adjusted to pH 8.1 ± 0.2 using 0.02 M NaOH.

**Porous media**

For the success of any CO2 sequestration project, the porous materials must be fully characterised to know whether the reservoir is suitable for the storage. In this work, three porous rock types were tested: silica sand (Minerals Marketing Company, Cheshire, UK), limestone (Tarmac Buxton Lime and Cement, Buxton, UK), and basalt sand (Aqua Maniac, Delaware, USA). The characteristics of porous sample such as porosity and average particle size were determined experimentally and are listed in Table 2. The properties of the silica, basalt and limestone sand were designed to be almost the same but could not be precisely be the same. For example, all the three materials were sieved manually with six sieves of sizes ranging from 762 to 1557 µm to obtain similar average particle size. The porosity of the material was determined by packing sand into a cylinder of known volume and saturating the bed with a measured amount of water. The porosity was then calculated using Eq. 1:

\[
\phi = \frac{V_t - V_s}{V_t} = \frac{V_v}{V_t} = \frac{V_w}{V_t},
\]

where $\phi$ is porosity, $V_t$ is the total volume of a porous media sample, $V_s$ is the volume of solids in the sample, $V_v$ is the volume of openings (voids), and $V_w$ is the volume of water that will occupy the voids space. Before use, the sands were rinsed with distilled water and dried to eliminate any clay content.

**Experimental rig**

A CO2 flow rig (Fig. 1) was designed and constructed in this work. The rig was composed of a bespoke 4 cm high sample holder (i.d. 10 cm) situated in a PID-controlled heating cabinet (West Control Solutions, Brighton, UK) connected to a CO2 syringe pump and controller (Teledyne ISCO Incorporated, Nebraska, USA). The stainless-steel sample holder, composed of a cell and end-pieces at the top and bottom, contained an inlet for CO2 at the top, and an outlet for water at the bottom, lined with a hydrophobic and...

| Parameters | Silica sand | Limestone sand | Basalt sand |
|------------|-------------|----------------|-------------|
| Porosity (%) | 39 ± 0.25 | 40 ± 0.30 | 42 ± 0.30 |
| Average particle size (µm) | 968 ± 253 | 1147 ± 270 | 1016 ± 296 |
hydrophilic membrane, respectively, to prevent water from exiting the top and CO₂ from exiting the bottom (Porvair Filtration Group Ltd, Hampshire, UK). Figure 1 shows a schematic diagram of the experimental setup with the TDR probe (Campbell Scientific Limited, Shepshed, UK) at the centre of the sample holder. Measurements from the probe and the transducers were transmitted to the computer via a datalogger.

Experimental procedure

Before each experiment, a small amount of the relevant brine solution was added to the sample chamber followed by 500 g of the relevant rock particles. The remaining brine was added until the sample was completely saturated and trapped air was removed by gentle pressing. The mass to volume ratio for each of the sand particles sample were ensured to be the same (i.e., 500 g of sand particles sample was used for each experiment). The chamber was sealed via the addition of the lid and tightening of bolts. The CO₂ syringe pump was filled with gaseous carbon dioxide at 55 bar and 23 °C from the pressurized cylinder (BOC gases, Leicester, UK). The temperature was set to 23 °C, and carbon dioxide was released into the chamber via the syringe pump at a flow of 2 mL/min.

The flow rate of exiting brine was mediated to give a low brine flow rate by adjusting the Nitrogen gas back-pressure from a pressurized cylinder (BOC gases, Leicester, UK) using valve V5. Once brine ceased to flow out from the chamber, the experiment was terminated. Before dismantling of the rig, the CO₂ was vented from the chamber through V2. Thereafter, the rock particles were evacuated, washed and recycled for use in further experiments. In addition, the chamber was rinsed with tap water to ensure that all sand particles were removed before subsequent experiments.

Results and discussion

Repeatability of experiments

Figure 2a, shows the reproducibility of results for σₐ and εₐ, respectively. As mentioned in previous study (Abidoye and Das 2015a), σₐ has been found in several studies (Huang et al. 2005; Plug et al. 2007; Keller 1966) to be a function of water saturation. It is inferred that σₐ increases with greater presence of water, because liquid water is a superior conductor of electricity than gaseous carbon dioxide.

Since permittivity (εₑ) of water is greater than the gaseous CO₂ and silica sand (Drnevich et al. 2001), it is this to which the trend shown in Fig. 2b can be attributed to. At high values of water saturation, εₑ is high, in accordance with the high dielectric constant value for water. As the CO₂ concentration within the sample holder increases, due to its high resistance (Breen et al. 2012), the dielectric constant decreases towards that of the silica sand. At the lowest value of water saturation, the dielectric constant approaches the value of 2.5–3.5 for silica sand (Drnevich et al. 2001). Results for dielectric constant show a comparable trend to that obtained by Plug et al. (2007). The maximum percentage difference is 50% but, in their work, they used distilled water; the present work utilised the brine water which is commonly found in the saline
aquifers. However, the maximum percentage of 3% was obtained for the experiment using distilled water (see, e.g., Rabiu et al. 2017).

Effect of salt concentration

As can be seen from Fig. 3a, b, salt concentration has a significant effect on both $\sigma_b$ and $\epsilon_b$. At a given $S_w$, the $\sigma_b$ is greater for higher salt concentrations, since $\sigma_b$ is a function of the concentration of ions present (Singha et al. 2012; Coury 1999). The difference between the conductivities at greater $S_w$ becomes more pronounced.

At a given $S_w$, $\epsilon_b$ is greater for higher salt concentrations. This is attributed to the presence of more ions; therefore, greater polarization induced when an electric field is applied. As can be noted from Fig. 3b, significant fluctuations are present within the $\epsilon_b$–$S_w$ curves. There is more fluctuation in $\epsilon_b$ at higher salt concentration making it impossible to find the values of $\epsilon_b$ as the $S_w$ approaches 1 for the 2% and 5% solutions. This can be explained by the large concentration of ions (and thus their increased mobility) interfering with the TDR dielectric constant measurements. Hu et al. (2011) discovered that this effect can be mitigated by coating the TDR probe with an insulating layer. There is little difference between the results for 0.5% and 2% salt concentration, especially at lower $S_w$. However, there is a sizeable difference between 5 and 2% salt concentrations, suggesting that the relationship between $\text{pH}$ and $\epsilon_b$ is not linear. Sea water has an average salinity of approximately 3.5% (http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/seawater.html), which is comparable to the concentrations used in the experiment. The values of approximately 5.3 S/m (Bullard, 1995) and 70–80 (Fores, 1999) for $\sigma$ and $\epsilon$ of seawater, respectively,
are in the same order of magnitude as the values obtained at maximum $S_w$.

As can be seen from Fig. 4a, b showing the effect of pH on the $\sigma_b$–$S_w$ and $\varepsilon_b$–$S_w$ curves, a change in the initial pH of the brine solution has no significant impact. Although $\sigma_b$ at $S_w = 1$ at pH 8.1 is slightly higher than $\sigma_b$ at pH 6.1 ($3.5 \pm 0.5$ S/m vs $4.6 \pm 0.4$ S/m), this difference is due to the increased ion concentration due to the higher pH. For both the $\sigma_b$ and $\varepsilon_b$, a significant difference in results was expected by changing the pH of the solution.

Effect of pH

It has been reported that alkaline pH favours the reactions in mineralisation (Druckenmiller and Mercedes Maroto-Valer 2005: Matter et al. 2007), hence reducing the ion concentration within the sample holder. As no changes in $\sigma_b$ were recorded, it can be assumed that no mineralisation reactions occurred. This is due to the fact that the ions typically required for CO$_2$ mineralisation (i.e., Ca$^{++}$, Mg$^{++}$, Fe$^{++}$, K$^+$) are not present within the solution (De Silva et al. 2015). In addition, the absence of mineralisation can also be attributed to the limited duration of the experiment, since mineralisation occurs over a longer period.

Effect of rock type

As can be seen from Fig. 5a, b, the rock type present in the sand body has a significant effect on both the $\sigma_b$ and $\varepsilon_b$ curves. While $\sigma_b$ in Fig. 5a is relatively similar for silica and basalt, sizeable differences are noticed in the limestone. At $S_w = 1$ the average $\sigma_b$ for limestone ($4.9 \pm 0.8$ S/m) is significantly higher than for silica or basalt sand ($3.7 \pm 0.5$ S/m and $3.6 \pm 0.6$ S/m, respectively). This trend is observed throughout the $S_w$ range (at 30% water saturation, the limestone
curve is above the silica and basalt curves). This effect can be explained by the fact that $\sigma_b$ for limestone is higher than that of silica (Duba, et al. 1978) and basalt sands (Hyndman and Drury 2007). Abidoye and Das (2015b) attribute the heightened $\sigma_b$ of the limestone to the dissolution of limestone in water and thereby increased concentration of dissolved ions (Plan 2005; Assayag, et al. 2009). Figure 5b shows the relationship between $\varepsilon_b$ and $S_w$ for the different rock types. As with the $\sigma_b$ curve, $\varepsilon_b$ for limestone is consistently higher than that for silica and basalt. This was also observed by Abidoye and Das (2015b). This is consistent with the bulk $\varepsilon_b$ values for the rocks (Dutta and De 2007; Martinez and Byrnes 2001; Rust et al. 1999; ElShafie and Heggy 2012). The difference in dielectric properties can be attributed to their chemical constituents (Abidoye and Das 2015a).

Nelson and Trabelsi (2012) state that the factors which influence the permittivity of the material include density, porosity, pore structure, material composition and signal frequency. However, since the porosity measurements of the materials were very similar (see Table 2), it can be argued that these do not affect $\varepsilon_b$.

**Effect of temperature**

Storing $\text{CO}_2$ in supercritical condition is generally acceptable because of its favourable properties (i.e., water related density and gaseous viscosity) which can make it to store significant amount of $\text{CO}_2$ (Metz et al. 2005; Petrik and Mabee 2011). Besides, it is safer to store $\text{CO}_2$ in supercritical phase, because it minimises the effect of leakage during buoyancy (Khudaida and Das 2014; Metz et al. 2005). However, a perturbation in the temperature of the reservoir can change the $\text{CO}_2$ phase completely, either into gaseous or liquid phase and this can have an effect on geoelectrical properties during the monitoring process. This work investigated the temperature effect on the $\sigma_b$–$S$ and $\varepsilon_b$–$S$ relationship and the results are displayed in Fig. 6a, b, respectively. It is observed that the $\sigma_b$ and $\varepsilon_b$ rise as the temperature increases in silica sand system. Similarly, the work on the effect of temperature on geoelectrical properties and water saturation relationship has been carried out on silica, basalt and limestone sand by injecting liquid and supercritical $\text{CO}_2$ (Rabiu et al. 2017; Abedian and Baker 2008; Or and Wraith 1999; Abidoye and Das 2015a). Gaseous $\text{CO}_2$ was injected in the current work, because it is assumed that a change in the $\text{CO}_2$ phase might have an effect on the geoelectrical properties. The results in Fig. 6a show an increasing trend in temperature as the electrical conductivity ($\sigma_b$). A similar trend was noticed in the work of Rabiu et al. (2017) and Abidoye and Das (2015a) but in their work, liquid and supercritical $\text{CO}_2$ phases were used. This can be attributed to the increase in the mobility of ions at high temperature. In addition, an increase in temperature results in an increase in dielectric permittivity ($\varepsilon_b$), and this can be related to the bound water released during the experiment (Abidoye and Das 2015a).

**Effect of surfactant**

In addition to being used in enhanced oil recovery, surfactants are also used in carbon sequestration to improve displacement efficiency and aqueous solubility of carbon (Magill 2009). As can be seen from Fig. 7a comparing the $\sigma_b$–$S_w$ curves for systems with and without surfactant, the presence of surfactant has a substantial effect on $\sigma_b$. At $S_w = 1$, $\sigma_b$ with surfactant is higher than with no surfactant ($6 \pm 0.4 \text{ S/m} \text{ vs} \ 3.8 \pm 0.4 \text{ S/m}$), likely due to the presence of additional ions in the solution. However, at $S_w < 0.75$,.

![Fig. 6](image-url)
σₜ with surfactant is lower than without surfactant. It could be hypothesized that it is related to the reduced mobility of the ions caused by presence of large surfactant molecules increasing the viscosity of the brine solution (Jewell et al. 2015; Wu et al. 2014).

The εₛ−Sₛ curve with surfactant shown in Fig. 7b is consistently below the εₛ−Sₛ without surfactant. This can be explained by the increased viscosity of the surfactant solution. This would increase resistance to the molecules lining up in response to the application of an electric field, resulting in reduced polarity. The experiments with higher concentration of surfactant have some limitations, for example, there is excessive foam which affects the accuracy of σₛ−Sₛ and εₛ−Sₛ relationships.

Comparison between gaseous CO₂ and ScCO₂

Carbon capture and sequestration is a viable technology to avert the problem of CO₂ emission from fossil fuel. However, more knowledge is required to fully understand the behaviour of the subsurface during geological storage of carbon dioxide. Ideally, CO₂ is stored in supercritical phase due to its favourable properties (i.e., higher density and viscosity). A significant amount of CO₂ is stored in this form in comparison to the injection of gaseous CO₂. On the other hand, the compression of gaseous CO₂ into supercritical CO₂ is very expensive. Besides, the high pressure of the supercritical CO₂ injection can affect the earth surface and consequently cause earthquakes (Bachu 2000; Metz et al. 2005). While the majority of CO₂ sequestration and monitoring processes have been carried out in supercritical condition.
(Rabiu et al. 2017; Abidoye and Das 2015a, b; Metz et al. 2005), there is a possibility of monitoring the gaseous CO₂ in the subsurface. Recently, Lamert et al. (2012) explored the monitoring of gaseous CO₂. In their work, gaseous CO₂ was injected into the subsurface for monitoring purposes. Figure 8a, b shows the $\sigma_b$–$S_w$ and $\varepsilon_b$–$S_w$ curves for systems with gaseous and ScCO₂. The $\sigma_b$–$S_w$ curve is higher in supercritical condition than in gaseous form. This effect can be attributed to the phase change and higher temperature in the supercritical phase. However, the $\varepsilon_b$–$S_w$ curve shows no significant difference between ScCO₂ and gaseous CO₂, although a slight increase is observed in supercritical phase when compared with gaseous phase. In the future work, high pressure and temperature will be used for ScCO₂ which will provide significantly different experimental conditions allowing analysis in a much broader range of conditions.

**Regression of experimental data**

The dielectric permittivity ($\varepsilon$) of air, sand particles and water are 1, 3 and 80, respectively. The differences in these values cause the bulk dielectric permittivity to be related to water saturation (Abidoye and Das 2015a; Rabiu et al. 2017). The experimental results from this study were fitted to Archie’s law (Archie, 1942). The equation is written as follows:

$$\sigma_b = \frac{s^n \sigma_w}{b^m},$$

(2)

where $S$ is the water saturation, $b$ is the sand porosity, $\sigma_b = \text{bulk conductivity}$, $\sigma_w = \text{the brine conductivity}$, $n$ is the saturation exponential and $m$ is the cementation exponential.

From the above Eq. (2), exponent $m$ and $n$ can be deduced using non-linear regression statistical analysis. The analysis was used to fit the value of $m$ and $n$ for each of the porous materials studied (silica, basalt and limestone). The logarithm linearization of Eq. (2) is shown in Eqs. (3) and (4):

$$\log \sigma_b - m \log b = \log \sigma_w + n \log S$$

(3)

$$n \log S + m \log b = \log \sigma_b - \log \sigma_w.$$  

(4)

The values of the exponents $m$ and $n$ for silica, basalt and limestone using Minitab statistical analysis are shown in Table 3.

The $m$ and $n$ values from the non-linear regression using the Minitab statistical software (Microsoft 2016) are in agreement with previous studies (see, e.g., Scudiero et al. 2012; Wang et al. 2014; Abidoye and Das 2015a; Rabiu et al. 2017; Liu and Moysey 2012). It can be deduced that Archie’s equation can be used to predict the experimental results.

Moreover, the statistical software was used to predict the value of dielectric permittivity ($\varepsilon_b$). The value of $\varepsilon_b$ is paramount, because it characterizes the degree of water saturation in the sand system. The bulk dielectric permittivity, $\varepsilon_b$ is, therefore, can be written as

$$\varepsilon_b = f(S, P, T, i),$$

(5)

where $S$ is the water saturation, $P$ is the pressure, $T$ is the temperature, and $i$ is the initial value of $\varepsilon_b$ before CO₂ injection.

The non-linear regression polynomial model equation is generated from experimental results using Minitab statistical software. The equation is shown in Eq. (6):

$$\varepsilon_b = -699.547 + 86.470S + 55.992T$$

$$+ 1.743P - 13.475i - 8.103S^2$$

$$- 1.015T^2 - 0.024P^2 + 0.244i^2.$$  

(6)

The regression results in using Eq. (6) are shown in Fig. 9a, b. The figures reveal that the model provides a good match for the experimental data, because most of the data are fitted accurately (coefficient of correlation ($R^2$) in Figs. 9a, b are 0.8570 and 0.8295, respectively). In particular Eq. (6) shows that $\varepsilon_b$ (and hence, CO₂ saturation) can be estimated based on four common measurable quantities of the geological formation, namely, saturation, temperature, water pressure and initial $\varepsilon_b$. Simple approximation of the process such as in Eq. (6) can help take managerial decisions faster and accurately. They also offer cost benefits over other complex methods of gathering the required information on the real process. It is, therefore, envisaged this model can be used to predict the behaviour of CO₂ in subsurface during CO₂ sequestration.

**Conclusions**

The effect of different factors on $\sigma_b$–$S_w$ and $\varepsilon_b$–$S_w$ relationships in porous rock media were investigated using a TDR probe. Salt concentration, rock type and presence of surfactant had an observable effect on the relationships; however, different initial values of pH (with silica sand) produced no significant change. Higher salt concentrations were shown to result in higher $\sigma_b$ and $\varepsilon_b$ values for a given $S_w$, which was attributed to the greater number of ions present. For any given $S_w$, limestone was found to give higher values of both $\sigma_b$ and $\varepsilon_b$, followed by basalt and silica, respectively. For $\sigma_b$, this can be explained by a greater level of

### Table 3: Exponents m and n values for silica, basalt and limestone (Archie 1942)

| Porous media | m (-) | n (-) |
|--------------|-------|-------|
| Silica       | 1.701 | 1.768 |
| Basalt       | 1.260 | 1.559 |
| Limestone    | 1.296 | 1.132 |
dissociation of the rock, resulting in a greater number of ions in solution.

In the case of $\varepsilon_b$, the difference can be attributed to their respective chemical compositions. Presence of surfactant resulted in lower $\sigma_0$ values at lower $S_w$ values and higher $\sigma_b$ values at higher $S_w$ values compared with solution absent of surfactant. $\varepsilon_b$ values were found to be lower in the presence of surfactant at any given $S_w$. These differences can be attributed to the increase in viscosity due to the surfactant. Although change in initial pH was found to produce no discernible change in the relationships with silica sand, it was hypothesized that an effect could be observed with a different rock type.

This work contributes to the understanding of the effect of salt concentration, pH, rock type and surfactant presence on $\sigma_0^{-}S_w$ and $\varepsilon_b^{-}S_w$ relationships. Measuring $\sigma_0$ and $\varepsilon_b$ is a viable option for monitoring CO$_2$ storage sites, and consequently understanding how these geoelectrical parameters relate to $S_w$ is essential. This enables an estimate to be made from the measured geoelectrical parameters, which in turn relates to the CO$_2$ content of the storage site. Therefore, by monitoring the geoelectrical characteristics, changes in CO$_2$ content indicative of leakage can be detected. The Archie equation was used to predict the experimental results and the outputs were corroborated with previous studies. Finally, a fit regression analysis was carried out on the experimental results and the model reveals a good reliability in the prediction of monitoring process in geological carbon sequestration.

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