Geological carbon sequestration in the context of two-phase flow in porous media: A review

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Abstract

In this review, various aspects of geological carbon sequestration are discussed in relation to the principles of two-phase flow in porous media. Literature reports on geological sequestration of CO_2 show that the aquifer storage capacity, sealing integrity of the caprock and the *in situ* processes, e.g., the displacement of brine by supercritical CO_2 ($scCO_2$), convection-diffusion-dissolution processes involving $scCO_2$ and brine, geochemical reactions, and mineral precipitation depend on the fluid-fluid-rock characteristics as well as the prevailing subsurface conditions. Considering the complexity of the interrelationships among various processes, experimental investigations and network of mathematical functions are required for the ideal choice of geological site with predictable fluid-fluid-rock behaviours that enhance effective monitoring. From a thorough appraisal of the existing publications, recommendations are made for improvement in the existing simulators to fully couple the entire processes involved in the sequestration operations and *in situ* mechanisms which include injection rate and pressure, brine displacement, simultaneous flow of free and buoyant phases of CO_2, various trapping mechanisms, convection-diffusion-dissolution processes, $scCO_2$-brine-rock reactions, precipitation of the rock minerals and the consequences on the hydraulic and hydrogeological properties in the course of time as well as the quantity of injected CO_2. Suggestion is made for the inclusion of leakage parameters on site-specific basis to quantify the risks posed by the prevailing fluid-fluid-rock characteristics as well as their immediate and future tendencies. Calls are also made for thorough investigations of factors that cause non-uniqueness of the two-phase flow behaviour with suggestions for the use of appropriate experimental techniques. The review comprehensively synthesizes the available knowledge in the geological carbon sequestration in a logical sequence.

Keywords: Carbon sequestration, global warming, capillary pressure, saturation, relative permeability, dynamic effects, modelling and simulation.

1. Introduction

The world is currently confronted with the issue of global warming arising mainly from the anthropogenic activities, especially man's excessive use of fossil fuels for energy. This has resulted in the unhindered emissions of several climate-unfriendly gases into the atmosphere. There are significant evidence which has shown that these emissions exacerbate the change in the climate 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 (Karl et al. 2009; Solomon et al. 2007). Owing to the increasing amount of global emission, carbon dioxide is of serious concern as it is considered to be the greatest culprit in the greenhouse effect (Metz et al. 2005; Marland and Rotty 1984). Sources of these pollutants include, e.g., fossil fuels and deforestation practises (Karl et al. 2009).

In the face of increasing global energy demands, the desire to mitigate the change in climate presents a daunting and interesting challenge as ninety per cent of world's primary sources of energy still comes from fossil fuels (DOE 2010). The world population still hopes for an improvement in the standard of living, education and health care. These aspirations are directly related to energy consumption. To check the steep rise in carbon emission since the industrial revolution (200 to ~385 ppm) and preserve the planet, CO_2 will need to be reduced to, at most, 350 ppm (Houghton et al. 2001; Hansen et al. 2008). In tackling the challenges, various technologies have emerged while many others are under investigations and implementations to reduce the emissions of these gases into the atmosphere, utilise alternative energies, improve carbon capture, or promote storage efficiencies and so on. Figure 1 shows the pilot and commercial scale carbon sequestration projects being executed worldwide.

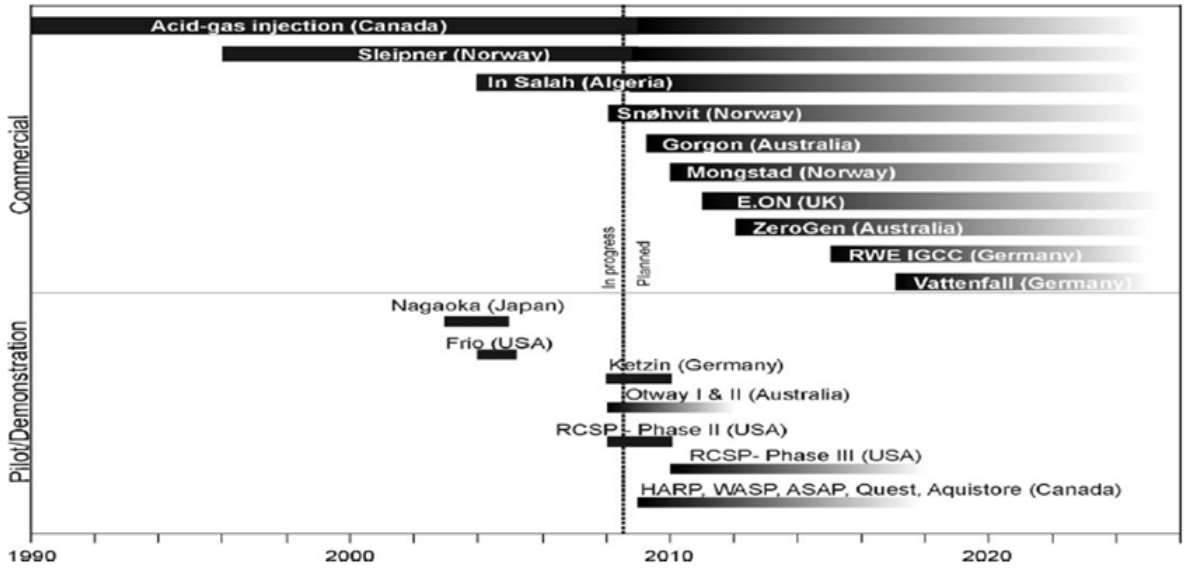

Figure 1: Carbon dioxide sequestration operations at pilot and commercial scales worldwide (Michael et al. 2010).

Popular sites identified as suitable for carbon storage include ocean, brine or saline aquifer, coal bed and depleted oil reservoir. However, the geological sequestration in saline aquifers is considered as the most viable option as it seems to have the largest carbon storage potential (Fujii et al. 2010; Zahid et al. 2011). Parts of the reasons for this choice include the stability, capacity and ubiquity of these aquifers. Stable sedimentary basins are necessary for dependable sequestration activities and such basins are found in most continents (Metz et al. 2005) with estimated capacities of around 1000 to 100,000 gigatonnes of carbon dioxide (Zahid et al. 2011). Researchers have thus dedicated many studies to determine storage capacities and fluid flow mechanisms at prospective sites. The ultimate choice of a particular geological site will depend on a combination of several characteristics which include aquifer size, porosity, permeability, depth, geology, hydrogeology, caprock integrity, petrophysical characteristics, geothermal gradient, proximity to emission sources and existing infrastructures, tectonic stability and faulting intensity (Espinoza et al. 2011).

Scenarios of the injected CO_2 in the brine aquifer for sequestration purposes involve several in situ mechanisms, one of which is the displacement of the resident brine by the invading CO_2 plume (Zhang et al. 2011; Juanes et al. 2006). Considering this as a kind of two-phase system, multiphase flow researchers have delved into supercritical CO_2-brine ($scCO_2$-brine) system with emphasis on capillary pressure-saturation-relative permeability relationships ($P^c - S - K_r$) (Plug and Bruining 2007; Plug et al. 2006;

Pentland et al. 2011; Pini et al. 2012; Tokunaga et al. 2013). Capillary pressure and relative permeability for wetting and non-wetting phases are parameters of key importance in modelling the two-phase flow processes encountered during transport of immiscible phases in the underground (Aggelopoulos and Tsakiroglou 2008) and they constitute critical parameters used to history match and design field-scale injection projects using reservoir simulators (Doughty 2007). Many publications are available on the behaviour of P^c-S relationships (Hassanizadeh and Gray 1993; Mirzaei and Das 2007; Nordbotten et al. 2008; Bottero et al. 2011; Goel and O'Carroll 2011; Das et al. 2007) while several others are based on the K_r-S relationship (Bennion and Bachu 2008; Water et al. 2006; Lenormand et al. 1998; Anderson 1987). Most of these publications consider the cases of oil-water and gas-water systems. So, it will be of specific importance to thoroughly understand how the $P^c - S - K_r$ relationships behave in $scCO_2$-brine system.

For characterising $scCO_2$-brine system in geological sequestration, two approaches are most commonly considered. Firstly, it involves the use of the theories concerning convection-diffusion-dissolution processes and secondly, it relates to the use of the principles of two-phase flow in porous media. In the first case, the dissolution of the $scCO_2$ in the aquifer brine is considered and it eliminates the need for determination of capillary pressure. In this process, the carbon dioxide-brine solution is defined to be slightly denser than the unsaturated brine causing negative buoyancy by moving to the bottom of the aquifer, enhancing safe and permanent storage, which reduces chances of leakage. The convective process promotes mixing of the brine and $scCO_2$ while enhancing further dissolution of carbon dioxide into the brine (Ozgur and Gumrah 2009). The second approach regards the supercritical carbon dioxide and brine as two immiscible fluid phases, which can be described by $P^c - S - K_r$ relationships. This assumes that there is a limited dissolution of CO_2 in the brine and that displacement process dominates at least for some period after CO_2 injection.

To consider the $scCO_2$-brine system as a two-phase flow system one requires the understanding of the interactions of the fluid-fluid-porous media (i.e., gas-liquid-solid or $scCO_2$-brine-rock) in the system. Analogous to an oil-water system, the immiscible displacement of $scCO_2$-brine/water system may be affected by the presence of heterogeneity in the media, viscosity and density ratios of the two fluids and the

123 geophysical as well as the geochemical conditions of the domain. For example, media
124 heterogeneities affect the $P^c - S$ and K_r-S profiles (Das et al., 2004; Aggelopoulos and
125 Tsakiroglou 2008; Mirzaei and Das, 2013; Khudaida and Das, 2014) while they also
126 raise the value of the irreducible wetting phase saturation (Das et al. 2006). In addition,
127 the heterogeneity (e.g., fractures) may create preferential flow path which increases the
128 effective permeability of the fluid (Aggelopoulos and Tsakiroglou 2008). The
129 permeability to fluid is also affected by the presence of micron-scale heterogeneity (e.g.,
130 lamina) where varying intrinsic permeability value the degree of heterogeneity affect the
131 average permeability of the domain (Alabi 2011). These scenarios are important in the
132 choice of geo-sequestration sites as they affect storage capacity of the aquifer and can
133 influence the risks of leakage.
134
135 Recent review papers on CO_2 sequestration consider the alternative sequestration in
136 limestone (Stanmore and Gilot 2005), technologies and costs (Abu-Khader 2006),
137 health and safety issues (Zakkour and Haines 2007), analogy between traditional liquid
138 waste disposal and carbon storage (Tsang et al. 2007), storage in marine environment
139 (Huh et al. 2009), pilot projects (Michael et al. 2010), $scCO_2$-brine relative permeability
140 experiments (Müller 2011), caprock integrity (Shukla et al. 2010) and present and future
141 challenges (Zahid et al. 2011). Shukla et al. (2010) acknowledge the influences of the
142 fluid-fluid-media characteristics of the $scCO_2$-brine system on trapping mechanisms,
143 breakthrough of the injected fluid and capillary sealing of the caprock. Also, Müller
144 (2011) notes that while there are similarities in the measurement of relative permeability
145 for oil-water and CO_2-water systems, exception exists in the reactivity of core materials
146 with CO_2, resulting in permeability, porosity and wettability alteration. These pointed to
147 the unique characteristics of the two-phase flow parameters in the geological
148 sequestration processes. However, Shukla et al. (2010) are primarily concerned about
149 caprock integrity while Müller (2011) investigates the relative permeability experimental
150 methods.
151
152 To reliably predict CO_2 storage phenomena, understanding the capillary behaviour of
153 supercritical CO_2 and its dependence on water saturation are essential (Tokunaga et al.
154 2013). Characterising a system for geological storage of CO_2 also comes with the
155 challenges of dealing with high gas pressure and temperature above ambient
156 conditions as CO_2 is stored at a depth of around 1 km or more from earth's surface
157 (Rutqvist 2011). In addition to changing property of CO_2 at slight variation of conditions

in the subsurface, these scenarios might cause non-uniqueness in the functional representation of the system such as those discussed by Das et al. (2006).

The above discussions introduce the practices of geological sequestration and the relevance of two-phase flow ($scCO_2$-brine) parameters. It is however equally important to illustrate the challenges and trends found in the literature concerning the determination, application and interpretation of relevant two-phase flow parameters in relation to the carbon sequestration processes. In addressing these issues, this review intends to examine the research activities relating to geological sequestration of CO_2 together with the issues involved in the determination of two-phase relationships for $scCO_2$-brine system from experiments, modelling and simulations. How $scCO_2$-brine-rock characteristics affect stability/instability of the system will be extensively discussed and suggestions as well as recommendations will be made in view of the identified gaps in knowledge. This work is based on the up-to-date reliable information available in the open literature

2. Characteristics of the geological sites

Geological sites hold the important properties that determine a successful geological CO_2 sequestration projects. In this regards, the geological media should meet some fundamental conditions to ensure successful storage of carbon dioxide. Three of these are capacity, injectivity and confinement (Gunter et al. 2009). Studying and modelling CO_2 sequestration in geological formation need a clear understanding of multi-phase flow characteristics and their behaviour in porous media. The above-mentioned parameters (i.e., aquifer capacity, injectivity and confinement) bear relation to media properties i.e., porosity, tortuosity, permeability, relative permeability, dispersion coefficient, capillarity, connectivity, adsorption and wettability as well as to two-phase flow characteristics in the medium. Some of these media properties in the context of the studies on CO_2 sequestration are discussed below.

2.1 Porosity and pore size distribution

In their review of characteristics of potential geological formations for CO_2 sequestration, Kopp et al. (2009) explain that geological formations are suitable for carbon dioxide storage if they demonstrate high values of porosity and permeability. These are crucial for storage of high amounts of carbon dioxide and allow its injection to be done economically.

Porosity is the fraction of the aquifer that is composed of voids (Bear 2013). The interconnected voids in the aquifer forms what is referred to as the effective porosity and it determines the effective storage capacity of the aquifer. Chadwick et al. (2008) suggest that the amount of CO_2 that can be stored in a given saline aquifer in terms of a capacity factor C is:

$$C = C^{gas} + C^{liquid} \quad (1)$$

Where $C^{gas} = \langle \phi . S_g \rangle$, $C^{liquid} = \langle \phi . S_l X_l^{CO_2} . \rho_l / \rho_g \rangle$ and C is the volume fraction of the reservoir available for storage. C is taken as the sum of the free supercritical CO_2 (C^{gas}) and CO_2 dissolved in the brine (C^{liquid}). ϕ is the effective domain porosity and, S_l and S_g are the fractional volumes of the pore space containing liquid and $scCO_2$ phases, respectively. $X_l^{CO_2}$ refers to the mass fraction of dissolved CO_2 in the brine, ρ_g and ρ_l are the densities of the $scCO_2$ and liquid phases, respectively. The angle brackets imply averaging over the spatial domain of storage. Equation 1 shows that the porosity, ϕ, plays a very important role in determining the capacity factor of an aquifer and it can serve as a factor to check suitability of an aquifer for storage. According to Espinoza et al. (2011), the volume of CO_2 injected, V_{CO_2}, in an aquifer is a function of average aquifer porosity as follows:

$$V_{bulk} = \frac{V_{CO_2}}{\phi} \frac{1}{\psi} \quad (2)$$

Where Ψ is a water or brine displacement efficiency coefficient and it is a function of the media and process characteristics. In essence, the effective porosity of an aquifer is a key factor in its capacity to store CO_2. According to Chadwick et al. (2008) a porosity greater than 20% is a positive indicator in a site selection while a value lesser than 10% porosity calls for caution. The porosity of sediment tends to decrease with depth as the effective stress on the sediment increases. The pore size and structure of an aquifer tend to change under the same influence as the pore size is a function of porosity and specific surface. Also, due to enormous complexity of the pore structure of any porous media in terms of the number of pores, their size, shape, orientation, and manner of interconnection of the pores, it often becomes important to consider

the pore size distributions of an aquifer. The pore size distribution is defined as a fraction, f, of total pore spaces within a range of pore diameter δ and $\delta + d\delta$ as expressed in the following distribution function:

$$\int_0^\infty f(\delta)\, d\delta = 1 \quad (3)$$

Information concerning the pore size distribution of a particular aquifer can be obtained from analysis of core measurements and even geophysical logs of adjacent wells. In such sample, the P^c required to force a liquid (e.g., mercury) into the pores can be used to approximate δ, with the following equation (Bear 2013):

$$\delta = 4\gamma \cos\theta / P^c \quad (4)$$

where, γ is the interfacial tension between the two fluids and θ is the contact angle. Pore size distributions are useful in the analysis of permeability reduction, e.g., as a result of clay swelling, microbial growth in pores, mineral precipitation, etc., (Tiab and Donaldson 2004). Theory for the penetration of non-wetting fluid into the pore was developed by Ritter and Drake (1945) while Burdine et al. (1950) applied it to study two-phase flow in reservoir rocks. In the absence of typical mercury injection information, pore size distribution information can be obtained from measurements made by porous semi-permeable diaphragm method (Burdine 1953). Other methods for determining pore size distribution, e.g., adsorption isotherm (Dollimore and Heal 1964; Seaton and Walton 1989) and induced polarization logging measurements (Vinegar and Waxman 1987) have been reported as well. Information on pore size distribution is important in the characterization of the displacement of brine by $scCO_2$ in the saline aquifer as it can be used to calculate the relative permeability of the phases (Burdine 1953).

Changing porosity, mineral precipitation, dissolution and change in effective stress are some of the factors that result in the evolution of pore size distributions of a reservoir. Mineral precipitation in the porous media is often affected by pore size (Emmanuel et al. 2010) and vice versa. While the large pores permit ready precipitation of minerals, the smaller pores might inhibit the process leading to reduced bulk reaction rate,

which in effect stabilises the porosity. Also, geochemical reaction with rock minerals is considered to be one of the trapping mechanisms for long term sequestration. The pore lengths and their distribution might affect how readily the reactions occur at different parts of the sediment. Precipitation of quartz was found to be inhibited in pores smaller than 10 μm in diameter. Also, the pore size distribution will also affect the dissolution rate which is another mechanism identified for trapping as varying solubility is applicable (Emmanuel et al. 2010). In addition, the standard deviation of pore size distribution affects CO_2 breakthrough into a medium (Espinoza et al. 2011).

2.2. Intrinsic, Relative and Effective Permeability

Permeability, as the name suggests, is an indication of how easily a fluid will pass through a porous medium. It can be defined by Darcy's law (Bear 2013; Virnovsky et al. 1995) for an incompressible fluid having viscosity, μ, which flows through a porous medium with length, L, and cross sectional area, A, at flow rate, q, and pressure difference of ΔP across the domain. The isotropic permeability, K, of the porous medium is defined as:

$$K = \frac{q\mu L}{A\Delta P} \quad (5)$$

Its value is dependent on the porous structure of the medium. Appropriate permeability needs to be maintained in the medium to ensure effective storage of CO_2 (Rutqvist 2012). However, the permeability of a medium is affected by the reactions, dissolution and precipitations of the rock minerals. Simulations have shown that following CO_2 injection, dissolution of carbonate cement initially increases the sediment porosity but subsequent reactions result in dissolution of feldspar and precipitation of carbonate minerals and clay leading to reduction in permeability and porosity (Gaus et al. 2005). This implies that the original permeability of the sediment may alter in the course of injection and will affect the prediction of the process behaviour.

Meanwhile, the flow processes (like that in geological sequestration system) can hardly occur with a single fluid. This reality leads to the concept of relative permeability that represents the two-phase relationships of $scCO_2$-brine system in a geological media. While the permeability is the intrinsic property of the medium, relative permeability is

the characteristic of the fluid-fluid-solid system and it comes to play when two or more fluids are present in the porous medium. The term describes the extent to which one fluid is hindered by the other. Though relative permeability is dependent on a number of factors, available experimental evidence indicates the concept of relative permeability that depends on only saturation is a good approximation for all practical purposes (Bear 2013). It is expressed through Darcy's law set up for individual phase i that flows in the pore space:

$$q_i = \left(\frac{KK_{ri}}{\mu_i} \right) A \frac{\Delta P_i}{\Delta x} \quad (6)$$

q_i, K_{ri}, μ_i, and ΔP_i refer to the flow rate, relative permeability, viscosity and the pressure drop, respectively for phase i. The ratio $\left(\frac{KK_{ri}}{\mu_i} \right)$ denotes the "mobility" of phase i.

Figure 2 shows the relative permeability plots of CO_2-water system. It consists of primary, secondary and tertiary drainage of the system (see, Bear (2013) for definitions of these processes). It can be seen that following primary drainage, the residual water saturation continues to decrease in subsequent drainages. This is attributed to dissolution property of CO_2 in water and a contrast was shown in N_2-water system which shows a fairly similar residual saturation for the subsequent drainages owing to lesser solubility of N_2 (Pistone et al. 2011). Water relative permeability, K_{rw} is higher for larger portion of the water saturation though the value reduces with subsequent drainages while that of CO_2 remains low. Relative permeability of CO_2, $K_{rg,}$ remains low owing to dissolution and diffusion into smallest pore spaces with no need to overcome the entry pressure. Evolution of CO_2 from this dissolution state displaces previously immobile water which further impedes CO_2 mobility (Pistone et al. 2011). Thus, the residual saturation of water continues to reduce following subsequent drainage.

Bickle et al. (2007) concluded that the relative permeability-residual saturation relations have a great influence on average carbon dioxide saturation as well as plume evolution velocity and as such, have a great effect on storage capacity. Hysteresis in relative permeability has the tendency to enhance residual trapping. This is defined, for a particular CO_2 saturation, as a reduction in relative permeability during imbibition

compared to drainage (Chadwick et al. 2008). Strong hysteresis in relative permeability results in 'sticky' plumes that leave behind relatively higher amounts of CO_2 trapped compared to weak hysteresis leaving behind small amount. This scenario was observed in the simulation of sequestration project at Sleipner (Norway) (Chadwick et al. 2008).

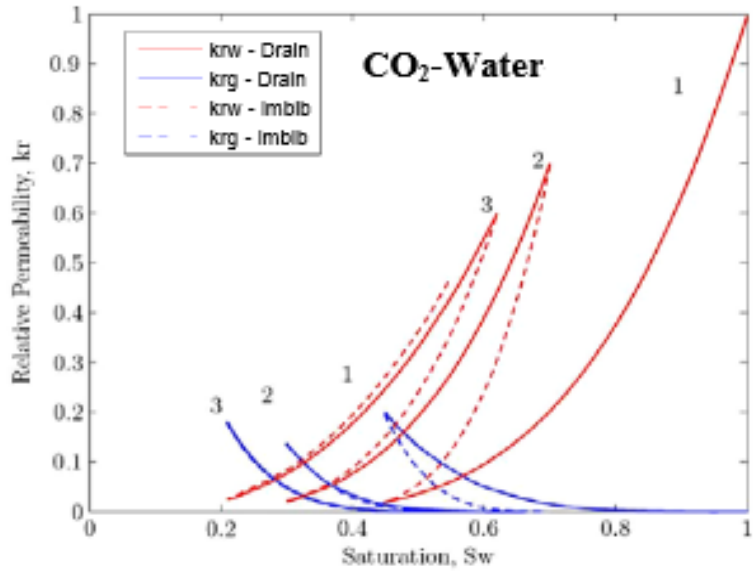

Figure 2: Relative permeability curves for CO_2 (blue) and water (red) (Pistone et al. 2011).

On the basis of a large number of drainage experiments with various types of media, Brooks and Corey (1964) suggest the following relative permeability function:

$$k_{rw} = (S_e)^{(2+3\lambda)/\lambda} = \left(\frac{P_b}{P^c}\right)^{(2+3\lambda)} \qquad P^c \geq P_b \tag{7}$$

$$k_{rnw} = (1-S_e)^2(1-S_e^{(2+\lambda)/\lambda}) = [1-(P_b/P^c)^{\lambda}]^2[1-(P_b/P^c)^{2+\lambda}] \tag{8}$$

where λ is the pore-size distribution index, P_b is referred to as the bubbling or threshold pressure or entry pressure. S_e is the effective saturation and can be expressed as $S_e = (P_b/P^c)^{\lambda}$ for $P^c \geq P_b$. Even though the above results are deduced for isotropic media, their validity makes them applicable to a wide range of pore-size distributions (Bear 2013). Several factors can affect the effective permeability of an aquifer. Pore size distributions, media heterogeneities and scale can be of considerable impact. This

was corroborated by Alabi (2011) investigating the difference in the flow rate of fluid in homogeneous media and different types of heterogeneous media. The author found out that the permeabilities of heterogeneous media are lower than the permeabilities of homogeneous media and that mixed heterogeneity has higher permeability than layered type. This implies that fluid flows faster in mixed heterogeneous sample than the layered type.

2.3 Threshold pressure (bubbling pressure)

In $scCO_2$-brine system, the pressure in the invading fluid (i.e., $scCO_2$) at the interface between fluid-fluid and rock system is required to exceed the minimum entry pressure of the sediment. This implies a certain pressure must be reached in the non-wetting fluid before it begins to penetrate the sample, displacing the wetting fluid contained in it (Bear 2013). The minimum pressure needed to initiate this displacement is called the threshold pressure (or bubbling pressure) or non-wetting fluid entry value or breakthrough pressure. This parameter is also a pointer to injectivity of a medium and its excessive magnitude can pose serious risk to the caprock.

Understanding of the threshold pressure of a caprock saturated with water is important when a gas is to be stored in the reservoir underneath the caprock. This is also the breakthrough pressure when CO_2 can enter through the caprock. Its value depends on the mean pore size related to specific surface S_s, standard deviation in pore size distribution and void ratio e as well as the wettability of the minerals in the presence of water and CO_2 (Espinoza et al. 2011); $e = e_{1kPa} - C_c \log(p'/1kPa)$ where p' is the *in situ* effective stress and e_{1kPa} is the critical state void ratio when the mean confining stress is 1kPa. Espinoza and Santamarina (2010) gave expression for breakthrough pressure, P^*_{thru}, by extension of Laplace's capillary pressure equation:

$$P^*_{thru} = \Psi \frac{S_s \rho \gamma \cos\theta}{e} \quad (9)$$

Ψ is a factor that depends on the clay fabric and grain size distribution and a value of $0.04<\psi<0.08$ applies to smectite clay barriers and, γ is the interfacial tension. This interfacial tension is an important property of the two-phase system. Its influence

depends on the prevailing conditions, e.g., temperature, pressure, salinity and cation valence. Detail discussions and the implication of these factors on γ will be found under subsection 5.2 in this work.

Aside the sediment where actual injection and storage occur, threshold capillary pressure is an important parameter of the caprock that gives indication about its sealing capacity or integrity of caprock. It combines with caprock permeability to determine possibility of leakage and its rate of occurrence (Fleury et al. 2010; Pusch et al. 2010). Thus, the threshold pressure for the sediment must be well below that of the caprock to avoid undue development. Also, since the injection and the *in situ* displacement processes result in pressure fluctuations within the system, the caprock entry pressure should be well in excess of any possible pressure increase for long-term safety. Practical caprock core from Sleipner (Norway) was reported to possess greater than 3.3 MPa capillary entry pressure to $scCO_2$ while that of another project from Schwarze Pumpe (Schweinrich) is predicted to be in the range 4 to 40 MPa (Chadwick et al. 2008).

2.4 Wettability

Wettability is the ability of a liquid to adhere to a solid surface due to their intermolecular interactions. It has a significant impact on the relative permeability-saturation relationships and can be determined from the combination of cohesion forces, which cause the drop to prevent contact with the solid surface, and adhesion forces that try to spread the liquid across the solid surface in a flow system. It is among the factors that determine the entry pressure of the geological media (Espinoza et al. 2011). If the medium is CO_2-wet, it becomes easier for the invading CO_2 to displace the resident brine. However, if the medium is water-wet, then higher entry pressure is required for the invading CO_2 to penetrate the medium. Publications on water-wet, CO_2-wet and mixed-wet media have been reported. In relation to carbon geological sequestration, many of the representative media samples, quartz, calcite, kaolinite, microcline and illite were reported to be water-wetting (Wang et al. 2012). The possibility of the alteration in wettability based on saturation history of the medium was also reported (Plug et al. 2006).

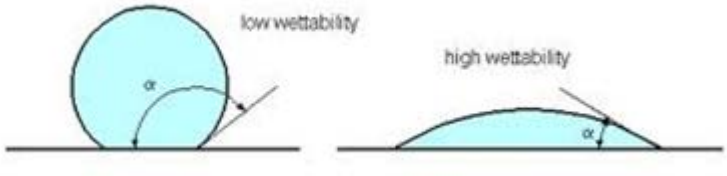

Figure 3: Wettability index of liquid as a function of contact angle (α): $\alpha > 90^o$ (non-wetting liquid), $\alpha < 90^o$ (wetting liquid). The possibility of $\alpha=0^o$ (perfectly wetting) is not shown.

Wettability is related to capillary effects and occurs at different degrees according to the angle at which fluid1-fluid2 interface meets with the fluid1-solid interface. This contact angle provides an inverse measure of wettability (Shafrin and Zisman 1960). Importance of wettability in the determination of $P^c - S - K_r$ relationships is great and the *in situ* alteration in wettability can lead to error in calculation and predictions if not considered. Wettability indices (e.g., USBM index, Ammott index and Hammervold-Longeron (HL) index) are employed in quantifying wettability and its changes for the drainage and waterflooding processes in the porous media using the P^c-S curves (Pentland 2011). Table 1 shows the wettability indices for oil–water system.

Table 1: Wettability indices for oil-water indices (Pentland 2011)

Index	Water-wet	Neutrally-wet	Oil-wet
Ammot (displacement by water ratio)	Positive	0	0
Hammervold-Longeron	1	0	-1
USBM	near 1	near 0	near -1

By implication, partial-wetting behaviour of CO_2 (e.g., limestone rock under reservoir condition) results in lower capillary pressure and higher mobility for brine and can lead into lower capillary breakthrough pressure of the caprock (Chalbaud et al. 2010).

3. *In situ* Trapping Mechanisms of Injected CO_2

Trapping mechanisms come under two major categories: physical and chemical trapping mechanisms. Physical mechanism involves the trapping by structural and

stratigraphic patterns of the aquifer sediment and caprock while chemical mechanisms include dissolution in the brine, complex mineralisation with host rock, adsorption on coal and CO_2 hydrate formation (Espinoza et al. 2011). Some of these trapping mechanisms are discussed below under the broad headings of structural, dissolution, capillary and mineral trapping.

3.1 Structural trapping

Structural trapping arises from physical nature of the aquifer, e.g., anticlines or faults intercepting the upward mobile plume of CO_2. Together with stratigraphic as well as hydrodynamic trappings, they constitute physical trapping mechanisms that control the initial period of CO_2 storage (White et al. 2001). Structural trapping occurs in the presence of a structural enclosure together with a seal forming low permeability cap-rock (Omambia and Y. Li 2010). The injected carbon dioxide rises to the upper layer of the aquifer above the resident brine by the power of buoyancy and is immobilised under the impermeable anticline structure. In a sequestration project at Sleipner (Norway) structural traps are the key features focused upon prior to CO_2 injection as they are key to favourable geological site characterisation (Chadwick et al. 2008). From 1996, the CO_2 plume had reached the top of the reservoir by 1999 at Sleipner (Shukla et al. 2010). Figure 5 depicts this mechanism in a reservoir as CO_2 trapped under caprock.

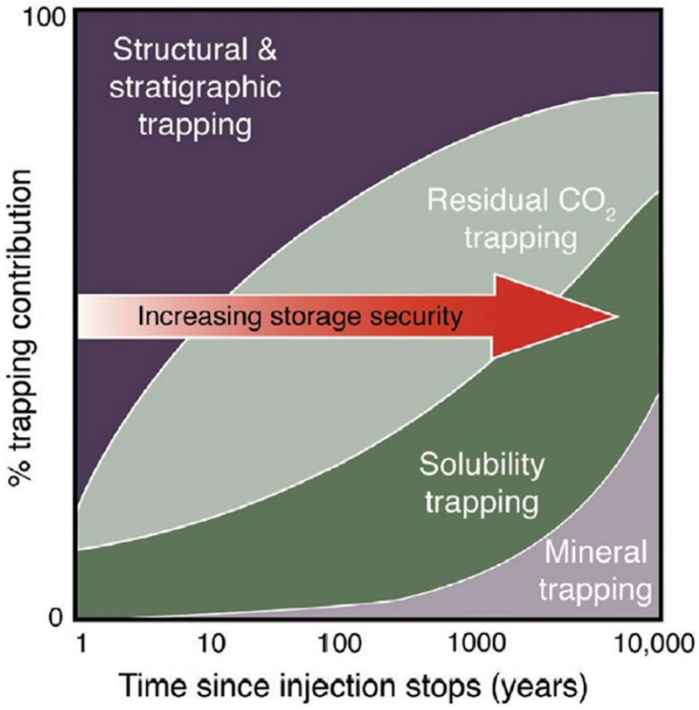

Figure 4: Mechanisms of CO_2 Trapping with time (Benson and Cole 2008).

3.2 Residual trapping

Residual trapping occurs as a result of a hysteresis effect in the permeability of the $scCO_2$ phase especially when the saturation direction is reversed. It is a quick process because of the tight and rigid sponge nature of the porous rock (Omambia and Li 2010). As the $scCO_2$ is injected into the deep aquifer formation, it displaces the resident fluid. When the $scCO_2$ continues to move, the previous brine takes its place trapping some of the $scCO_2$ adhered to the pore surface and stay behind trapped in the pore spaces as residual droplets rendered immobile like water in a sponge (Ide et al. 2007). It is depicted in Figure 5.

The trapping of a phase in this manner can be characterised by the relationship between initial and residual saturation, known as the capillary trapping curve. This phenomenon can be characterised by maximum trapped saturation and the form of the capillary trapping curve as these depict the physics of this phenomenon and also give an important indication of system wettability.

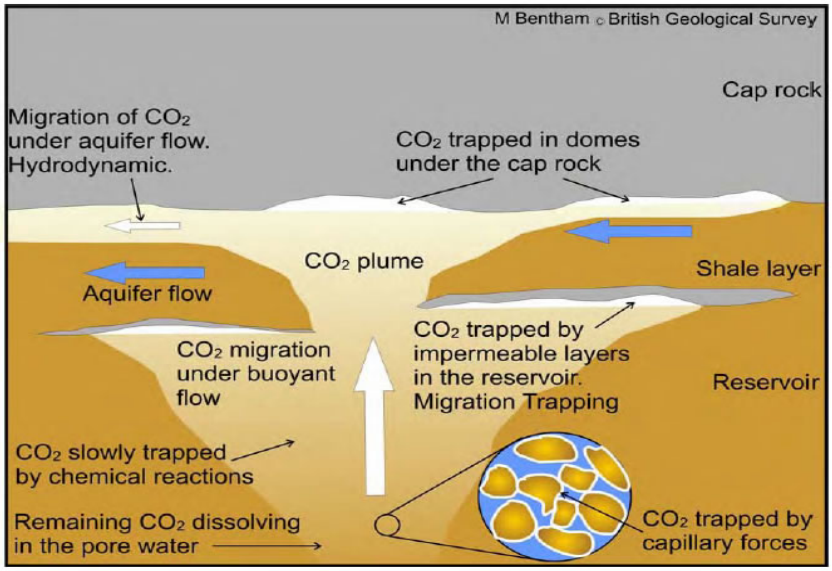

Figure 5: Various mechanisms of CO_2 trapping in the reservoir (Bentham 2006)

3.3 Solubility trapping

It is envisaged that the long-term sequestration of CO_2 in deep saline aquifers will occur via dissolution in the brine and/or chemical complexation with the formation (White et al. 2003). Solubility trapping occurs when CO_2 in gaseous or supercritical state dissolves in the aquifer brine at the prevalent conditions of temperature, salinity and pressure (Omambia and Y. Li 2010). This results in the increase of the solution density and

lowered pH as shown in Figure 6. As the CO_2 dissolves in water, part of this mixes with the water and form the carbonic acid which goes on to produce bicarbonate with hydrogen ions. This reduces the pH of the system at reservoir conditions to approximately 3. The following steps represent the ionization process:

$$\begin{aligned} &CO_2(g) \Leftrightarrow CO_2(aq) \\ &CO_2(aq) + H_2O(l) \Leftrightarrow H^+ + HCO_3^-(aq) \\ &HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}(aq) \end{aligned} \quad (10)$$

Being heavier than other surrounding fluids as a result of the dissolved CO_2, convective currents are created causing the denser solution to settle at the bottom of the aquifer trapping the CO_2 more securely. The lighter brine with less dissolved CO_2 then rises to the top of the rock formation (Silin et al. 2008). The mass density of brine-CO_2 solution, ρ_{sol} (kg/m^3), can be estimated from equation (11) (Espinoza et al. 2011):

$$\rho_{sol} = \rho_w + m_{CO_2}\chi_{CO_2} - \chi_{CO_2}\rho_w V_\varphi \quad (11)$$

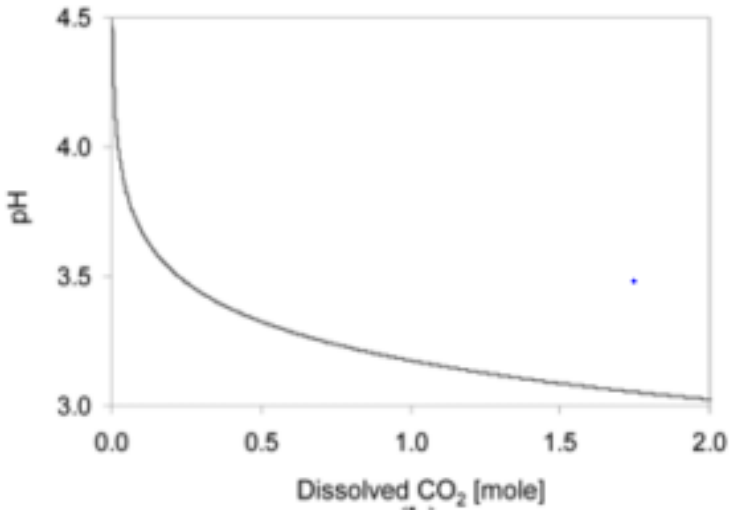

Figure 6: Solution pH as a function of solubility of CO_2 in brine (Duan and Sun 2003).

ρ_w (kg/m^3) is the density of pure water, χ_{CO_2} (mol/m^3) is the CO_2 concentration in water, m_{CO_2} (kg/mol) is the molecular weight of CO_2, V_φ (m^3/mol) is the apparent molar volume of CO_2 as a function of temperature, T(C) expressed by Garcia (2001) as $V_\varphi = 37.51\cdot10^{-6} - 9.585\cdot10^{-8}T + 8.740\cdot10^{-10}T^2 - 5.044\cdot10^{-13}T^3$. Densification of the

brine-CO_2 solution promotes the convective mixing in the aquifer, which improves the effectiveness of this trapping mechanism. This continues until the system reaches equilibrium condition.

Solubility is affected by the temperature and pressure of the system, pore size distribution. So, the choice of basins with higher density of large pores will aid this mechanism (Emmanuel et al. 2010). The dissolution increases with pressure and decreases with temperature as shown in the chart presented by Dodds et al. (1956) with different patterns of dissolution below and above critical conditions. Also, salt concentration of the brine has been shown to affect the solubility of CO_2. There appear to be an indirect linear relationship between CO_2 solubility and salt concentration as shown in Figure 7. This implies that aquifer with lower brine concentration favor s this dissolution mechanism.

A dimensionless number, namely, Rayleigh number (Ra) is important in the dissolution-convection processes involved in the solubility trapping. Ra is particularly associated with buoyancy-driven flow. It is dependent on the fluid property and the characteristic length of the system expressed as (Farajzadeh 2009): $Ra = \frac{\beta_c g \Delta c R^3}{\nu D}$. β_c is the volumetric expansion coefficient (m^3/mol), g is the acceleration due to gravity (m/s^2), c is the gas concentration (mol/m^3) , R is the characteristic length of the system (m), ν is the kinematic viscosity (m^2/s) and D is the diffusion coefficient (m^2/s). As Ra increases mass transfer of CO_2 into the brine-saturated porous medium increases and the concentration front moves faster (Farajzadeh 2009). Low Ra results into the steady-state concentration while its high value leads to the system instability (Ouakad 2013).

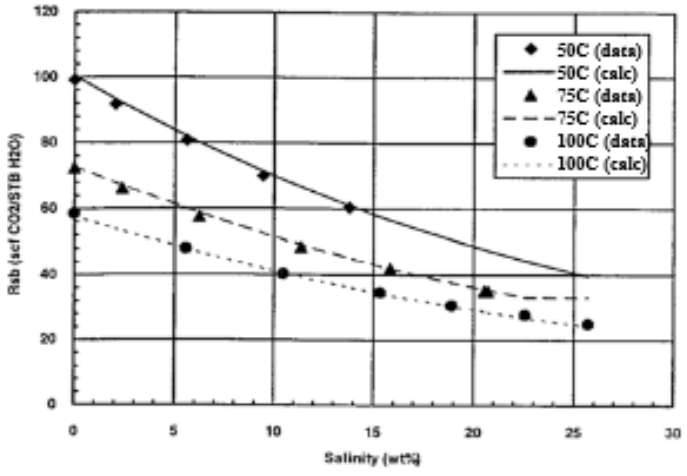

Figure 7: CO_2 solubility as a function of salinity (Chang et al. 1998)

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3.4 Mineral trapping

When carbon dioxide is dissolved in brine, it decreases the pH of the solution leading to acidification as expressed in equation (10). This acidified solution in contact with host rock results in mineral dissolution, precipitation and reactions, which are the processes that induce mineral trapping. With time, the reactions of the acid with dissolved ions and rock minerals in the aquifer lead to chemical complexes such as magnesite, dolomite, calcite, drawsonite and siderite. These occur as products of dissolution and complexing, resulting in chemical precipitation of solid carbonate minerals (secondary carbonates). It is regarded as a permanent sequestration process. However, it is a slow process with significant contribution occurring only in the geological time scale.

Reaction between CO_2 and alkali aluminosilicate minerals will generate a soluble alkali bicarbonates as well as carbonates promoting the mechanism of solubility trapping. In this line of series, parallel and complex reactions and processes, pH of the system changes dramatically as the dissolution of carbonates ions raises it up to 5 while aluminosilicates can take the pH up to 8 (Espinoza et al. 2011).

Beni et al. (2012) evaluated the potential of mineral trapping on CO_2 sequestration in the sandstone formation near Minden in Germany. They found that after about 200 years, this mechanism contributes significantly in the storage and the prospect increases even more with time.

Typical reaction with silicate mineral is represented below (Drever and Stillings 1997):

$$\begin{aligned} & SiO_2(s) + 2H_2O \Leftrightarrow H_4SiO_4 \\ & \Leftrightarrow H^+ + H_3SiO_4^- \\ & \Leftrightarrow H^+ + H_2SiO_4^- \end{aligned} \quad (12)$$

Equation (12) has a reaction rate of 1.26×10^{-14} $mol.m^{-2}.s^{-1}$ (White et al. 2004) and the reaction is not affected by dissolution of CO_2. But the reaction with aluminosilicates (including feldspars, micas, clays) turns the system alkaline with pH up to 8 (Li et al. 2006) while faster carbonate reactions raise the pH up to 5 (Algive et al. 2009).

4 Modelling and simulations of scCO$_2$-brine-rock system

Modelling and simulations of geological sequestration processes are highly required to assess the feasibility of CO_2 sequestration into particular aquifer or reservoir. Modelling the sequestration entails considerations for the technicalities of the storage systems and the economics. This ranges from capture, transport and storage together with the associated costs brought together in a discounted cash flow calculations (Chadwick et al. 2008). However, the interest of this section is to discuss the basics of modelling and simulations involved in geological sequestration.

Generally, the geological sequestration systems can be described using multiphase and multi-component processes with consideration for non-isothermal conditions occurring near the injection region owing to CO_2 expansion with Joule-Thompson effects (Class et al. 2009). Basic multiphase equations are built upon mass and momentum conservations as well as various constitutive equations. For the simultaneous flow of CO_2 and water, the governing equations can be expressed as:

$$\phi \frac{\partial S_i}{\partial t} + \nabla . q_i = 0 \quad (13)$$

'i' stands for the phases; CO_2 (g) or brine/water (w). S is the phase saturation and q the velocity and ϕ, the porosity. . The velocity q is given by the extended version of Darcy's law; $q_i = -\frac{K_{ri}K}{\mu_i}[\nabla P_i + \rho_i g \nabla z]$. For radial injection in the aquifer (Saripalli et al. 2001); $q_{r,i} = \frac{Q_i f_i(S_i)}{2\pi r h}$. K_{ri} represents the relative permeability for phase i and K is the medium intrinsic permeability. P is the phase pressure, ρ the density and g is the acceleration due to gravity, ∇z is the gradient of upward unit vector. Q is the injection rate and f is the phase fractional flow. For the injected phase, substituting for radial velocity in equation (13) results into two-phase displacement theory based on the Buckley-Leverette theory (Saripalli et al. 2001):

$$\frac{Q_g f_g}{2\pi r h \phi}\frac{\partial S_g}{\partial r} + \frac{\partial S_g}{\partial t} = 0 \quad (14)$$

595 In addition to the above, a detailed description of the constitutive equations for the
596 sequestration system requires several mathematical expressions which include the CO_2
597 saturation in the expanding radial plume and its derivative, equation of state for the
598 phase partitioning behaviour of CO_2-H_2O mixture, models for dissolution of CO_2 in brine
599 and vice versa with their derivatives along the horizontal and vertical regions and
600 pressure distribution in the region of the plume. While the radial flow of the injected
601 phase is inserted as velocity in the equation (14) (Saripalli et al. 2001), the buoyant flow
602 of the process needs a separate velocity expression as a function of radius.
603 Furthermore, incorporating expressions for leaks is desired for robust modelling and
604 analysis of injection and sequestration processes.
605
606 For CO_2 leaks scenarios, two significant processes are of concern: vertical migration as
607 a free phase through fractures and buoyancy driven flow through permeable zones of a
608 water-saturated caprock were identified (Huo and Gong 2010; Saripalli et al. 2001).
609 Young-Laplace relation for capillary pressure provides a handy expression for
610 determining the entry capillary pressure from the values of two-phase interfacial tension
611 and pore size obtained for the caprock (Singh et al. 2010). Thickness of the CO_2 bubble
612 layer near the caprock will provide the needed parameter for the exerted pressure on
613 the confinement and expression for free phase flow of CO_2 through the aperture is
614 required for the complete description of the leak scenario. In very robust case,
615 incorporating chemical reactions from dissolution, mineral precipitations, various
616 trapping mechanisms are highly desired. The above scheme can be simplified for easy
617 solution depending on the level of analysis desired but the more processes that are
618 incorporated into the model the better the simulation and the more robust and better its
619 application. This calls for the assessment of the currently available simulators. Though,
620 it is recognised that the solution methods become complicated with complex multi-
621 process models.
622
623 Popular approaches to the solution of mathematical modelling are analytical, semi
624 analytical and numerical techniques. For example, Woods and Comer. (1962) obtained
625 analytical solution to equation (14) for radial injection of gases into initially water-
626 saturated reservoir. Similarly, Nordbotten et al. (2005) provide analytical solution to the
627 space-time evolution of CO_2 plume. However, for very complex problems, non-linearity
628 in constitutive relations often defies analytical solution. As such, numerical solution is
629 often applied. Numerical solution allows simulations that incorporate diverse injection

630 wells with varying injection rates, heterogeneous geologic formations, and simultaneous
631 chemical reactions as well as mass transfer processes. If sufficient data are available,
632 achievable CO_2 saturation, local or regional pressure constraints, dissolution as well as
633 residual saturation can be assessed with numerical simulation as they are dependent
634 mainly on the reservoir and fluid properties as well as injection strategies (Chadwick et
635 al. 2008).
636
637 Software designed for hydrocarbon systems in the oil industries are easily adaptable to
638 CO_2 storage as evident by code inter-comparison study (Pruess et al. 2003). However,
639 currently many numerical simulators have emerged in the field of sequestration
640 processes with function-specific as well as general applications. They include NUFT-
641 SYNEF (Morris et al. 2011a; Morris et al. 2011b), STOMP (White 2002), FEMH (Bower
642 and Zyvoloski 1997), ECLIPSE-VISAGE (Ouellet et al. 2011), OpenGeoSys (Wang and
643 Kolditz 2007), TOUGH2 (Pruess et al. 1999), TOUGHREACT (Xu et al. 2006), TOUGH-
644 FLAC (Rutqvist 2011; Rutqvist et al. 2002), CODE-BRIGHT (Olivella et al. 1994;
645 Vilarrasa et al. 2010), DYNAFLOW (Preisig and Prévost 2011), STARS (Bissell et al.
646 2011). Also, COORES, DuMux, GPRS, MUFTE, MoReS, ROCKFLOW and ELSA are
647 some of the models with capability for simulating different carbon sequestration
648 scenarios and are involved in the benchmark study for the inter comparison of
649 mathematical and numerical models in the context of geological carbon sequestration
650 (Class et al. 2009). In some (e.g., TOUGHREACT) fluids and heat flows are coupled
651 with reactive geochemistry to enhance applications in geological carbon sequestration.
652
653 The simulation code, ‘subsurface transport over multiple phases (STOMP)’ developed
654 using advance computational tools by Pacific Northwest National Laboratory (PNNL,
655 Washington) has the ability for simulating fully coupled mass and heat transport with
656 kinetic and/or equilibrium controlled chemical reactions, temporal and spatial responses
657 to injection, injectivity , hydrogeological and fluid properties change (White and McGrail
658 2005). Class et al. (2009) emphasised the investigation of influence of gridding, model
659 concepts and mechanisms to ensure quality control and assessment of numerical
660 simulators. However, further developments are required in the ability of the simulators
661 to quantify and relate leak factors on a site-specific basis. This should establish the
662 threshold values that may compromise the reservoir integrity. For example, one needs
663 to determine what quantity of CO_2, in conjunction with gas-brine-rock interactions and
664 time will result in leakage. Ability to easily predict this scenario will afford the

researchers the opportunity to establish site-specific limit of injection. For example, the work of Schwartz (2014) using TOUGHREACT presented a leakage factor: transmissibility. This was established for a potential leak zone as a product of width and permeability with a threshold value of $1.7x10^{-3}$ m^3. This is established based on the media property. However, such threshold established on gas-brine-media and time factors together with associated geophysical and geochemical processes will serve a caution on the limit of sequestration for site-specific assessments.

5. P^c-S-K_r relationships and phase characteristics in $scCO_2$-brine system

Some properties of CO_2–water system had been discussed above and are shown to be temperature and pressure dependent. Among them, the interfacial tension of CO_2-water had been shown to decrease with increasing pressure and attains a plateau in the supercritical state (Espinoza and Santamarina 2010; Kvamme et al. 2007). In contrast, contact angle of the system also changes with pressure relative to the wettability of the medium. It increases with pressure on oil-wet surfaces and decreases slightly on water-wet surfaces (Chiquet et al. 2007; Espinoza et al. 2011). The implication of this behaviour on two-phase flow characteristics can be discerned based on Young-Laplace relation: $P^c = \frac{2\gamma^{wn}\cos\theta}{r}$ where P^c decreases with decrease in interfacial tension, γ^{wn}, and increase in contact angle. Researchers of multiphase flow have reported patterns of $P^c - S - K_r$ relationship for multiphase flow and expatiated on number of factors affecting these relationships. Most of the works are published for oil-water system but of recent, we can find some studies relating to carbon sequestration. Changes in the interfacial tension as well as the contact angle will have impact on capillary pressure, residual saturation, evolution of flooding, capillary effects and relative permeabilities (Espinoza et al. 2011). Below, we examine the reports presented and the approaches adopted.

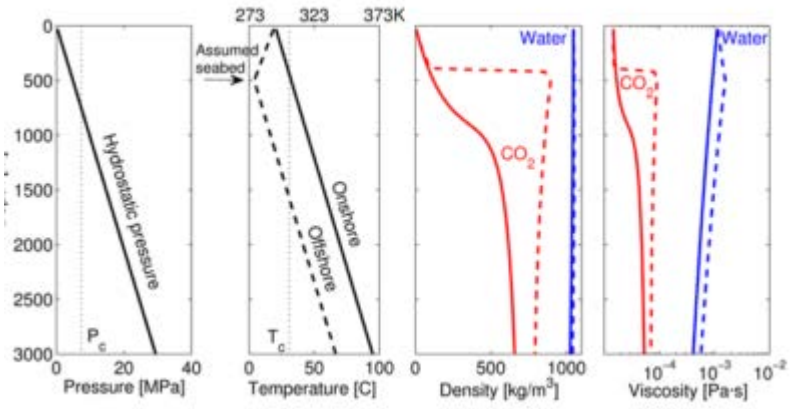

Figure 8: Density and viscosity of water and CO_2 with depth (Espinoza et al. 2011)

5.1 Effects of viscosity and density ratios of CO_2 on P^c-S-K_r relationships

The density and viscosity of the CO_2 have been shown to vary under different conditions of pressure and temperature. In Figure 8, the density of CO_2 can be seen following nonlinear rise from the surface to the injection bed about 1 km below ground and then follow a fairly straight line into a deeper injection field about 3 km down for the onshore sequestration. For the offshore operation this pattern changes as the density rises rapidly around the sea bed and then remains almost constant henceforth and larger at the same depth compared to onshore. In another part of the figure, the viscosity of CO_2 in offshore and onshore follows similar though with slight variation in values. On the other hand, the figure shows that the density of water remains constant with depth while there is slight variation in its viscosity with depth. Implication of the above properties behaviour is that at different depths of injection of CO_2 for sequestration, the ratios of viscosity and density of CO_2 to that of brine will vary. Viscosity and density ratios are some of the parameters identified to affect two-phase flow in porous media (Das et al. 2007; Goel and O'Carroll 2011). In the context of carbon sequestration, viscosity ratio refers to the ratio of the viscosity of non-wetting phase i.e., $scCO_2$ (μ_{CO_2}) to that of the wetting phase i.e., water or brine (μ_w). This ratio is mathematically expressed for viscosity as: $\mu_r = \frac{\mu_{CO_2}}{\mu_w}$ and density as: $\rho_r = \frac{\rho_{CO_2}}{\rho_w}$, respectively. While discussing the rate dependency of the $P^c - S - K_r$ relationships for oil-water system, Joekar-Niasar and Hassanizadeh (2011) stated that the invading front in a two-phase system becomes unstable if the viscosity ratio is less than one under drainage or if greater than unity under imbibition while the front becomes stable if the ratio is higher than one in drainage and lower than one in imbibition. This implies that the displacement of brine by $scCO_2$ may face instability and the lower the viscosity ratio at shallower depth, the higher the instability at the displacement front.

Das et al. (2007) pointed out that density ratio effect on $P^c - S - K_r$ relationships is dependent on the flow direction. The saturation-rate dependency of the relationships also known as dynamic effect increases as density ratio increases if the flow is in downward direction while the trend is still on the increase for decreasing density ratio if the flow is in the upward direction (Das et al. 2006). Implication of the above discussion

in the characterisation of $P^c - S - K_r$ relationships for the $scCO_2$-brine system in different geological media will require applicable mathematical functions, which in no doubt will be complex. Otherwise, the relationship will be determined for individual site.

5.2 Instability in the displacement of fluid/fluid interface in $scCO_2$-brine-porous media system

In a two-phase system in porous media, instability at the displacement front can occur because of the higher mobility phase displacing a lower mobility phase as in the case of $scCO_2$-brine system leading to fingering of the displacing phase (Berg and Ott 2012). This can be observed in both miscible and immiscible displacement conditions (Meurs 1957; Taylor 1958). Analytical model by Van Wunnik and Wit (1989) had earlier shown the source of this condition to be as a result of viscous pressure gradient leading to a steeper pressure gradient of the lower-mobility phase letting the finger grow. Among the factors controlling this condition, mobility is defined as the ratio of the relative permeability (K_r) of the phase to its viscosity (μ) and mobility ratio (m) as the ratio of the mobility of the displacing phase to that of the displaced. For CO_2 displacing brine, m is expressed in equation (15):

$$m = \frac{K_{rn}/\mu_n}{K_{rw}/\mu_w} \quad (15)$$

K_{rn} and μ_n are the relative permeability and viscosity of $CO_{2)}$, respectively while the K_{rw} and μ_w are the respective relative permeability and viscosity of water. It determines the stability and the efficiency of the displacement (Berg and Ott 2012) which becomes unstable at high m resulting in viscous fingering (Salimi et al. 2012). This is enhanced by the much lower viscosity of the CO_2.

Furthermore, capillarity was identified as another factor of importance affecting instability growth rate (Yortsos and Hickernell 1989; Babchin et al. 2008) causing ‘capillary dispersion’ (Riaz and Tchelepi 2004) by which a sharp front becomes transformed into a diffused zone with elongated tail (Berg and Ott 2012). This dispersion effect acts to suppress finger (Homsy 1987). In addition, the scale of consideration determines the influence of this capillarity as the dispersion occurs at the

same length scale as the shock front. Capillary number, Ca, is used to quantify the influence of this force and it is defined as the ratio of the viscous to capillary forces expressed as: $Ca = \mu V / \gamma$, μ is the viscosity of the displacing fluid, V the characteristic velocity and γ is the interfacial tension between the two phases. Change in Ca has been shown to affect the stability of the two-phase displacement patterns at different values of m. Numerical simulations results by Lenormand et al. (1988) showed that at high m and low Ca (-8<Log Ca<-6), capillary fingering dominates the displacement which becomes stable at high Ca (Figure 9a). At low m (Figure 9b), there exists a crossover region as the Ca increases. At this region the displacement mechanisms switches from the capillary to viscous fingering. Noticeable from the figure, at high m, is the improved saturation of the displacing phase as the displacement transitioned to stable displacement at appropriate Ca. Also, the figure showed the possibility of inefficient storage that may result from operating under viscous fingering at low m. Wang et al. (2013) demonstrated the influence of the Ca and the significance crossover on the displacement of water by $scCO_2$. They found increase in $scCO_2$ saturation as the logCa increases from -7.61 to -6.61 where capillary fingering dominates. At higher injection rates, viscous fingering dominates, and the $scCO_2$ saturation remains nearly constant.

Furthermore, the Ca equation, shown above, indicates the importance of the interfacial tension in the two-phase flow system. This also tells us some information about the stability of the system. For example, in the numerical simulation by Berg and Ott (2012), low interfacial tension in the range of 0-0.05 mN/m generally leads to unstable displacement while marginal stability is recorded at 0.1 mN/m. For interfacial energy that is greater than 1 mN/m, it becomes stable at an experimental scale.

Various factors have been reported to affect the γ between CO_2/water or CO_2/brine system. These include the temperature, pressure, salt concentrations and type of ions in the system. Under similar conditions, γ for CO_2/water and CO_2/brine show similar evolution with respect to temperature and temperature (Chun and Wilkinson 1995; Chalbaud et al. 2010). It decreases with pressure at constant temperature and this is more significant at lower pressure near the critical region (Nielsen et al. 2012; Shojai Kaveh et al. 2011) especially at low temperature (Chalbaud et al. 2010). At higher pressure, plateau is reached at the value of γ for the system that slight increases with

salt concentration at constant temperature (Chalbaud et al. 2010). This behaviour has been attributed to the solubility effects of CO_2 which increases with pressure at low pressure and remains nearly unchanged at higher pressure when the difference in densities between CO_2 and brine remains constant. Considering the dissolution effect on the density difference (Δρ) become more important at high pressure since γ calculation is a linear function of Δρ (Chalbaud et al. 2010; Chiquet et al. 2007). For a given height of stored CO_2, underestimating the γ between CO_2/water will lead to overestimating the displacement efficiency making it seem like there is more space for storage than in reality (Chalbaud et al. 2010). The valence of the cations present in the gas-brine-rock system has been shown to be important in the value of the γ. For CO_2-water system, γ is more than twice higher for the divalent cation (e.g., Ca^{+2}) than the monovalent type e.g., Na^{+} (Aggelopoulos et al. 2010).

In addition, the viscosity ratio and the non-wetting phase saturation have relation to the Ca and the stability of the two-phase system. Zhang et al. (2011) observe higher incident of viscous fingers in the two-phase flow at high Ca. For very low viscosity ratio, unstable displacement dominates with the viscous fingers for all Ca. For moderately low viscosity ratio, there exists a value in Ca at which there is a crossover from unstable to stable displacement. This condition corresponds to $\log \mu_r > 0$ (Zhang et al. 2011). Based on Figure 8, at moderate depths of the aquifers (between 500 to 1000m), stable displacement is enhanced at offshore sites where CO_2 viscosity is higher.

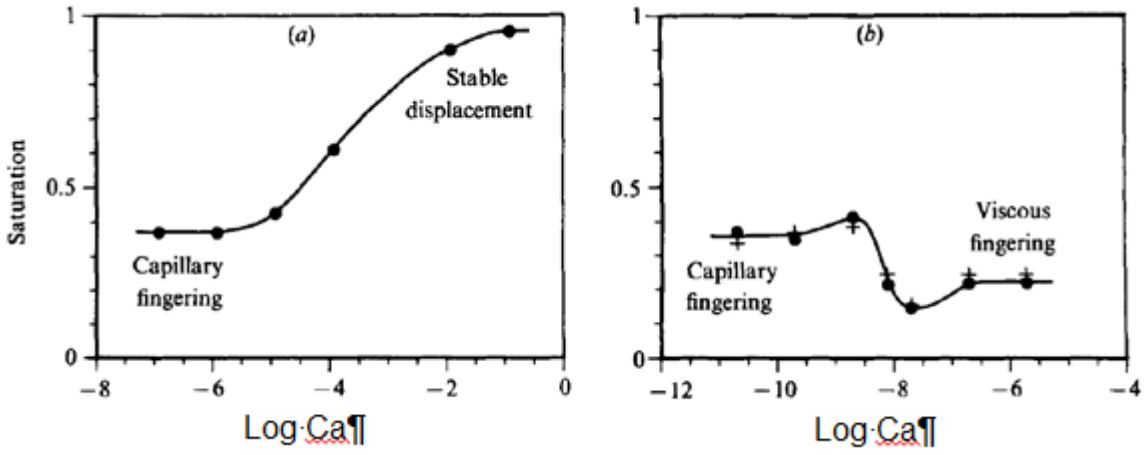

Figure 9: Capillary number and the displacement in the two-phase system (a) high viscosity ratio (log m = 1.9), (b) low viscosity ratio (log m = - 4.7). Vertical axis represents the saturation of the displacing phase (Lenormand et al. 1988).

Authors like Plug and Bruining (2007) and Plug et al. (2006) acknowledge that the supercritical CO_2 state is prone to phase transition together with property fluctuation. These behaviours may not be unexpected to affect the stability and the $P^c - S - K_r$ relationships for the system. Plug and Bruining (2007) observed irregular P^C-S relationships for supercritical CO_2 (at 40^0C and 85 bar) under drainage while usual P^C-S curve pattern was obtained for liquid CO_2 (27^0C and 85 bar). This was attributed to CO_2-wet behaviour or occasional imbibition of water during the process. This behaviour can also be viewed as part of the manifestation of the above-described instability in the displacement. $scCO_2$ phase undergoes irregular transition in properties and characteristics at slight change of temperature, pressure and velocity which are difficult to maintain constant in the system. The fact that this is absent in liquid case points to the fact that reduced interfacial tension in $scCO_2$ (Nielsen et al. 2012; Espinoza and Santamarina 2010) may be responsible judging from the report of Berg and Ott (2012). Both authors (Nielsen et al. 2012; Espinoza and Santamarina 2010) reported that the interfacial tension of CO_2-water system reduces with pressures but levels off above the CO_2 critical condition (~7 MPa) at fixed temperature (Nielsen et al. 2012). However, the work of Kaveh et al. (2013) show that the decrease continues up to 100 bar. Furthermore, the sharp deviation in contact angle from the subcritical to supercritical regions of CO_2 (Saraji et al. 2013) show that phase transition holds important information about the phenomena in the $scCO_2$-brine system. Considering these cases, phase transition in the geological media in conjunction with numerous subsurface processes associated with $scCO_2$-brine and porous media systems may be complex and point finger at the system stability and reliability.. This calls for more understanding of the fluid-fluid-media system and characteristics, e.g., P^C-S-K_r relationships under the varying conditions. K_r-S functions is essential for accurate analyses of the CO_2-water displacement process (Berg and Ott 2012).

5.3 Influence of pressure, dissolution and wettability

The comparisons made between N_2 and CO_2 experiments by the Plug and Bruining (2007) showed that CO_2 dissolution in water results in lower residual gas saturation. This is similar to the findings of Pistone et al. (2011). Also, the capillary pressure of $scCO_2$ was found to be lower if compared to gas and liquid CO_2 at every corresponding saturation. Several authors (Tokunaga et al. 2013; Plug and Bruining 2007) are

unanimous in their observations that the $P^c - S$ relationships decrease as pressure increases owing to decreasing interfacial tension (Chun and Wilkinson 1995; Espinoza et al. 2011) while for secondary imbibition the negative P^c at around high water saturation was attributed to alteration in wetting behaviour (Plug and Bruining 2007). Though the effects of dissolution were more pronounced for the CO_2 injection compared to N_2, the capillary pressure was said not to be affected by the dissolution since the P^c curves in both cases appear in the same range. But, it is well known that the dissolution effects act to reduce the surface tension of a two-phase system as earlier pointed out by Bennion and Bachu (2008) for CO_2-brine and H_2S-brine systems. Therefore, it is difficult to rule out the effect of dissolution on the observed differences in P^C-S at higher pressures. For $scCO_2$, small perturbations in the system dynamics cause sudden events resulting in the spontaneous imbibition of water into the system during drainage (Plug and Bruining 2007). This results in a decreasing capillary pressure and an irregular drainage curve. Also, wettability effect showed that the sand remains water-wet going by the positive drainage capillary pressure measured for all temperature and pressure conditions considered. Plug et al. (2006) showed that coal bed was water-wet in primary drainage but increasing pressure changes this to CO_2-wet condition in medium rank coal. They found that the effects of adsorption were not very pronounced with the significant CO_2-wet condition re-occurring for the imbibition processes conducted. Their reports concluded that imbibition experiments provide good qualitative information regarding the wettability of coal.

5.4 $P^c - S - K_r$ relationships in consolidated porous rocks

The work of Pini et al. (2012) reported $P^c - S$ for consolidated media, namely, the Berea and Arqov sandstone samples. Discussing the relation in reference to temperature, the $P^c - S$ curves for the Berea sandstone showed that capillary pressure decreases as temperature reduces and this behaviour was attributed to increase in CO_2 dissolution as the temperature decreases reducing the interfacial tension. By implication, the supercritical CO_2 will have a higher P^c than liquid CO_2. But this will contradict the conclusion of other authors that the liquid CO_2 has higher P^c than $scCO_2$ (Plug and Bruining 2007). Also, the $P^c - S$ profile in Berea sandstone, described as well sorted and homogenous sample, was consistently low for wide range of saturation with sharp rise in $P^c - S$ values close to irreducible saturation. In comparison, the Arqov sample described as heterogeneous in nature displays a sharper rise and

broader distribution in $P^c - S$ while the profile remains considerably higher than in Berea sandstone for most of the saturation values. This brings to mind the influence of heterogeneities in $P^c - S$ relation as earlier reported for oil-water system (Mirzaei and Das 2007) as the micro-heterogeneities are abundant in oil reservoirs (Van Lingen et al. 1996; Pickup et al. 2005). A list of experimental methods, fluid and media characteristics and various equipment applications by various authors in connection with $P^c - S - K_r$ determination for $scCO_2$-brine system in the context of geological sequestration is shown in Table 2.

6.0 Leakage risks and monitoring

Risks of leakage of stored carbon dioxide portend serious dangers to the potable water aquifers that may lie along the escape paths. Also, on the earth's surface, living species are susceptible to CO_2 inhalation while leakage through the ocean with consequent acidification poses harm to marine life. Technically, leaks could occur as results of gravity override together with viscous instability causing the carbon dioxide to move to the top of the injection layer bypassing large quantities of brine (Gasda 2008; Saripalli et al. 2001; Metz et al. 2005). If the caprock however has favourable pathways, the carbon dioxide could escape vertically compromising the intention of the process. The vertical buoyant pressure applied on the caprock by the carbon dioxide is as a result of difference in density between the formation waters and the carbon dioxide, and the thickness of the carbon dioxide plume accumulation.

Monitoring technologies are widely discussed in the literature. They are built upon the physico-chemical properties of the CO_2-brine-rock system or the detection of the reaction by-products or even the coupled process effects such as micro-seismicity (Espinoza et al. 2011). Methods like electrical resistivity and wave propagation are most often employed in deep reservoir applications (Nakatsuka et al. 2010) while application of tracers like SF_6 aid the monitoring of fluid movement. The monitoring methods should extend several hundred meters beyond the injection region to safely check the advancing plume of CO_2. In addition, monitoring the deep region around the aquifers should be coupled with near surface and surface monitoring.

To this end, available technologies should be adequately utilised. These include: electromagnetic techniques (Nakatsuka et al. 2010), temperature signals (Bielinski et al.

2008) and infrared monitoring (Charpentier et al. 2009) that have been demonstrated either in the laboratory or pilot applications for subsurface monitoring. Methods like electromagnetic techniques utilise the wide gap between the dielectric permitivitties of CO_2 and water to create contrast with reference the CO_2 saturation in the domain. Non-isothermal effects such as CO_2 dissolution and change of phase are made use of in the temperature signal method while the characteristic infrared wave absorption property of CO_2 is harnessed in the infrared monitoring technique. Near surface monitoring is also essential as stated before and this involves the analysis of near surface water, air and soil samples on a regular basis as CO_2 leaks can acidify the water and create conspicuous contrast between the original and current soil and air compositions. On the surface, the use of gravity method (Alnes et al. 2008) as CO_2 is heavier than air and lighter than water, remote sensing of air composition (Leuning et al. 2008) and surface analysis of carbon content by Inelastic Neutron Scattering (INS) (Wielopolski and Mitra 2010) have been reported. Overall, monitoring protocols are essential for effectiveness of success of geological sequestration of CO_2.

7.0 Concluding remarks

To address the issues of climate change and the problems of global warming requires meticulous scientific and engineering approaches. The current opinions favour geological sequestration option. Therefore, scCO_2-brine-rock interactions together with the *in situ* processes and trapping mechanisms should be quantified accurately as they play significant roles in determining the efficiency and safety of these processes. . Out of many candidate sites, choosing an appropriate geological site requires optimizing the process functions relating to the media, fluid and operational characteristics. This is more so as these characteristics directly or indirectly affect the processes which determine safe CO_2 storage, e.g., dissolution and structural trapping, reaction and mineral precipitation, etc. CO_2 solubility is influenced by the porosity and pore size distribution (Emmanuel et al. 2010). So, developing the optimization protocols will aid the general practices in this regard. In relation to this, mathematical modelling and simulation tools have played significant roles, providing insightful predictions of the fate of the stored carbon and various processes including the trapping mechanisms. But, the site-specific indicators of CO_2 leakage, and predictable compromise of reservoir integrity with the quantity and dynamics of CO_2 in the reservoir are desired to be integrated in the system software with fully-coupled geochemical, fluid-fluid-solid, hydrogeological, physical and chemo-physical conditions. Such indicator or factor

should consider the impact of man-made leakage zone (see, e.g., (Humez et al. 2011; Tao and Bryant 2014)) as well as natural-leakage zone (see, e.g., (Schwartz 2014)). Affordable and commercial availability of the software products will drive research and field developments.

As a special kind of two-phase flow system, $P^c - S - K_r$ relationships for $scCO_2$-brine-rock system are important in the modelling and analysis of the sequestration operations. But, the list of available experimental publications is far from sufficient especially when viewed from possible factors that can affect $P^c - S - K_r$ relationships from closely related process as encountered in the studies of oil recovery, oil spill remediation, contaminant transport and so on. Wettability of the medium is shown to be responsible for the irregularity in the pattern of $P^c - S - K_r$ relationships (Plug and Bruining 2007) with the possibility of *in situ* alteration in media wettability. This needs further investigation in order to keep the function applicable in the modelling and prediction of sequestration process and storage safety.

Most of the $P^c - S - K_r$ relationships reported are related to quasi-static or equilibrium conditions. The dynamic behaviour of the system particularly at the immediate time following injection prior to the attainment of equilibrium needs to be better understood. In this regards, the difference in the quasi static or dynamically measured $P^c - S - K_r$ relationships will be of interests. Researchers of multiphase flow had dedicated past decades to the study of various dynamic effects in system properties of multiphase flow. Part of the investigations dwelled largely on the saturation-rate dependency of the system properties and a number of publications had resulted (Hassanizadeh and Gray 1993; Das et al. 2007; Mirzaei and Das 2007; Hanspal and Das 2012; Dahle et al. 2005; Goel and O'Carroll 2011; Das and Mirzaei 2013). Particularly for $P^c - S$ relationships, the dynamic coefficient, τ, used in quantifying this phenomenon has been said to be dependent on media permeability (Mirzaei and Das 2007; Tian et al. 2012; Hanspal and Das 2012; Dahle et al. 2005), microheterogeneity (Mirzaei and Das 2007), fluid properties (Das et al. 2007; Goel and O'Carroll 2011), scale of observation (Dahle et al. 2005; Bottero et al. 2006 ; Bottero et al. 2011; Nordbotten et al. 2007), etc. Though, the observations and reports were made largely in relation to oil-water system, investigating the same effects for the rock-$scCO_2$-brine system will broaden the present state of

study while improving the applicability and integrity of $P^c - S - K_r$ relationships as a modelling function for the rock-scCO_2-brine system.

For example, different media permeabilities are encountered and hardly can two porous media share the same permeability even at a contiguous sediment. A look at Table 2 reveals this reality as each experiment has different media permeability unique to it. Even within an aquifer or reservoir, media anisotropy may be assumed but the reality dictates otherwise (Pickup et al. 2005; Nordbotten et al. 2007; Aggelopoulos and Tsakiroglou 2008). Micro-heterogeneities are another closely related property of the porous media. These are abundant in the reservoir (Van Lingen et al. 1996; Pickup et al. 2005) and they affect the micro and macro scale quantity of the system variables while τ is said to increase with its intensity (Mirzaei and Das 2007). Aquifer or reservoir exhibits these properties or characteristics with few exceptions and are worth investigating in the context of carbon sequestration, especially the way they affect the $P^c - S - K_r$ relationships.

To determine $P^c - S$ relationships for two-phase flow in any aquifer or reservoir, pressures in both phases need to be measured separately and saturation simultaneously determined. From the literature discussed in this review, it seems that the common laboratory measurement methods used for determining the $P^c - S$ parameters for scCO_2-brine/water system can be better described as pressure drop across the domain to get the P^c and the measurement of the outflow water or brine for the saturation. An advanced *in situ* saturation measurement method was presented by Pini et al. (2012) using a medical X-ray CT scanning instrument with good resolution. This has the additional ability to determine the sample porosity. But the cost of this instrument and technicalities may pose challenges to many promising investigations. To overcome this, instruments like time domain reflectometer (TDR) can be recommended. They had been variously used to obtain *in situ* saturation measurement for decades (Das and Mirzaei 2013; Goel and O'Carroll 2011; Camps-Roach et al. 2010; Topp et al. 1984). Most of these experiments were conducted for oil-water and air-water systems mostly at near ambient condition but the instrument is still easily adaptable to the supercritical condition of carbon sequestration. The TDR probe has the capacity to determine the bulk electrical conductivity of the system in addition to the dielectric constant used in determining water saturation.

1022 **Table 2:** Typical P^c-S-K_r experiments for $scCO_2$-brine/water system in the literature (D: diameter L: Length)

Author(s)	**Porous Materials**	**Fluid**	**Permeability (m^2)**	**Porosity**	**Process Condition(s)**	**Equipment Type**	**P^c Measurement Method**	**Sample Dimensions (cm)**
Plug and Bruining (2007)	Unconsolidated sand	$scCO_2$ - water	2×10^{-10}	0.36	21-40 (^oC), 1-85 (bar)	Porous plate and micropore technique	Pressure difference across domain	8.4 (D) 2.5 (L)
Plug et al. (2006)	Unconsolidated sand, coal		–	0.36-0.38 (sand), 0.42-0.45 (coal)	21-40 (^oC), 1-85 (bar)	Porous plate and micropore technique	Pressure difference across domain	8.4 (D) 2.5 (L)
Tokunaga et al. (2013)	Unconsolidated sand		3.9×10^{-11}	0.381	45 (^oC) 85-120 (bar)	Porous plate	Externally controlled fluid-fluid interface adjustment in relation to reference plane	8.2 (D) 3 (L)
Pentland et al. (2011)	Consolidated sandstone	$scCO_2$ - brine	4.6×10^{-13}	0.22	70 (^oC) 90 (bar)	Porous plate	Pressure difference across domain	3.85 (D) 7.53 (L)

Pini et al. (2012)			2.7 x10^{-13}	19.5	25-50 (^{o}C) 90 (bar)	Modified porous plate		5 (D) 9 (L)

It has been argued that external measurement of capillary pressure loses significance near residual saturation (Morrow and Harris 1965; Bottero 2009) as the non-wetting phase pressure dominates at this period when the wetting phase experience disconnectivity and thus making the measured wetting phase pressure appear larger. This makes the P^c smaller than supposed. But, the challenges of *in situ* phase pressure measurement are not simple, considering the high pressure and above ambient temperature of the supercritical CO_2. At this state, most of the semi permeable membranes used by many authors (Das and Mirzaei 2012; Bottero et al. 2011; Hou et al. 2012) or porous ceramic discs (Camps-Roach et al. 2010; Goel and O'Carroll 2011) employed in oil-water or air-water systems will fail to distinguish any phase under supercritical condition as they were designed to operate under ambient conditions. However, there is hope in some of the metallic materials recently used by some authors under similar conditions even though they were not used to measure phase pressures. For example, C276 Hastelloy porous plate used by Tokunaga et al. (2013) and aluminium silicate by Pentland (2011) were described as semi permeable hydrophobic and hydrophilic discs, respectively under the supercritical conditions. Many other materials may still be available from membrane manufacturers to achieve this aim.

The effect of scale on dynamic effect in $P^c - S - K_r$ relationships is also well reported (Dahle et al. 2005; Bottero et al. 2011; Camps-Roach et al. 2010). Most of the experiments available for $scCO_2$-brine-rock system are, at most, at the core scale size. How these relationships vary with size of the aquifer or field scale will be of great importance in the complete assessment of the factors affecting the $P^c - S - K_r$ functions and will improve the versatility of their applications. The following bullet points will help to emphasis some suggestions based on this review:

- There are needs for experimental investigations of the effects of media characteristics e.g., domain scale, on the $P^c - S - K_r$ relationships for $scCO_2$-brine system at conditions applicable to geological carbon sequestration.
- To promote our understanding of caprock integrity, investigations of the pore size distribution on relative permeability of CO_2 needs to be made clearer in

conjunction with interfacial tension of the $scCO_2$-brine system. For example, one may ask, 'how does the combination affect the entry pressure of the caprock?' Such investigations need to be conducted in the context of pressure, temperature, salt concentration, cation valence that are known to influence the interfacial tension. Contributions of the long-time mineral precipitation to change in salinity, combinations of cation valences and their effects on the above parameters will be very enlightening.

- Use of surfactants to curtail migration of $scCO_2$ in saline aquifer and promote residual trapping will deserve future investigations, e.g., can surfactants check viscous and capillary fingerings in $scCO_2$-brine-rock systems? There are many works on the use of surfactant and CO_2 in literature which are related to enhanced oil recovery (EOR).
- Inclusion of leakage parameters on a site-specific basis in the modelling and simulation of the system should be encouraged.
- The dynamic capillary pressure effects for the $P^c - S - K_r$ relationships should be investigated in relation to $scCO_2$-brine-rock system and these relationships should be incorporated in the relevant simulators for the geological carbon sequestration.
- The wettability alteration and the caprock integrity from the perspective of the alternation of the $scCO_2$-brine-rock system conditions from neutrality to acidity and alkalinity as a result chemical complexation and mineral dissolution deserve more investigations. As different cationic valences change the interfacial tensions, how do similar changes in the subsurface conditions affect the wettability? This will be an important question to answer in future investigations.
- How continuous or intermittent injection and its rates influence residual trapping of injected CO_2 will be a subject of interesting investigations.
- Cheap and simple CO_2 leakage detection system should be developed for common household to be used for the independent assessment of CO_2 gas accumulation, especially for residents closer to transport pipeline or geo-sequestration sites.

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