Geo-electrical Characterisation for CO_2 Sequestration in Porous Media

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Running title: **Monitoring CO_2 Stored in Silicate, Carbonate and Basalt Media**

Abstract

Developing monitoring strategies for the detection and monitoring of possible CO_2 leakage or migration from existing and anticipated storage media are important because they can provide an early warning of unplanned CO_2 leakage from a storage site. While previous works have concentrated on silicate and carbonate porous media, this work explores geoelectrical techniques in basalt medium in a series of well-defined laboratory experiments. These were carried out to identify the key factors which affect geoelectrical monitoring technique of CO_2 in porous media using low cost and efficient time domain reflectometry (TDR). The system has been set up for simultaneous measurement of the bulk electrical conductivity and bulk dielectric permittivity of CO_2-water-porous media system in silica sand, basalt and limestone. Factors investigated include pH, pressure, temperature, salinity, salt type and the materials of the porous media. Results show that the bulk electrical conductivity and dielectric permittivity decrease as water saturation decreases. Noticeably, electrical conductivity and permittivity decrease due to the changes in water saturation and the relationship remains the highest in limestone except at the start of the experiment. Also, an increase in temperature, pressure and salinity tend to increase the bulk electrical conductivity (σ_b) and permittivity (ε_b) of the CO_2-water-porous media system during the drainage experiment. On the other hand, pH and concentrations of different types of salt do not seem to have significant effect on the geoelectrical characteristics of the system. It was evident that Archie's equation fit the experimental results well and the parameters obtained were in good agreement with those in the literatures. The regression shows a good reliability in the prediction of electrical properties during the monitoring process of CO_2 sequestration.

Keywords: pH, electrical conductivity, dielectric permittivity, CO_2 leakage, water saturation.

1 Introduction

Carbon dioxide is known to be a major contributor to the greenhouse effect. It causes excessive heating of the earth's atmosphere and, thus, contributes to the global climate change (Abidoye et al. 2014; Aliakbar et al. 2016; Mariyamma et al. 2015; Terzi et al. 2014). CO_2 emissions from various sources such as power generation plants and automobiles have increased by more than 30 percent over the last decades (Bachu 2000; Metz et al. 2005; Shalek 2013; Socolow et al. 2004). Therefore, the removal of the emitted CO_2 is important to prevent the environmental disaster such as change in precipitation patterns, the rise in sea levels, polar caps disruption, and acidic oceans (Adefila and Yong 2013; Mariyamma et al. 2015). The approach of carbon capture and sequestration (CCS) has been suggested to be one of the most promising ways of reducing the present level of this emission into the atmosphere (Abidoye et al. 2014; Folger 2009; Kilgallon et al. 2014; Metz et al. 2005). Other methods include use of energy efficient system and renewable energy but these techniques have been suggested to be less-effective when compared to CCS (Abidoye and Das 2015a; Alvarez 2014).

The CO_2 storage using CCS can be grouped into three categories: (i) geological storage; (ii) mineralization; and (iii) ocean storage. The CO_2 geological storage (CGS) is considered as a promising CO_2 sequestration method in developed countries; the geological formation includes deep saline aquifer, unmineable coal deposits, depleted and mature oil and gas reservoirs while the mineralization process is the conversion of CO_2 into solid inorganic carbonates during the reaction of CO_2, brine and rock minerals. Mineralization method provides permanent storage of CO_2; however, the conversion of CO_2 into solid carbonate is very slow while the high cost of implementation is a concern (Druckenmiller and Maroto-Valer 2005).

The major problem of CO_2 storage in geological aquifer is the possible risk of CO_2 leakage from the storage reservoir to shallower potable-water aquifer, which consequently may become a threat to the living organisms (Abidoye and Das 2015b; Dafflon et al. 2013). The leakage may be as a result of detrimental permeability pathways around the well or faulty caprock (Abidoye and Das 2015b). But, if the reservoir is well characterised before CO_2 is injected, the problem of leakages could be minimised. Khudaida and Das (2014) reported that injecting supercritical CO_2 into porous formations would minimise CO_2 leakage during geological sequestration of CO_2, because storing CO_2 in supercritical phase will reduce the buoyancy, since the density of supercritical CO_2 will be similar to that of brine (Khudaida and Das 2014). Also, monitoring of CO_2 storage site before, during and after injection is very important for any CCS project (Kilgallon et al. 2014) because this can provide an early warning of unplanned CO_2 leakage from a storage site.

In the context of monitoring CO_2 sequestration, simultaneous measurement of electrical conductivity and dielectric permittivity can provide accurate early warnings for the presence of CO_2 in the water bodies, because an increase in CO_2 concentration signals a decrease in geoelectrical properties (i.e., dielectric permittivity and electrical conductivity) as compared to pure water (Abidoye and Das 2015a; Abidoye and Das 2015b). Previous works have been conducted on the geoelectrical characterizations of CO_2-water/brine flow in porous media (see, e.g., Abidoye and Das 2015a; Abidoye and Das 2015b; Lamert et al. 2012; Dethlefsen et al.

2013); however, these investigators did not exhaust the interplay of different factors that can affect the behaviour of bulk electrical conductivity (σ_b) and bulk dielectric permittivity (ε_b) of the fluid-fluid-solid system (i.e., CO_2-water-porous media system) in porous media, especially in basalt medium. These factors include pressure and temperature of the system, in-situ fluid salinity, materials of the porous medium, chemical characteristics of the in-situ salt (brine) and soil pH.

Majority of the previous work on geophysical monitoring techniques utilised seismic methods, electrical resistivity, borehole geophysics (see, e.g., Wagner 2016; Lamert et al. 2012; Schmidt-Hattenberger et al. 2011; Bergmann et al. 2011; Borner et al. 2015). A limited number of laboratory studies have focused so far on studying the effects of important parameters such as temperature, salt composition, pH, fluid pressure and salinity on the monitoring techniques in basalt, using bulk electrical conductivity (σ_b), dielectric permittivity (ε_b) and their respective relationships with water saturation (S_w). While geo-electrical monitoring techniques can provide an efficient and effective monitoring method (Lamert et al. 2012; Abidoye and Das 2015a; Abidoye and Das 2015b), other geophysical monitoring techniques such as seismic are time consuming and expensive (Zhang 2013).

Furthermore, the work of Wang and Tokunaga (2015) characterised CO_2 distribution, trapping and leakage potential using capillary pressure - saturation relations. But their investigation was conducted on limestone medium. Earlier, the works of Pentland et al. (2011) as well as Zuo and Benson (2014) investigated CO_2 trapping in quartz-rich medium (sandstone). Similarly, the works of Abidoye and Das (2015a, b) were based on silicate and carbonate media. Thus, it can be inferred that most of the existing publications concentrate on silicate and carbonate porous media. Meanwhile, Wang and Tokunaga (2015) are of the opinion that mineral contents of the porous media determine the trapping capacity of the medium during geological carbon sequestration. Basalt primarily consists of magnesium and calcium silicate minerals which provide divalent metal cations necessary for the formation of solid carbonates (Matter and Kelemen 2009; Snæbjornsdottir and Gislason 2016).

Therefore, question may be asked as to how basalt medium will affect CO_2 distribution, trapping and leakage potential during geological carbon sequestration? This work explores this gap in knowledge by investigating geoelectrical characteristics of CO_2-brine-porous medium system in basalt medium as well as silicate and carbonate porous media.

This work determines the effects of temperature, pressure, pH, salinity, salt types and porous material on geoelectrical characteristics of the CO_2-water-porous media system at high pressure and temperature relevant to geological carbon sequestration. In addition to examining the influence of porous media on the characteristics of CO_2–brine-porous media system, this work also aims to investigate how inexpensive and effective time domain reflectometry (TDR) could be used as tool for early detection of CO_2 migration in an engineered CO_2 storage reservoir.

2 Methodology

The laboratory experiment was designed to monitor the CO_2 level in porous media such as silica sand, limestone and basalt. The characteristics of the samples used are described in Table 1. The relationship between geo-electrical properties, i.e., bulk electrical conductivity and bulk dielectric permittivity (σ_b and ε_b) and water saturation (S_w) makes it possible to monitor the amount of CO_2 in the storage reservoir (Knight 1991, Abidoye and Das 2015a). Geological conditions of CO_2 storage reservoirs, i.e., at high pressure and temperature relevant to geological conditions, are to be mimicked in the experiments. The effects of various parameters such as pressure, temperature, salt types, salt concentration, pH and porous material on the geo-electrical monitoring performance were investigated.

Geo-electrical measurement techniques made use of locally fabricated three-pin time domain reflectometry (TDR) probe and measured both dielectric permittivity and electrical conductivity, simultaneously. TDR can measure electrical parameters simultaneously and was employed to acquire in-situ laboratory experimental data on σ_b and ε_b, for CO_2-brine-porous media system in analogy to geological CO_2 sequestration in brine aquifer. In-situ experimental data acquired by the TDR were automatically transferred to the data acquisition system (CR10X datalogger, Campbell Scientific Ltd, Shepshed, UK).

2.1 Materials and Methods

This work investigated three unconsolidated sand samples: silica sand (Minerals Marketing Company, Cheshire, UK), basalt sand (Aqua Maniac, Delaware, USA) and carbonate sand (limestone) (Tarmac Buxton Lime and Cement, Buxton, UK). The physical properties such as porosity, density, permeability, and average particle size of each mentioned porous materials were determined experimentally and are listed in Table 1. SEM (Zeiss 1530VP) images were taken before the experiment to examine surface morphology and roughness of the porous materials used. As shown in Figure 1, basalt sand has hexagonal shape; limestone has round shape while silica sand is more angular. All the sand materials were washed with tap/deionised water to remove excessive clay content.

Table 1 Characteristics of the porous media used in the experiments

Parameters	**Silica Sand**	**Carbonate sand**	**Basalt Sand**
Porosity (%)	39±0.25	40±0.30	42±0.30
Intrinsic permeability (mD)	84±0.60	50±0.20	80±0.30
Average particle size (µm)	968±253	1147±270	1016±296

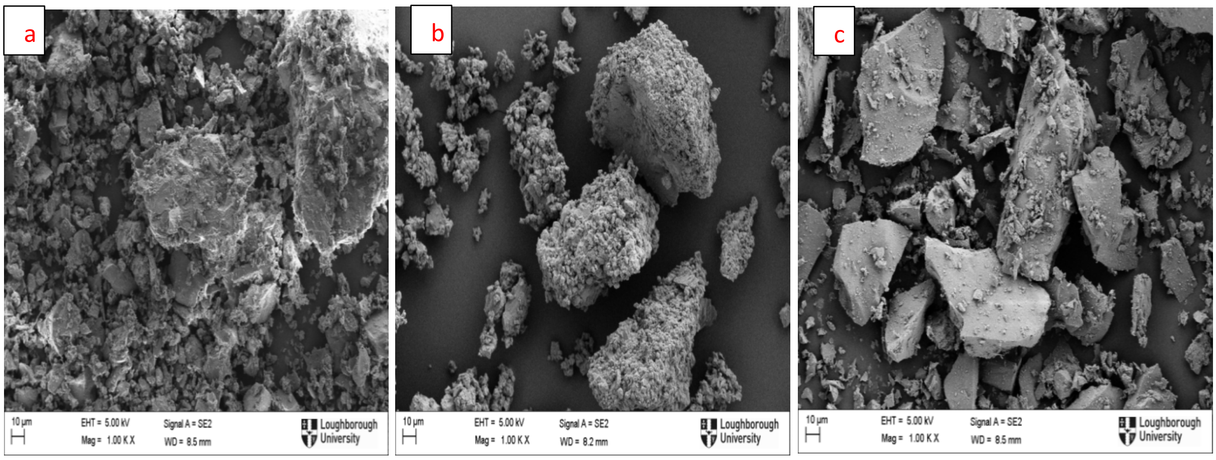


Fig. 1 Scanning electron microscope (SEM) images of: (a) Basalt; (b) Limestone; and (c) Silica sand particles

2.2 Set-up of the Experimental Rig

The time domain reflectometry (TDR) equipment consists of three-pin probes which are held together with high temperature polytetrafluoroethylene (PTFE) that can withstand high pressure and temperature experimental conditions. The TDR probes cable was connected to a multiplexer that was attached to TDR100 reflectometer (Campbell Scientific Ltd, Shepshed, UK) and connected to CR10X datalogger (Campbell Scientific Ltd, Shepshed, UK). The 12V and 50 Hz dual rail power supply (Rapid Electronics Ltd, Essex, UK) supplied power to the CR10X datalogger. The data-acquisition system was connected to the desktop computer into which data were stored automatically from the TDR probes that were inserted into the porous material during the experiment. Before the start of any experiment, the TDR device was calibrated using Campbell Scientific Instruction manual and the acquired readings from the calibration were used in developing the program. This program was used by the TDR 100 reflectometer to communicate with the datalogger. Figure 2 shows a schematic diagram of the experimental rig used in this work. The pressure transducers (PTs) and the time domain reflectometry (TDR) probe were attached to the centre of the stainless steel cell (porous medium holder). The PTs measured the in-situ system pressure while the TDR measured the geo-electrical properties of the saturated sand. The stainless steel chamber holding the saturated porous material was positioned in the heating cabinet having PID temperature controller (West Control Solutions, Brighton, UK) to regulate the system temperature. The steel sample holder had dimensions of 4 cm height and 10 cm diameter with top and bottom end-pieces that were made of stainless steel. The inner part of the top end piece was overlain with hydrophobic polytetrafluoroethylene, PTFE (0.1 µm) and the bottom end piece with hydrophilic nylon (1 µm). The membranes were obtained from Porvair Filtration Group Ltd (Hampshire, UK). It has been reported that a hydrophilic membrane minimizes $scCO_2$ escape from the bottom of the sample holder, while hydrophobic membrane was used to reduce the inflow of water into the $scCO_2$ pump (Abidoye and Das 2015a).

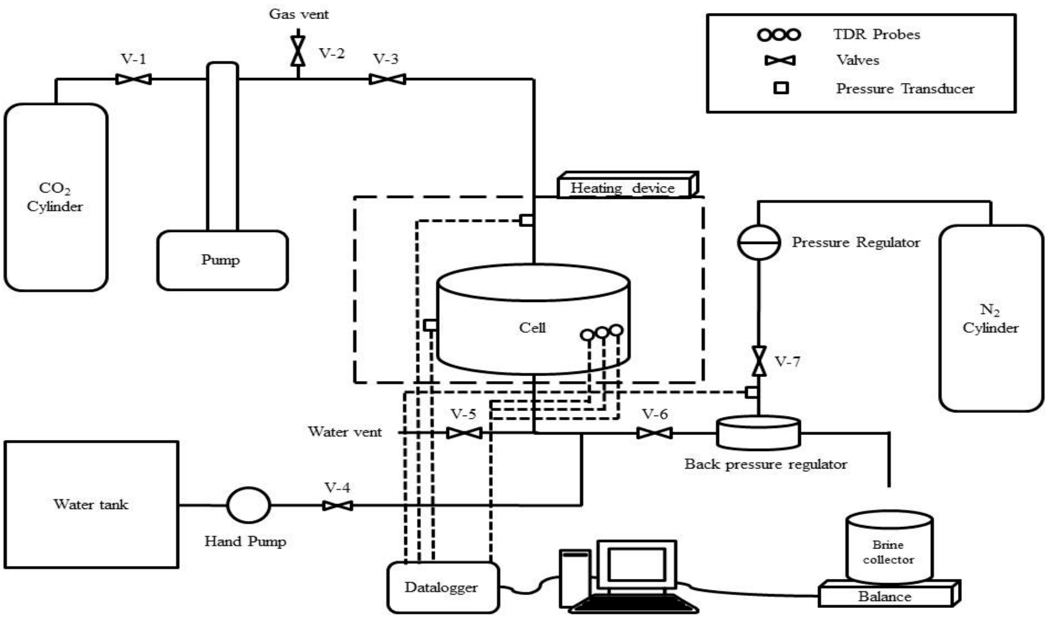


Fig. 2 A schematic diagram of the experiment rig

Moreover, a metering valve (Swagelok, Kings Langley, UK) was used for smooth flow control of water/brine from the experimental rig into the water collector situated on the measuring weigh balance. Back pressure regulator (BPR) (Equilibar, Fletcher, USA) was also connected to the system and this maintained the system by stabilizing the outflow of the water/brine at the set pressure. The back pressure regulator was loaded with nitrogen gas from a nitrogen cylinder (BOC gases, Leicester, UK).

2.3 Experimental Methods

All experiments were conducted in a fabricated stainless steel of 4 cm height and 10 cm diameter. The sample holder was placed on the bottom end piece with overlaying of the hydrophilic membrane and tightens the bolt firmly to avoid leakage. Brine water is prepared in the laboratory by mixing distilled water and sodium chloride salt obtained from Fisher Scientific (Loughborough, UK). For other salt, namely, magnesium chloride (Fisher Scientific, Loughborough, UK) used in this work, a similar procedure was observed. Equation (1) was used for preparing solutions of different brine concentrations. The salt concentrations used in this work were 0% w/w, 0.5 %w/w and 2 % w/w, respectively.

$$\% w/w = \frac{mass\ of\ solute}{mass\ of\ solution} \times 100 \qquad (1)$$

Small quantity of brine water was poured into the domain and the measured sand was passed through a metal sieve of appropriate size. Same quantity of sand (500g) was used in all the experiments. Thereafter, more brine water was added to make the porous media saturated. It was ensured that the sand was well compacted and the cell was covered by the stainless steel top end piece overlain with the hydrophobic membrane. All the joint bolts were tightened very well to avoid any leakage during the experiment. Before starting each experiment, the pH of brine water collected from saturated porous media was measured with a pH meter (Jenway, Fisher Scientific, Loughborough). For example, the initial pH of saturated basalt sand is 6.5±0.2. For the experiments at different pH, i.e., pH 12, the pH of the saturated rock media was adjusted to pH 12.0±0.2 using 0.02 M NaOH. Carbon dioxide (99.9% purity) used in this work was purchased from BOC gases (Leicester, UK). The $ScCO_2$ fluid pump (Teledyne Isco, Lincoln NE) was set to refill mode and filled with liquid CO_2 from the CO_2 cylinder by opening valve 1 (V-1; Figure 1). Afterward, V-1 was closed and the $ScCO_2$ fluid pump was set to the experimental pressure. The heater was switched on and also set at the experimental temperature. When temperature and pressure reached the predetermined values, i.e., when there was equilibrium in experimental condition (both temperature and pressure), V-3 and V-6 were opened (see Figure 1) and the displacement of brine began by CO_2. The experiment was stopped when there was no more brine coming out of the porous media sample in the sample holder (steel cell). Then, the porous media sample was removed from the cell for subsequent experiment. The sand removed from the cell was recycled by washing it with large volume of tap or deionized water. Table 2 shows the experimental conditions that mimic the geological conditions in which CO_2 is being stored.

Table 2 Experimental conditions that were utilized in this work

S/n	Pressure (bar)	Temperature (^{0}C)	CO_2 Phase
1	65	23	Liquid CO_2
2	75	23	Liquid CO_2
3	75	35	$ScCO_2$
4	90	35	$ScCO_2$

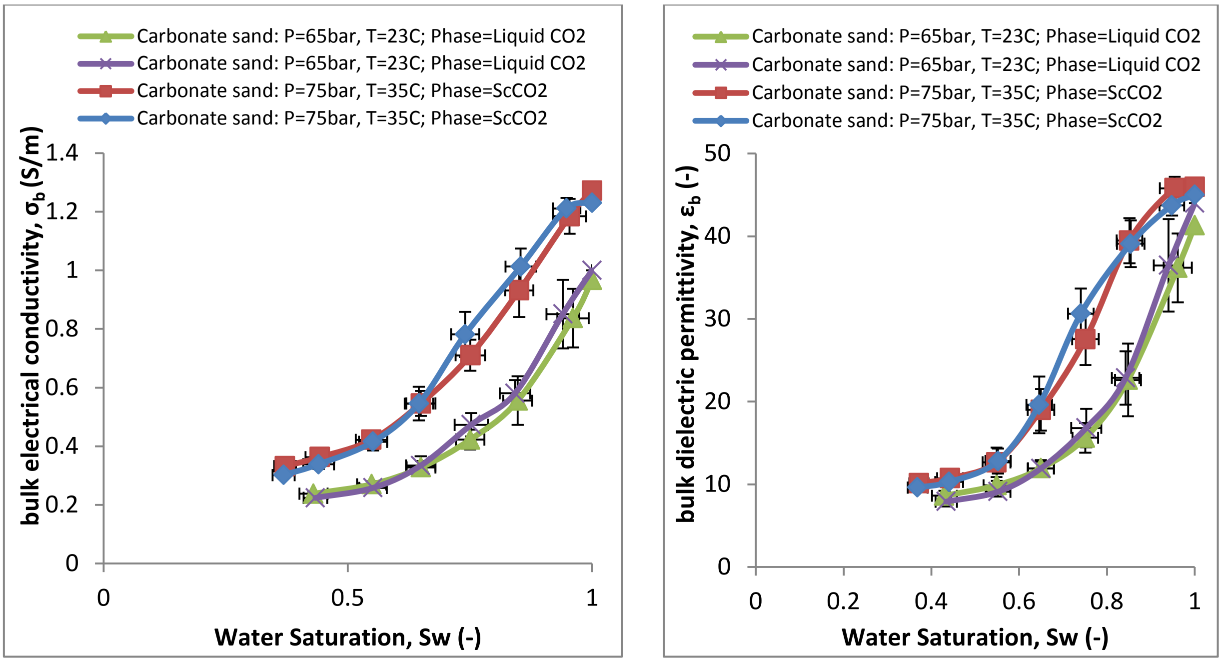
3 Results and Discussion

3.1 Electrical Conductivity and Dielectric Permittivity

Electrical conductivity and dielectric permittivity have functional relationships with water saturation (Plug et al. 2007; Abidoye et al. 2014; Abidoye and Das 2015a) and these can be used in monitoring the quality of fluids in the reservoir.

Our study focused on the effects of salt types, pH, porous material, salinity, pressure and temperature on the geoelectrical characteristics of CO_2-brine-porous media system. The results of various factors investigated in connection with the σ_b-S and ε_b-S relationships for $scCO_2$-brine-porous media system are discussed below.

Figures 3a and 3b show that the experiments are repeatable under different injection conditions corresponding to both liquid CO_2 and supercritical CO_2. The figures show results from two separate measurements for σ_b-S and ε_b-S relationships under similar conditions for both liquid CO_2 and $scCO_2$. The figures further show that the ε_b-S and σ_b-S relationships are functions of water saturation as indicated by the fact that they decrease as the water saturation reduces. For the σ_b-S relationship (Figure 3a), the decrease in σ_b-S relationship might be as a result of water being a better conductor of electricity than CO_2. For the case of ε_b-S relationship (Figure 3b), the decrease in permittivity and water saturation trend should be connected with the high permittivity of water compared to CO_2 (Drnevich et al. 2001).

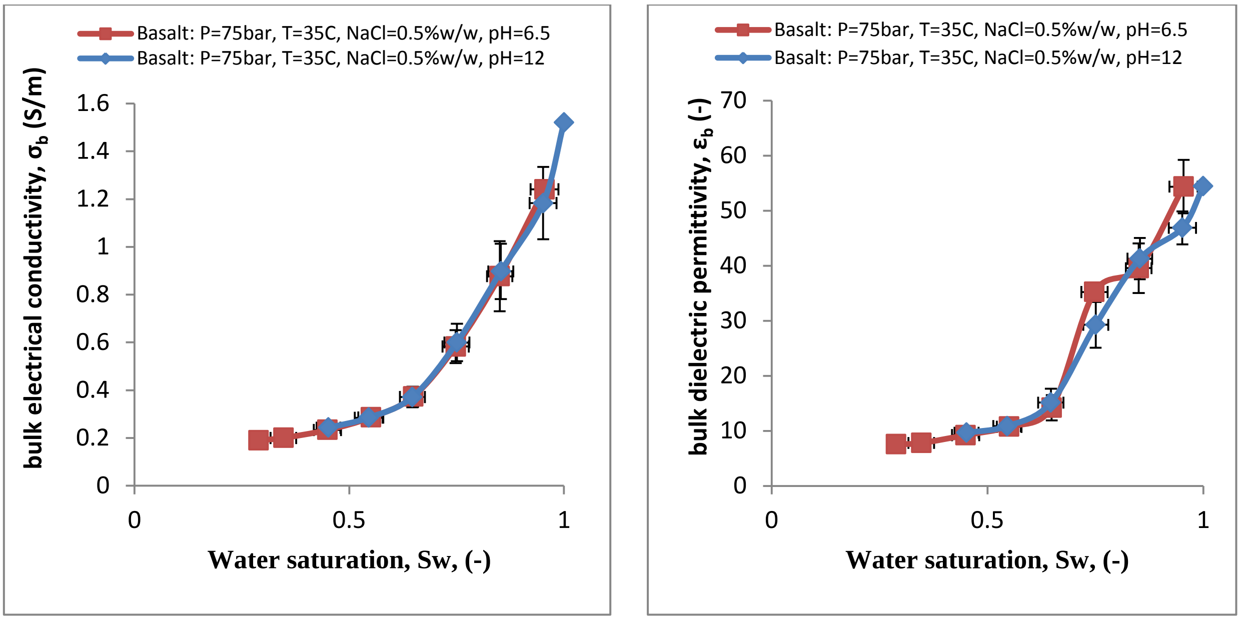


(a) **(b)**

Fig. 3 Repeatability plot for (a) σ_b–S and (b) ε_b–S relationships for liquid CO_2 / $ScCO_2$ – water - carbonate sand system

3.2 Effect of pH on Geo-electrical Properties

It has been reported that pH has effects on mineralisation (Druckenmiller and Maroto-Valer 2005; Liu and Maroto-Valer 2011). High pH is considered to speed up the mineralisation and it can be expected that this will affect the geoelectrical properties of the system. However, our work shows that there is no significant effect of pH. This is probably owing to the short time of the experiment during which significant mineralisation might not have occurred. Presumably, if the experiment was left for longer period of time, there might be a significant effect of mineralization and change in pH on the measured geoelectrical characteristics of CO_2-water-porous media system. Figures 4a, b display the results of pH effects on the σ_b-S and ε_b-S relationships in basalt sand. At different pH values, e.g., 6.5 and 12, pH does not have any significant effect on the ε_b-S and σ_b-S relationships. Although, according to Abidoye and Das (2015b), pH has effect on conductivity under static conditions, when dissolution is higher, but the flow condition in this work does not reveal similar effect.

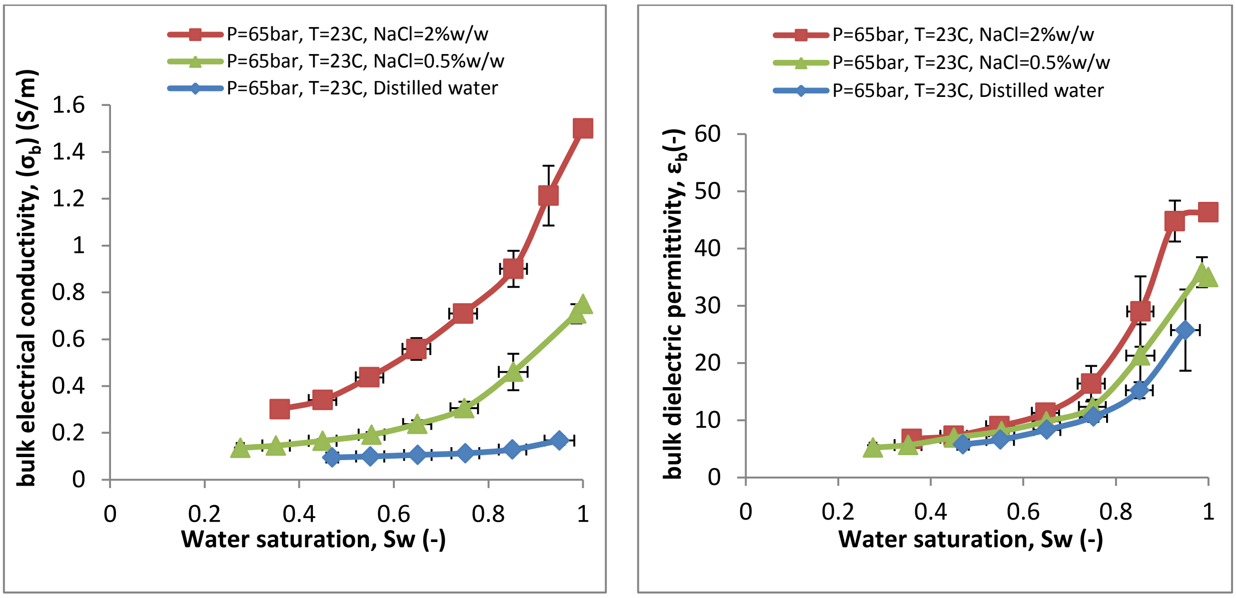


(a) (b)

Fig. 4 Effect of pH on (a) σ_b–S and (b) ε_b–S relationships for CO_2–water–basalt sand system

3.3. Effect of Salt Concentration

All saline aquifers contain brackish water and the amounts of salt concentration in them vary depending on their locations, i.e., concentrations between 0.5 and 153 g/L are found in most of the deep saline aquifers (Abidoye et al. 2014; Abidoye and Das 2015a; Buttinelli et al. 2011). The effects of salt concentration on geoelectrical properties and water saturation (σ_b-S and ε_b-S relationships) are examined in this study. The σ_b-S and ε_b-S relationships at different salt concentrations in silica sand are shown in Figures 5a, b. As expected, σ_b and ε_b increase with the increase in salt concentration. The increases in σ_b and ε_b values correspond to the increase in ions as salinity increases. This trend is more significant in the σ_b-S relationships (Figure 5a). However, for the ε_b-S curves (Figure 5b), there is only a slight change with different salt concentrations. The sensitivity of σ_b-S relationship to change in salt concentration can be attributed to the increase in ions in aqueous solution which raise the conductivity of the system. Furthermore, the figures reveal that the salt concentration is an important factor when compared to distilled water having less aqueous ions. The σ_b-S relationship increases when the concentration of brine is raised to 0.5 %w/w (NaCl) and the trend further increases when the concentration of the brine increases to 2 %w/w (NaCl). The results are similar to the results from Abidoye and Das (2015a), but they limited their work to σ_b-S relationships only. The current work focuses on simultaneous measurement of σ_b-S and ε_b-S relationship in porous materials.

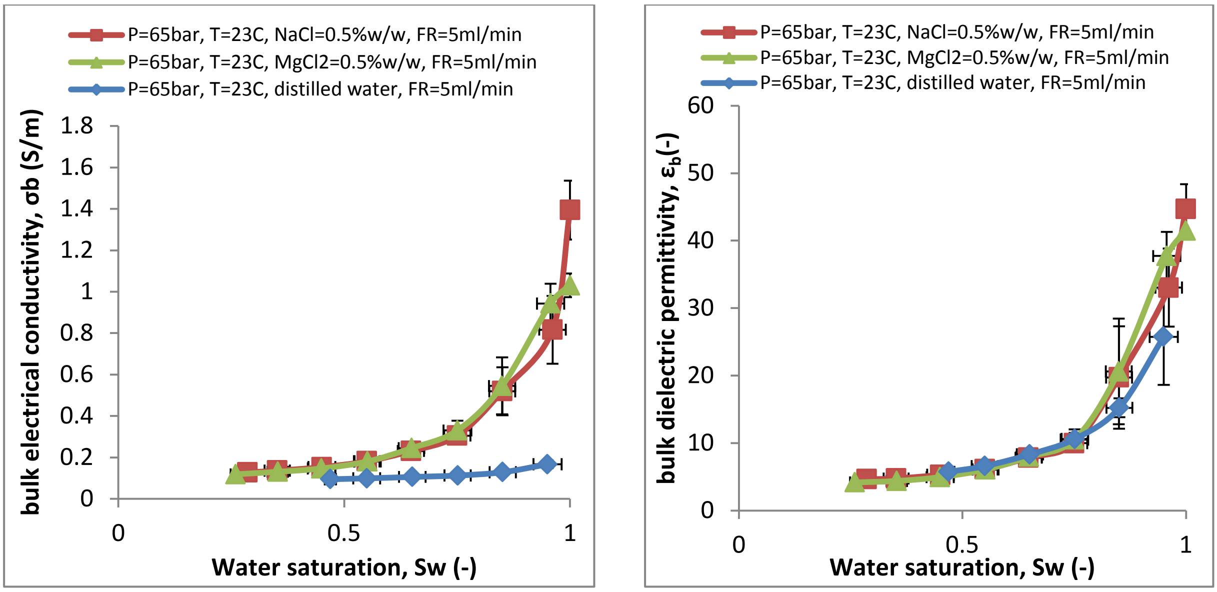


(a) **(b)**

Fig. 5 (a) σ_b–S and (b) ε_b–S relationships at different salt concentrations for liquid CO_2 in silica sand

3.4 Effect of Salt Types

The effect of salt types on σ_b-S and ε_b-S relationships in silica sand was also studied. Figures 6a and 6b display the influences of salt types on geoelectrical properties ($\sigma_{b,}$ ε_b) and water saturation (S_w). It can be deduced that salt types do not have any significant effects on geoelectrical properties ($\sigma_{b,}$ ε_b) and water saturation relationships when similar concentrations of different salt types (NaCl and $MgCl_2$) are used. This is clear from the figures; the only shifts in the curve occur when compared with distilled water. Thus, different salt types have similar effects on the σ_b-S and ε_b-S relationships.



(a) **(b)**

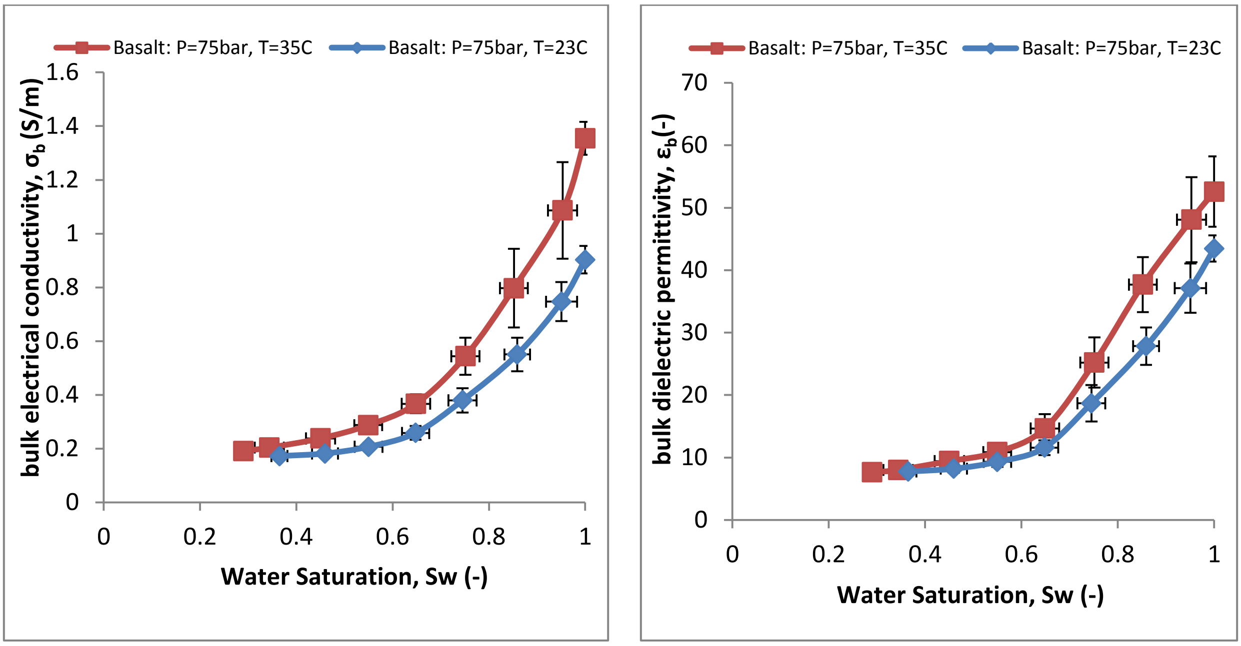
Fig. 6 (a) σ_b–S and (b) ε_b–S relationships for different salt types for liquid CO_2 in silica sand

3.5 Effect of Temperature

In the earth's crust, pressure and temperature gradually increase with depth. The geothermal gradient and hydrostatic pressure vary depending on the locations. Generally, CO_2 is stored at the depth of 800 to 1000 metres and at this depth the pressure is about 75 bar and the temperature is about 34^{o}C (Abidoye et al., 2014). At these conditions, CO_2 is in supercritical phase. In this work, the impact of temperature on the σ_b-S and ε_b-S relationship was investigated and the results are shown in Figures 7a and 7b, respectively. It is found that the σ_b and ε_b increase as the temperature increases in basalt sand system. Similar work on the effect of temperature on geoelectrical properties and water saturation relationship has been carried out on silica sand and limestone sand (Abedian and Baker 2008; Or and Wraith 1999; Abidoye and Das 2015a) but the current work utilises basalt sand because it is assumed that mineralisation takes place in basalt sand more rapidly than silica and carbonate sand media (Petrik and Mabee 2011). This may be the reason that Snæbjörnsdóttir et al. (2014) explored the permanency and potential of storing significant amount of CO_2 in basaltic rocks during carbon sequestration (Petrik and

Mabee 2011; Matter and Kelemen 2009; Snæbjörnsdóttir et al. 2014; Snæbjornsdottir and Gislason 2016).

The result in Figure 7a shows that an increase in temperature tends to increase the electrical conductivity (σ_b). This is possibly due to increase in the mobility of ions or the dissolution of the medium at higher temperature. Also, increase in temperature results in increase in permittivity (ε_b) and this can be attributed to the release of bound water, as claimed by Or and Wraith (1999). The same trend for ε_b-S has been observed by Drnevich et al. (2001) for clay but they observed decrease in dielectric permittivity with increasing temperature in sandstone (Drnevich et al. 2001; Or and Wraith, 1999).

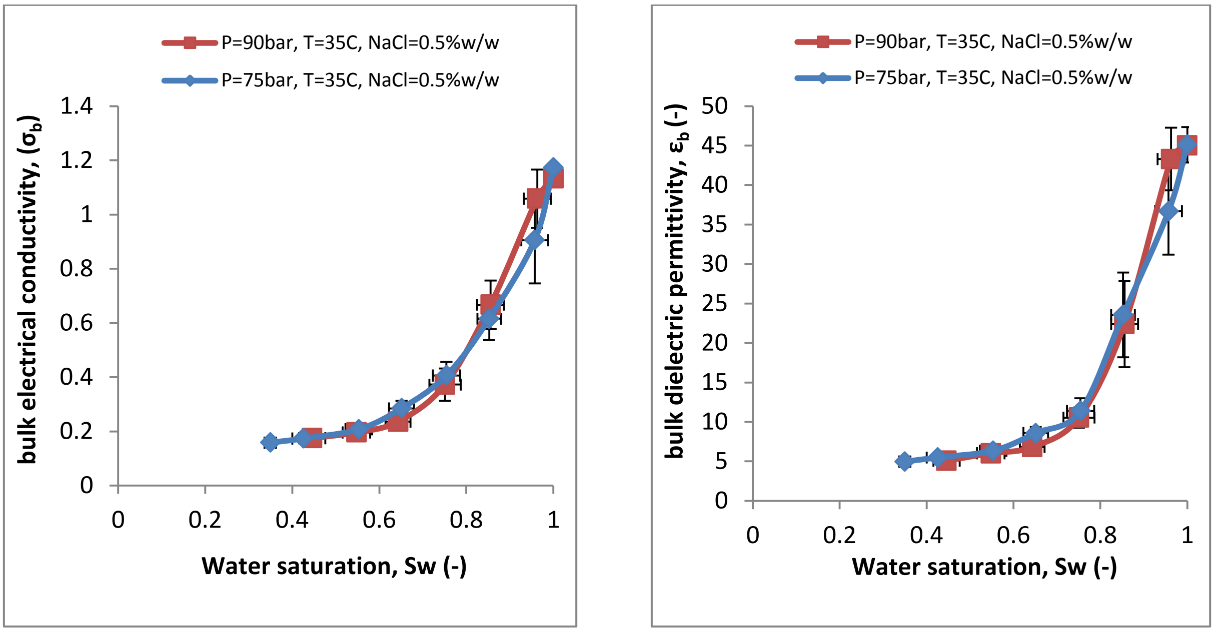


(a) **(b)**

Fig. 7 Effects of temperature on (a) σ_b–S and (b) ε_b–S relationships for CO_2–water–basalt sand system

3.6 Effect of Pressure

It is paramount to understand the effect of pressure on the geoelectrical characteristics of $scCO_2$-water-sand system, because geological carbon sequestration takes place at different depths. Different injection pressures that correspond to varying injection depths were used in the laboratory to simulate these different injection conditions. Figures 8a and 8b show the relationships between geoelectrical properties (ε_b and σ_b) and water saturation. The results revealed that ε_b-S and σ_b-S relationships increase slightly with increasing pressure especially at higher water saturation (80% and above) for σ_b-S relationships; and 90% and above for ε_b-S relationships.

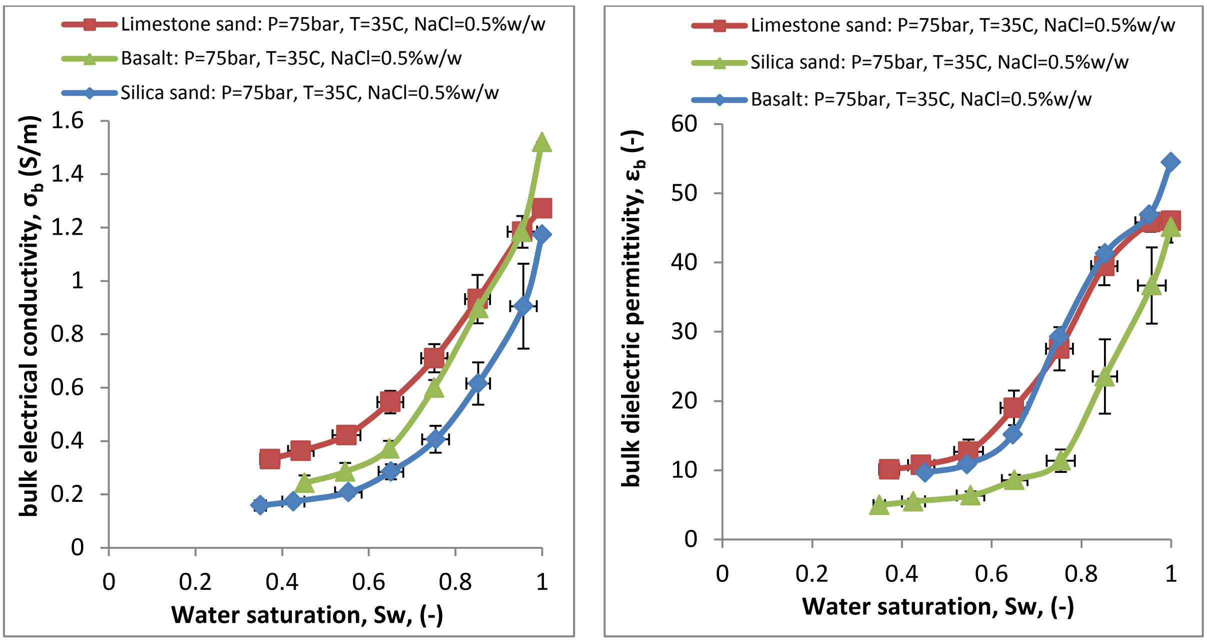


(a) **(b)**

Fig. 8 Effects of pressure on (a) σ_b –S and (b) ε_b–S relationships in $ScCO_2$-water-silica sand system

3.7 Effect of Rock Type

Figures 9a and 9b show the effect of porous materials on ε_b-S and σ_b-S relationships. It can be deduced that the type of rock present in the porous rock body has a noticeable effect on both the σ_b-S and ε_b-S curves. Abidoye and Das (2015a) attribute the high conductivity in the (carbonate sand) limestone-water-CO_2 system to the dissolution of carbonate sand in water with subsequent increase in concentration of dissolved ions (Plan 2005; Assayag et al. 2009). Figures 9a and 9b show the σ_b-S and ε_b-S relationships for different rock types (i.e., basalt, carbonate and silica sand). In the σ_b-S relationship, the curve is highest than others for limestone, except at the start of the experiment. At the start of the experiment, basalt sand is shown to have higher σ_b-S curve (i.e., at saturation of 1) than carbonate and silica sand, respectively. The explanation for this is that at the start of the experiment (S_w=1), less limestone has dissolved, thus the limestone presence does not affect σ_b-S at this time. After some time, more dissolution has occurred. Since dissolution of carbonate is higher than others, electrical properties may be more affected in carbonate than others. This was also observed by Abidoye and Das (2015a) but their work was limited to only carbonate and silica sand. The current study utilises three porous materials, i.e., basalt, carbonate and silica sand. It is concluded that different porous materials behave differently on geoelectrical properties and water saturation relationships.



(a) (b)

Fig. 9 Effect of porous media samples on (a) σ_b–S and (b) εb–S relationships in $scCO_2$– water silica/limestone/ basalt sand system

3.8 Regression of the Experimental Result

This section discusses the results of the geoelectrical parameters (σ_b and ε_b) for $scCO_2$-water/brine system. An attempt was made to fit the experimental results to Archie's law (Archie 1942), and thus, predict the bulk conductivity σ_b in the silica sand, basalt sand and limestone. Archie's equation can be written in terms of conductivity as follows:

$$\sigma_b = \frac{S^n}{\emptyset^{-m}} \sigma_w \quad (2)$$

where,

S = water saturation, $\emptyset = porosity, \sigma_w =$ brine conductivity, $\sigma_b =$ bulk conductivity,

m = cementation exponential, n = saturation exponential.

The equation can be used to fully predict water saturation (S) from porosity ($\emptyset$), brine conductivity (σ_w) and bulk conductivity (σ_b) measurements. Also, adjustable parameters m and n are the Archie's empirical parameters, which depend on formation characteristics and are used for the optimization of the model (Kennedy and Herrick 2012). From the silica, basalt and carbonate sand used in this work, the exponents m and n were determined from the experiments. Equation (2) was linearized using logarithm rules to form Eqs. (3) and (4). XLfit was then used to solve for m and n exponents.

$$log\ \sigma_b - mlog\emptyset = log\sigma_w + nlogS \quad (3)$$

$$nlogS + mlog\emptyset = log\sigma_b - log\sigma_w \quad (4)$$

Table 3 shows the values of m and n exponents using Microsoft XLfit.

Table 3 Archie's (1942) exponents and correlation coefficients (R^2) for each of the porous material tested

Porous media sample	n	m	R^2
Limestone	1.1	2.0	0.87
Silica sand	0.8	1.7	0.75
Basalt sand	0.9	1.8	0.70

The exponent values in Table 3 are in good agreement with the reports from the literature**.** Values of 1.0 to 2.2 were reported for both m and n exponents in carbonates and sandstones (Scudiero et al. 2012; Wang et al. 2014). According to Abidoye and Das (2015a), the values of m for sandstone and carbonate are 1.2 and 1.4, respectively. Also, n has the value of 1.2 and 1.5 for silica sand and carbonate sand, respectively (Abidoye and Das 2015a). On the other hand, Scudiero et al. (2012) give the range between 1.3 to 2.5 for the values of m, and n value to be 2.0. In addition, Liu and Moysey (2012) give the range between 0.7 and 1.96 for n value. It can be concluded that the exponent values for m and n from the model generated from our experiment is similar to others.

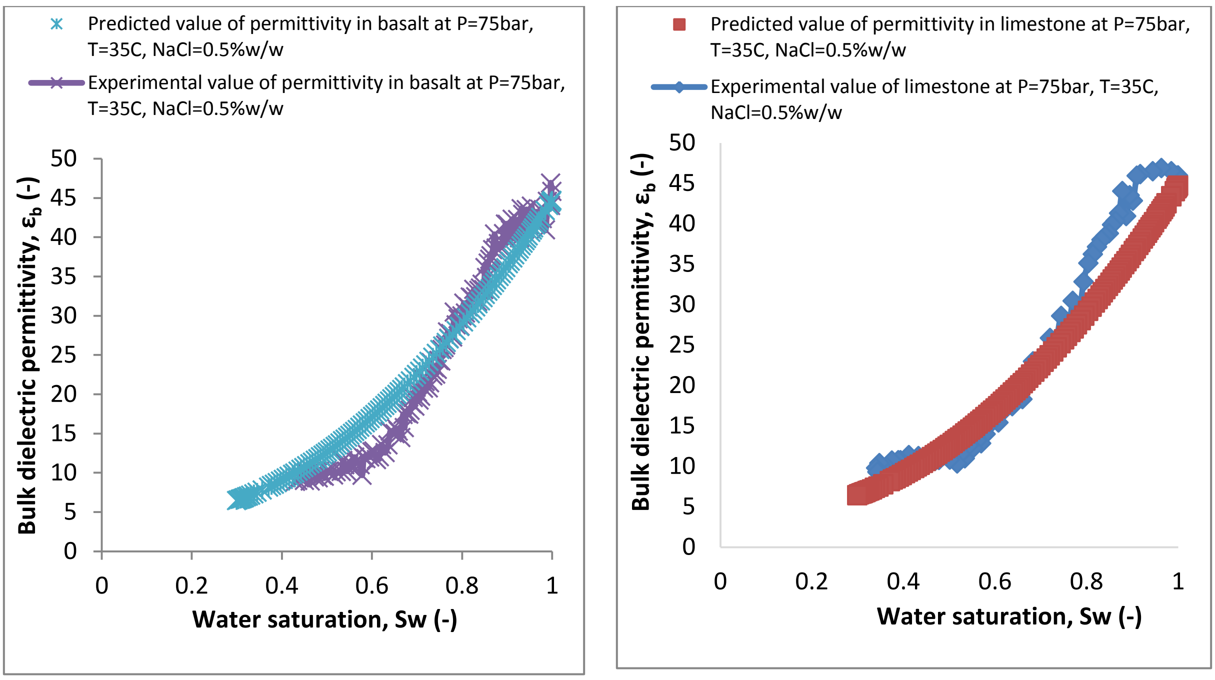
Additionally, the bulk dielectric permittivity (ε_b) is a function of various parameters, such as water saturation (S), pressure (P), temperature (T), and the initial value of ε_b (i). The initial value of ε_b is the value of dielectric permittivity of porous materials saturated with water before injection of CO_2. This value of ε_b is very crucial, because it shows the original state of water saturated medium, which eventually determines the ε_b-S profile. Therefore, ε_b can be written as:

$$\varepsilon_b = f(S, P, T, i) \quad (5)$$

The Minitab statistical software (Microsoft 2016) was used to determine dielectric permittivity (ε_b). The nonlinear regression polynomial model is shown as Eq. (6):

$$\varepsilon_b = -47.11 - 7.69S - 0.0057P + 1.156T + 0.237i + 47.94S^2 \quad (6)$$

The results of the regression using Eq. (6) are shown in Figures 10a and 10b. The figures show that the model is in agreement with the observed values because they capture most of the data accurately. It can be hypothesised that the nonlinear regression presented in this work using fit regression model is very reliable in predicting ε_b-S relationship for two-phase flow in porous media. This model can be used to predict the monitoring process of CO_2 sequestration.



(a) **(b)**

Fig. 10 Prediction of permittivity values in (a) CO_2-water-basalt and (b) CO_2-water-limestone systems at 75bar and 35^0C using non-linear regression

4. Conclusions

Monitoring CO_2 in geological storage reservoir is crucial in the context of carbon capture and sequestration. To this end, this work explored the effects of pressure, temperature, salt types, salinity, pH and porous media on the geo-electrical characteristics of the CO_2-water-porous media flow system, with a view to enhancing effective subsurface monitoring of the system. Time domain reflectometry (TDR) method was used for simultaneous analysis of the in-situ characteristics of the bulk dielectric permittivity and electrical conductivity for CO_2-water-porous media system, for liquid and supercritical CO_2 in silica sand, basalt sand and carbonate sand. The bulk electrical conductivity and dielectric permittivity decrease as water saturation decreases in the porous media. Results show that an increase in temperature, pressure and salinity tend to increase the bulk electrical conductivity (σ_b) and permittivity (ε_b) relationships with in-situ water saturation. On the other hand, pH and salt types do not show any significant effect on the geoelectrical parameters (σ_b, ε_b). Effects of porous materials on both the bulk electrical conductivity and permittivity curves show that the profile values are highest in limestone medium, followed by basalt and then silica sand, under similar conditions. This effect can be attributed to the different chemical compositions contained in silica, carbonate and basalt sand media. Archie equation using XLfit (Microsoft 2016) was used to model the experimental results and the outputs were in good agreement with previous studies. In addition, a polynomial fit developed in this study took into consideration the other parameters such as pressure, temperature and initial bulk permittivity. The fit regression model shows a good reliability in the prediction of geoelectrical characteristics of the system during the monitoring process of the geological CO_2 sequestration.

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