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**TNO report**

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**Caprock Integrity of Deep Saline Reservoirs and  
Coupled Processes**

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## Abstract

The anthropogenic greenhouse effect is becoming an increasingly alarming consequence of enormous emissions of human-made greenhouse gases, of which CO<sub>2</sub> is emitted in the largest quantities. Geological disposal, more specifically deep saline aquifer disposal, is a potential storage mechanism to prevent its emission into the atmosphere. On-going research into the potential of aquifer disposal has identified the sealing ability of the overlying caprock as one of the most important determining factors related to its storage effectiveness over geological times.

This report presents an up-to-date examination of caprock integrity associated with CO<sub>2</sub> storage. The fundamental responses of mudrock and shale caprocks with respect to geomechanical deformations, geochemical equilibrium, and changes in physical flow patterns are presented. Further, the report gives examples from natural analogue sites, laboratory testing, modeling, and a current field study of aquifer storage underway in Norway's North Sea. The discussion is limited to permanent storage of CO<sub>2</sub>, under caprocks which are water-saturated. Further, although evaporites also have large potential to provide adequate sealing, as proven in various hydrocarbon accumulations, they are not addressed in this report. Sealing efficiency with respect to argillaceous materials is the focus.

Clay-rich compact sediments have posed various engineering and hydrogeological challenges in the past. Strong physio-chemical interactions between the water molecules and mineral surfaces, very low permeabilities, and large specific mineral surface areas all contribute to the very specific behaviour of clay-rich materials. Fabric structure, physical transport properties, porefluid chemistry, geomechanical behaviour, geochemical equilibrium, and other complex parameters and processes influence the seal efficiency of caprocks. The required information is often difficult to obtain; even the controlling processes are not always well understood. Erroneous assumptions can lead to misconceptions about the sealing efficiency.

Discontinuities, fractures and faults, can result in permeabilities several orders of magnitude larger than of intact rock. Seal continuity and fracture sizes and density are therefore important parameters to characterize. Identifying the nature of fractures, and the class of materials most likely to fail under brittle deformation is important to predict the behaviour of caprocks. Various authors have provided such a framework under the theories of soil behaviour known as critical state soil mechanics. Geochemical reactions with stored CO<sub>2</sub> can significantly impact the rock fabric, resulting in changes to both its physical flow properties and its geomechanical response.

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# 1 Introduction

The anthropogenic greenhouse effect results from the human-made sources of greenhouse gases (GHG) such as chlorofluorocarbons, methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) released into the atmosphere. The large amounts of CO<sub>2</sub> emitted into the atmosphere from energy production and fossil fuel combustion, have led the focus of GHG emission discussions to CO<sub>2</sub>. Various technologies are currently being investigated in an effort to mitigate the anthropogenic GHG effect; one of these is the storage of CO<sub>2</sub> in various geological media. Potential recipients currently investigated include depleted oil and gas reservoirs, old salt caverns, deep oceanic beds, deep coal seams, and deep saline aquifers. The storage of CO<sub>2</sub> in deep saline aquifers is the focus of the present report.

CO<sub>2</sub>, currently found in the atmosphere at concentrations of 360 ppmv (Houghton, 1997), is a known contributor to the natural greenhouse effect. CO<sub>2</sub> is a nonpolar molecule with molecular weight of 44.009g/mol, and a critical pressure, temperature and specific volume of 7.31MPa, 31.1°C, and 2.147cm<sup>3</sup>/g respectively (Fogg and Gerrard, 1991). The CO<sub>2</sub> phase diagram is illustrated in Figure 1.1. Storage of CO<sub>2</sub> in a supercritical state is thought to be the most efficient use of aquifer storage capacity due to the increased density of supercritical CO<sub>2</sub>. Supercritical refers to the region in the phase diagram with temperature and pressure higher than those of the critical point (Felder and Rousseau, 1986). In other words, at supercritical conditions there is no distinct phase transition. Duan et al (1992) developed an Equation of State valid for temperatures between 0 and 1000°C, and for pressures between 0 and 8000 bar.

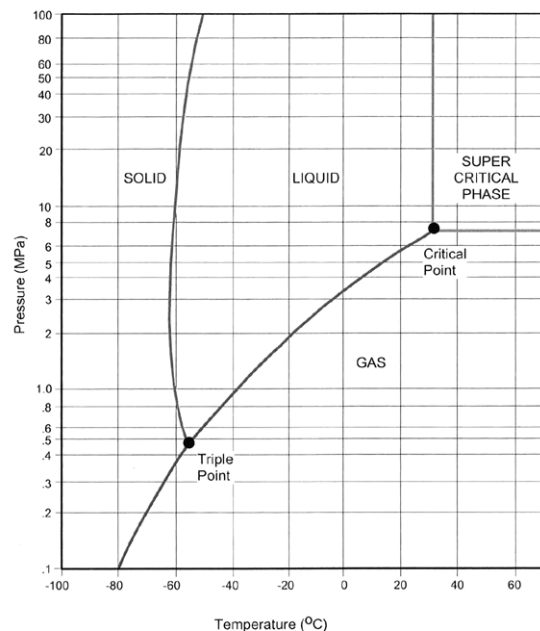


Figure 1.1 CO<sub>2</sub> phase diagram (adapted from Bachu et al., 2000).

It has been suggested that significant volumes of GHG could be securely contained over geological time frames within the porous space of deep saline aquifers. A number of criteria have been identified for successful aquifer sequestration (Gunter et al., 1993; Bachu et al., 1994; Holloway et al., 1996; van der Meer, 1992):

- The aquifer should be located near the source of the carbon dioxide, with large enough capacities to sequester significant volumes of CO<sub>2</sub>
- The top of the aquifer should be below 800 m, to ensure the CO<sub>2</sub> is in supercritical state
- The region near the injection well should be relatively permeable to allow for high injectivity of carbon dioxide
- A secure aquitard/caprock must overly the aquifer to ensure safe entrapment of CO<sub>2</sub> because CO<sub>2</sub> is less dense than the surrounding porefluid, and will migrate to the top of the aquifer.

There has been some debate whether lateral containment would be necessary. Hydrogeological trapping and mineralization reaction mechanisms within the aquifer could ultimately trap the CO<sub>2</sub> over geologically long periods (Gunter et al., 1993). We will not further comment on this issue but focus our discussion on the properties of the required seal.

Caprock integrity, its ability to seal against migration, is thought to be one of the most important factors in the safety assessment of long term GHG storage in deep aquifers. The effectiveness of the seal over geological time periods controls its ability to prevent migration into potential hydrocarbon sources, into potable water sources, or migration eventually back into the atmosphere. This report considers the storage of CO<sub>2</sub> in deep saline aquifers with specific emphasis to the integrity of the overlying aquitard or caprock. It is a complex issue because of the interactions between CO<sub>2</sub> and the seal, as they will be in direct contact due to buoyancy. Therefore, not all factors have been addressed in the current report. The following limitations need to be noted:

- Only permanent storage of CO<sub>2</sub> is discussed. Temporary repositories, whereby CO<sub>2</sub> is stored and removed for agricultural and industrial purposes, have not been considered. Therefore, dynamic and static stress conditions of caprock seals have been omitted from this study.
- Discussion is limited to the state of caprock integrity as the ultimate factor in risk assessment of aquifer disposal. Aquifer conditions are not discussed in great detail.
- Caprocks in deep saline aquifers are water-saturated, and disposal of CO<sub>2</sub> is likely to occur under supercritical conditions. Unsaturated caprock conditions are very unlikely, with some exceptions of very shallow disposal sites. Thus, transport mechanisms are discussed here under saturated caprock conditions only.
- The most common caprock lithologies are argillaceous sediments and evaporites. Despite their vast potential to provide adequate sealing, as proven in various hydrocarbon accumulations, evaporites are not addressed in this report. Sealing efficiency with respect to argillaceous materials is the focus.
- Fractures result in significant increases in permeability, but specific situations may also lead to the development of smear clay faults that provide relatively impermeable sealing characteristics. For caprock seals, however, brittle failure is the most important, and the focus of the current report will thus be on brittle crack failure.

The report first discusses the relevant caprock characteristics in Chapter 2. These are analogous to shales sealing hydrocarbon reservoirs and to rocks selected for nuclear waste repositories. Then the transportation mechanisms of CO<sub>2</sub> through the seals are discussed (Chapter 3), and how these are influenced by solubility, geomechanical characteristics and geochemical reactions (Chapters 4, 5, and 6). Chapter 7 presents a brief discussion of sealing mechanisms present in natural accumulations of CO<sub>2</sub>. Chapter 8 presents a current field study of aquifer storage in the Norwegian sector of



the North Sea. Chapter 9 summarizes the coupled processes playing a role in caprock selection and discusses the criteria for it. The report closes with a discussion of required research and with conclusions (Chapters 10 and 11).

## 2 Caprock

Any type of lithology can theoretically act as a caprock, however, shales and evaporites are the most common. Caprocks are responsible for the trapping of hydrocarbon gases in reservoirs, the presence of natural gas accumulations such as N<sub>2</sub>, CO<sub>2</sub> etc., and overpressured reservoirs. Lithology, thickness, ductility and fracture density are all factors which influence the seal properties, and are determined by microscopic and macroscopic properties of the seal.

### 2.1 Classification

Watts (1987) used the failure mechanism of caprocks to classify them into two categories: membrane and hydraulic seals (Figure 2.1).

Membrane seals refer to caprocks whose sealing capabilities are controlled by capillary entry pressure, and fail due to capillary leakage. Capillary forces are exerted at the interface between the non-wetting phase (CO<sub>2</sub>) in a reservoir and the wetting phase (water or brine) in the overlying top seal. Leakage occurs once the pressure of the non-wetting fluid exceeds the capillary forces. The minimum gas entry pressure, or the weakest point of a membrane seal, is largely controlled by the throat radius of the largest interconnected pore. As a generalisation, in capillary-pressure controlled membranes, the sealing capacity of the caprock increases with decreasing pore size, decreasing wettability, increasing gas-water interfacial tension, and greater down-dip flow from the caprock to the reservoir (Downey, 1984; Watts, 1987). Once the displacement capillary pressure has been exceeded flow may occur by two-phase Darcy flow, and leakage becomes a function of matrix permeability, as the porous space becomes more CO<sub>2</sub>-wet. Wettability of the caprock is thus especially important in membrane type seals. Wettability and interfacial tension between the fluid and the porewater significantly affect breakthrough behaviour of fluids through saturated media (Hildenbrand et al., 2002).

In contrast, hydraulic seals exhibit sufficiently high capillary entry pressures, such that the mechanical strength of the intact rock is exceeded before fluid pressures reach the capillary displacement pressure. Tissot and Pelet (1971), translated by Hedberg (1974), may have been the first who described the mechanism of oil and gas movement through water-saturated low permeability materials as a hydraulic seal failure. In their work they described the difficulty of hydrocarbon migration through materials with exceedingly high capillary entry pressures. They suggested that the seal could only be broken if the pressure within the fluids, formed in the porous space of the rock matrix, increased to a point where the mechanical strength of the seal was exceeded. The process would result in the formation of microfissures, allowing hydrocarbon migration through the caprock seal. The caprock thickness is therefore an important parameter in building confidence about the integrity of a hydraulic seal, since the probability of continuity of a seal is greater with increasing caprock thickness. Uncertainties remain around the mechanisms which promote the formation of microfractures in argillaceous materials, and evidence of their formation is largely inferred by the behaviour of fluid pressures in reservoirs as described by leakoff tests (Dewhurst et al., 1999). Both shales and evaporites are materials classified as hydraulic seals, as their intact structure promotes very high capillary entry pressures.

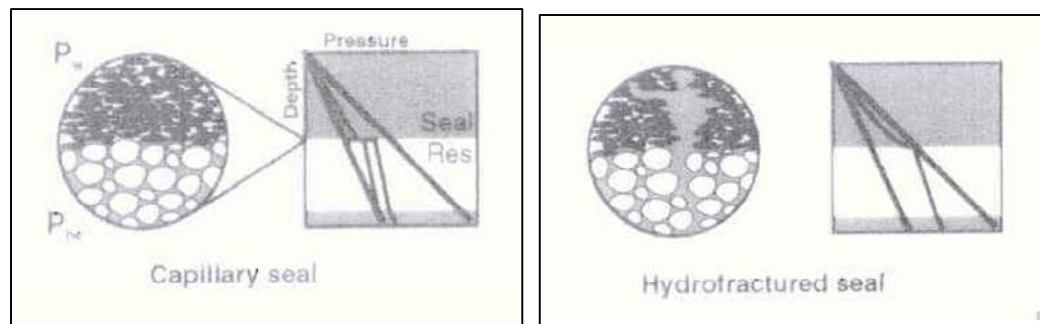


Figure 2.1 Membrane, i.e. capillary seals (left) fail due to capillary leakage while hydraulic seals (right) exhibit higher capillary entry pressures and fail due to hydrofracturing (Ingram et al., 1997).

## 2.2 Seal Effectiveness

Crucial factors in determining the effectiveness of a hydraulic seal include the lithologies and properties of the caprock, diagenesis, ductility, and its local and regional continuity. Stable and relatively ductile lithologies covering extensive areas cap major reserves and resources of hydrocarbons worldwide (Grunau, 1987).

### 2.2.1 Lithology

The lithology is thought to be the most important factor in good seals (Nederlof and Mohler, 1981). Varying lithologies have significant impact on the response of the seal under varying mechanical, chemical and hydrological conditions. Of the 25 largest gasfields in the world, nine are sealed by evaporites, and the remaining are sealed by shales (Grunau, 1987). The actual volumes of gas secured by evaporite versus shale caprocks are unknown, but it appears that shales may secure larger volumes.

Evaporites, typically marine derived sediments, with the exception of very specific conditions in lakes, are remarkably good ductile seals under several thousand feet of overburden, but they can exhibit brittleness at shallow depths (Downey, 1984). Anhydrites ( $\text{CaSO}_4$ ), usually associated with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), are commonly found in sedimentary rocks, and are the most abundant evaporite minerals. Anhydrite is a fibrous, granular crystal of white with grey/blue colouring (Whitten and Brooks, 1972). The Bravo Dome  $\text{CO}_2$  field in New Mexico, USA is an example of a gas accumulation overlain by anhydrite caprocks (Pearce et al., 1996). Rock salt, or halite ( $\text{NaCl}$ ), is colourless to grey in colour, with a solubility of 26.4% at  $20^\circ\text{C}$ , and typically exists as layered formations or as domes. Past studies suggested that rock salt was impermeable below a depth of 300m (Baar, 1977); however, more recent research has found that permeability of rock salt to brine is dependent on the depth of the formation. Deeply buried salt, at 3-4km burial depth, was shown to exhibit some permeability despite the low porosity (Lewis and Holness, 1996). Rock salt has been suggested as a host material for radioactive wastes due to its low permeability, low porosity, generally low moisture contents (~1%), and high self-sealing capacity (Rodwell et al., 1999). Salt rock is unique in that it is highly soluble in water, therefore moisture has a large impact on its strength and sealing characteristics. The excellent potential sealing of evaporite seals is demonstrated by large volumes of hydrocarbons, which are capped by evaporites (Grunau, 1987).

Argillaceous rocks, viz. mudstones, clays and shales, are commonly found as top seals in natural  $\text{CO}_2$  accumulations (Stevens et al., 2001) and hydrocarbon reserves (Grunau,

1987; Caillet, 1993). They have also been identified as suitable host rock materials for nuclear waste storage (Rodwell et al., 1999). Clay rich materials exhibit interparticle spaces of submicroscopic dimensions, they possess very large specific mineral surface areas, exhibit strong physio-chemical interactions between the water molecules and the mineral surfaces, have extremely low permeabilities and a very pronounced coupling between the hydraulic and mechanical responses. Small interparticle spaces and low permeability of intact materials make fluid transport by advective flow an unlikely dominating transport mechanism. Clay-rich materials are further complicated by the strong interactions between the water and dissolved ions in the porous space and the clay minerals. These processes are often described by diffuse double layer theories, most notably the Gouy-Chapman and Stern models, which describe the flocculation and de-flocculation behaviour of smectitic clays in monovalent electrolytic solutions. These models are also useful in illustrating the generic distribution of water and ions on the surfaces of clay minerals (Mitchell, 1993). The water molecules are thought to be so strongly adsorbed to the mineral surfaces that the force required to expel the water may be greater than the confining pressure to which the rock is subjected. The capillary pressures required to displace water for gas, in traditional two phase Darcy flow, is then so high that it can exceed the overburden pressure fluid flow through such materials, placing these materials in the class of hydraulic seals. The applicability of Darcy's law with respect to gas flow in water saturated clay-rich sediments has been disputed, because of the distinct effect between the clay mineral surfaces and the adsorbed water molecules. Fluid flow is also associated with the effective and overburden stresses, which the formation is subjected to.

It has been shown that multiple sequences of anhydrite and clay-rich rock formations are very effective seals against leakage. The Miocene Anhydrite caprock in the Zagros Fold-Belt of Iran is an example of multiple seals, where the final top cap is an evaporite seal (Grunau, 1987). The natural accumulation of CO<sub>2</sub> in the St. Johns Dome along the Arizona/New Mexico border in the USA is another example of a securely stored reservoir of gas overlain by a complex sequence of anhydrite and shale layers (Stevens et al., 2001). However, even multiple seal sequences have been inadequate in areas of high tectonic activity and increasing formation of fractures. An example is the Werra Potash basin in Germany, which is a complex sequence of anhydrites and claystones overlain by a rock salt bed (Pearce, 2001).

Behaviour of anhydrites and clay-rich rocks is significantly different. The current study only addresses the complexities involving the behaviour of argillaceous rocks, which is the most common sediment type found in nature.

### 2.2.2 *Thickness*

Although a few inches of shale is theoretically thick enough to provide an adequate seal, it is unlikely that such a thin layer would be continuous and unbroken over the area of the reservoir. In general, for hydraulic membranes, thicknesses exceeding 50m in areas of low tectonic activity are considered good (Grunau, 1987). The greater the thickness the more likely a secure, unbreached seal would be provided by the shale or mudrock formation. Typical thicknesses for major hydrocarbon reservoirs worldwide range from tens to hundreds of meters.

### 2.2.3 *Diagenesis*

Chemical reactions, which have occurred or will occur, are important in determining the current state of the seal and its ability to maintain a seal over geological times.

Knowledge of the rock fabric, mineralogy, and porefluid chemistry is important in properly modeling the physio-chemical behaviour of the seal. The influence of these reactions on the permeability, pore size and shape, connectivity, fabric, surface area, and mechanical strength are important in assessing the security of CO<sub>2</sub> storage in deep saline aquifers (Section 6).

#### 2.2.4 *Ductility*

Ductile lithologies can increase the chances of hydrocarbon retention in areas of intense deformation and fracturing. The behaviour of the seal under deformation will vary with the lithology, shear failure geometry, and dilatant or non-dilatant behaviour of the caprock. Brittle materials will develop dilatant fractures upon fracturing, and thus the effective permeability will increase. Ductile materials undergo plastic deformation under increasing pore fluid stresses, without an increase in the permeability of the material, thus producing non-dilatant, sealing fractures (Ingram et al., 1997), as illustrated in Figure 2.2. Dilatant behaviour is encouraged by high fluid pressures, overconsolidation, and increasing rock strength (Dewhurst et al., 1999).

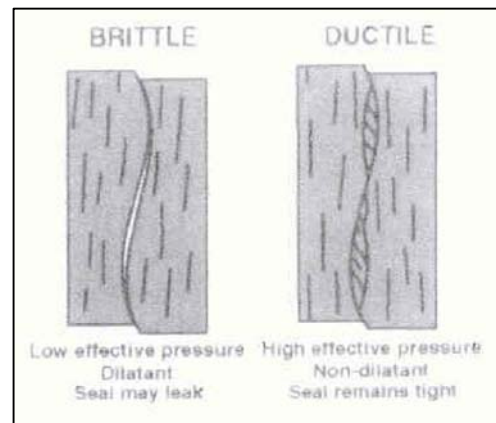


Figure 2.2 Ductile versus brittle seals (Ingram et al., 1997).

In the case of fractured argillaceous rock, flow can often take place through interconnected discontinuities. In the event that gas pressures are allowed to approach or exceed the total stress, as in by-product gas in nuclear waste facilities, dilation of flow paths may occur, resulting in gas flow through the rock. Creation of microfissures by high gas pressures may allow gases to preferentially flow by a mechanism known as hydrofracturing. Creation of microfissures and the dilation of pre-existing fissures has been previously documented as a potential source of hydrocarbon migration or pressure relief, however, the mechanism is generally poorly understood (Dewhurst et al., 1999). Presence of discontinuities, and geomechanical behaviour under shear failure can result in significant increases to the intact permeability (Section 5).

#### 2.2.5 *Local and Regional Continuity*

It is difficult to assess the continuity of a caprock formation without making significant assumptions, which will ultimately affect the understanding of its sealing efficiency. Deduction of caprock continuity is based on accurate information about the caprock's microstructure and macrostructure. Microstructure (section 5.1) refers to the depositional history, stress history, diagenetic processes and weathering. An understanding of the microstructure will provide information about the mineralogy, stress state, and failure mechanisms. Macrostructure (section 5.2) refers to the influence of discontinuities in the rock matrix, resulting in changes in permeability and strength,

as well as its lithology, ductility, thickness, and stability. It is thought to be the critical factor in risk assessment of caprock integrity over geologic time (Grunau, 1987).

#### 2.2.6 *Diffusion*

Even an intact seal, without faults, fissures, or microfractures, is not an ultimate barrier to transport of CO<sub>2</sub>. Indeed, the presence of a concentration gradient will induce diffusion. However, the debate around diffusion deals with its efficiency as a gas transport phenomena. The theories are split between those which suggest that diffusion plays a dominant role in gas migration, and those which consider diffusive fluxes as negligible gas transport mechanisms over geological times. Diffusion is affected by several factors which may make it the dominant or an insignificant transport mechanism (Section 3.4). The rate of diffusion is dependent on the gas molecule, the porefluid characteristics of the caprock, the concentration gradient, and time. Caprock seals must be evaluated on the potential diffusion of gases through the seal, and fracture development as a function of the intensity of geomechanical deformations.

### 2.3 **Concluding Remarks**

The assessment of caprock integrity is not straightforward. Microstructure, macrostructure, porefluid chemistry, geochemical equilibrium, physical transport properties, and other complex parameters and processes influence the seal efficiency. Parameters may vary from basin to basin. Accurate caprock properties – ductility, thickness, and continuity (both regional and local) – are often difficult to obtain. Erroneous assumptions about these properties can lead to misconceptions about the sealing efficiency of the caprock. Laboratory measurements of sealing capacity are valuable in assessing the fundamentals with respect to the caprock in question, however, extrapolation of laboratory data to reservoir caprocks can be incorrect. Bad sample preparation and storage can lead to erroneous conclusions. It is also important to bear in mind that average values of seal capillary entry and/or hydrofracture pressures are not valid on a field scale. The weakest point of a seal is the most important in assessing caprock integrity.

### 3 Physical Transport

There are several theories, which seek to describe the movement of gases in low permeability materials, in relation to hydrocarbon migration, migration of nuclear repository gases, and in greenhouse gas storage. These theories include Darcy's law of fluid flow for multiple phases (Ingram et al., 1997; Schlömer and Krooss, 1997; Hildenbrand et al., in press), diffusion (Krooss and Leythaeuser, 1997), flow through microfissures created from excess gas pressure (Harrington and Horseman, 1999), and the colloidal bubble ascent mechanism (Brown, 2000; Price, 1986). Flow through microfissures is usually described by Darcy's law with an effective permeability.

As described in Section 2, caprocks are classified in two categories depending on their mode of failure: hydraulic seals and membrane seals. A hydraulic seal fails by microfissuring due to overpressurization of the caprock. Hydraulic seals generally have capillary threshold pressures so large that they can theoretically exceed the overburden pressure. Puncturing of such a membrane due to high capillary pressures is then impossible. These membranes are believed to fail when microfissures are created due to increased pore fluid pressures and the associated decreased net stresses. Both shales and anhydrites, the most commonly found materials in hydrocarbon caprocks are thought to behave as hydraulic seals due to their tight porous structure. However, naturally fractured media can exhibit fracture openings several orders of magnitude larger than those of the porous spaces in low-permeability materials. It is widely believed that tight caprocks, in the absence of fissures, are best described by a hydraulic seal, whereas naturally fractured media are best described by a membrane seal.

#### 3.1 Darcy Flow

Darcy's law describes the migration of fluids through porous media. It states that the fluid flow is proportional to the pressure gradient. An extension of Darcy's law incorporates multiphase flows, such as gas flow through water saturated porous media, as described in the following by Equation for compressible flow.

$$v_{nw} = \frac{k_{rmw} k_i \rho_{bw}}{\mu_{nw}} \frac{dh_{nw}}{dl} \quad (3.1)$$

The subscript nw represents the nonwetting fluid, CO<sub>2</sub> in this scenario,  $k_i$  is the permeability of the rock matrix,  $k_{rmw}$  is the relative permeability,  $v$  is the darcy velocity,  $\mu$  is the viscosity, and  $dh/dl$  is the hydraulic gradient (Fetter, 1993). The application of Darcy's law requires that all fluids obey it for the porous space they occupy. The relative gas permeability theory suggests that partial displacement of water within the pore space will occur in order to make room for the incoming gas phase. The displacement pressure, or capillary threshold pressure, is the difference between the gas pressure and the porewater pressure, and describes the force required to gas to enter the porous space. It is dependent on the size of the pore throats, the intrinsic permeability, and the interfacial tension between the fluids. Hildenbrand et al. (2002) summarize various terms and definitions of displacement pressure from the literature. Once the capillary displacement pressure is exceeded, flow of the non-wetting phase will occur by two phase Darcy flow (Ingram et al., 1997; Schlömer and Krooss, 1997; Hildenbrand et al., 2002).

Drainage and imbibition (i.e. absorption) experiments in fine grained materials of varying lithologies examined, revealed that only very small transport porosities ( $10^{-2}$  to  $10^{-5}\%$ ) are necessary for gas migration (Figure 3.1, Hildenbrand et al., 2002). Once capillary entry pressures were exceeded, gas flow occurred which was well described by Darcy flow with effective permeabilities.

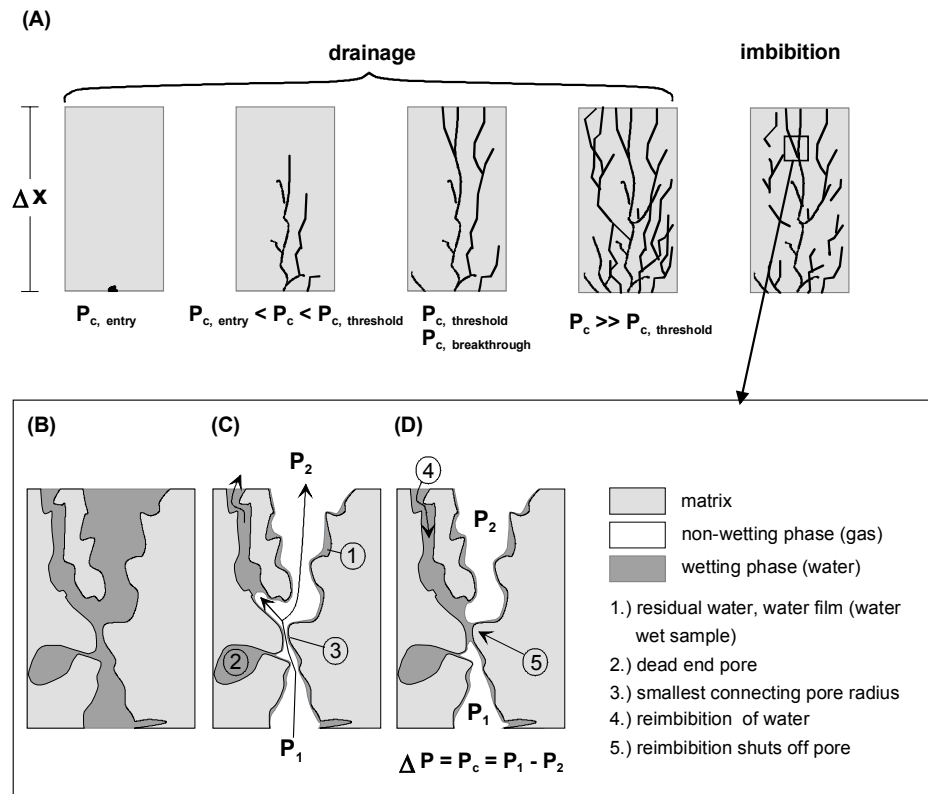


Figure 3.1 (a) Stages of capillary gas breakthrough (drainage) and re-imbibition process in fine-grained rocks (schematic); (b) initially water-saturated sample; (c) gas breakthrough, (d) re-imbibition. (after Hildenbrand et al., 2002).

Parameters and processes which are thought to influence gas migration through clay-rich rocks include porosity, pore size distribution, surface adsorption, capillary entry pressure, matrix suction, stress history and total and effective stress (Rodwell et al. 1999). The pore throat size distribution is related to the stress history and the maximum burial depth. Equivalent pore size radii were shown to vary significantly with interfacial surface tension and wetting angle of two fluids, in this case  $\text{CO}_2/\text{water}$  and  $\text{N}_2/\text{water}$  (Hildenbrand et al., 2002). Low-permeability mudstones, shales, and other clay-rich, heavily overconsolidated materials will exhibit extraordinarily high displacement pressures due to its tight porous structure. Harrington and Horseman (1999) conducted gas flow experiments in water-saturated Boom clay under uniform and isotropic stress conditions, and high gas pressures. Exceedingly high gas pressures required for gas injection resulted in high pore pressures. As a result, the sum of the effective stresses and pore pressure exceeded the boundary stresses and hydrofracturing created preferential gas pathways. These pathways tended to propagate along the bedding planes in naturally sedimented material, and gas breakthrough pressures were generally lower in samples that were parallel to the bedding rather than normal to the bedding. In reconstituted materials, where there was no oriented fabric, gas pathways tended to propagate normal to the minor principal stress, but a trend indicating gas pathways formed in the direction of the maximum stress gradient was also observed. In the



experiments conducted by Hildenbrand et al. (2002) hydrofracturing of the samples was avoided through the application of sufficiently large total stresses, well above the gas pressure. In samples with extremely low permeabilities, the lack of hydrofracturing was confirmed by the nonmeasurable low values of the Darcy permeability. Transport in these samples was due to diffusion and no gas breakthrough was observed.

### 3.1.1 *Drawbacks to Darcian Theory*

Despite the widespread use of Darcy's law, and some experimental support that desaturation of the water phase occurs during gas injection (Lindeham, 1989), it has some significant shortcomings with respect to clay-rich sediments. Darcy's law is unable to account for the complex coupled behaviour between water and clay minerals. In Darcian flow, increasing gas content is thought to occur at the expense of the saturated water phase. Various theories however, most notably the Guoy-Chapman and Stern models, describe the distribution of ions and water molecules along the surfaces of clay minerals (van Olphen, 1977; Mitchell, 1993; Horseman et al., 1996). Unlike non-clay materials, the term "water" does not simply refer to free water in the pore space. Rather, water in clays is distinguished by its position relative to the clay mineral. Figure 3.2 illustrates the four types commonly mentioned. Interlayer refers to water present within the clay mineral structure (a). Structured water refers to the water, which is strongly adsorbed to the clay surface, and in hydrated shells of the Stern layer cations (b). As water molecules move away from the surface of the clay mineral, it becomes less strongly attracted to the mineral surface, this loosely held water is known as the diffuse layer (c). Free water resides in the porous space, and is the water which participates in transport (d).

Water molecules closer to the clay surface are more strongly occluded to the mineral. As dewatering occurs closer and closer to the adsorbed layer, greater force is required, and pressures greater than the overburden pressure are sometimes required. In low-porosity clay sediments, the majority of water molecules are adsorbed to the clay mineral, and little water is available in the free phase. Displacement of water due to influx of gas is thought to be difficult due to the greater percentage of water in clays present as structure water. Desaturation is dependent on the proximity of the water molecules to the clay mineral surfaces, that is how strongly adsorbed the water molecules are to the clay minerals. It is unlikely for the gas phase to displace the porefluid, unless it exerts a force greater than the compaction force (Rodwell et al., 1999). Thus, the total stress at burial is the force required to desorb water from compact clays, illustrated in Figure 3.3. Various mechanisms, hydrogen bonding, hydration of exchangeable cations, attraction by osmosis, charged surface-dipole attraction, and attraction by dispersion forces, have been used to describe the interaction between clay minerals and water, and the various types of water.

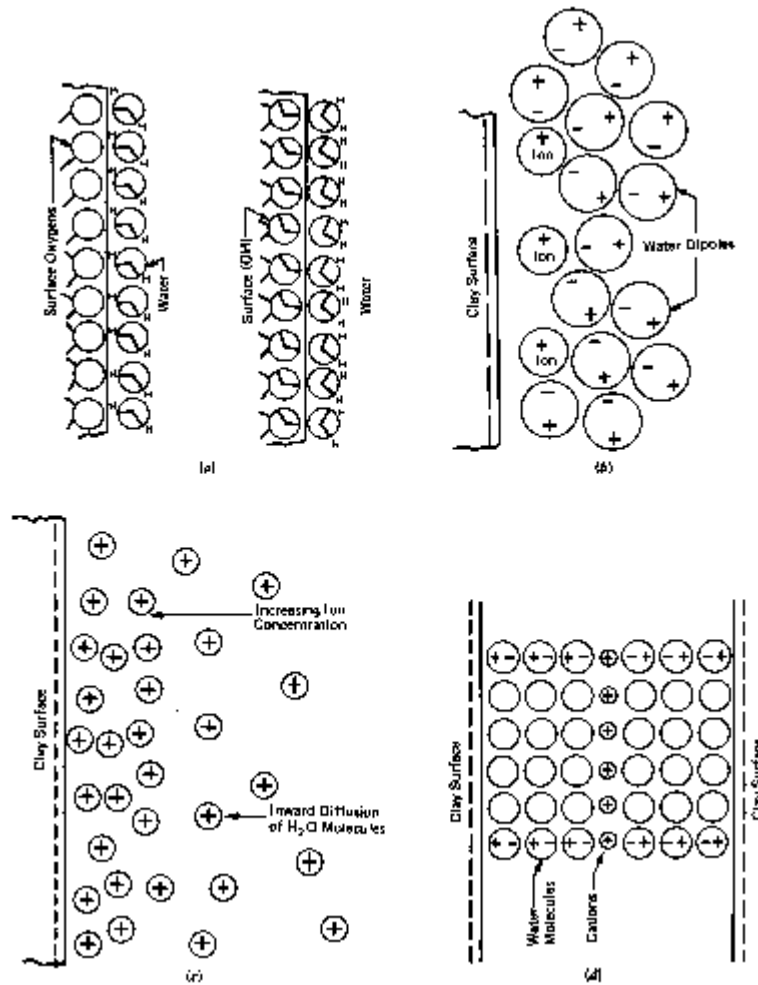


Figure 3.2 Types of water in clays (after Mitchell, 1993).

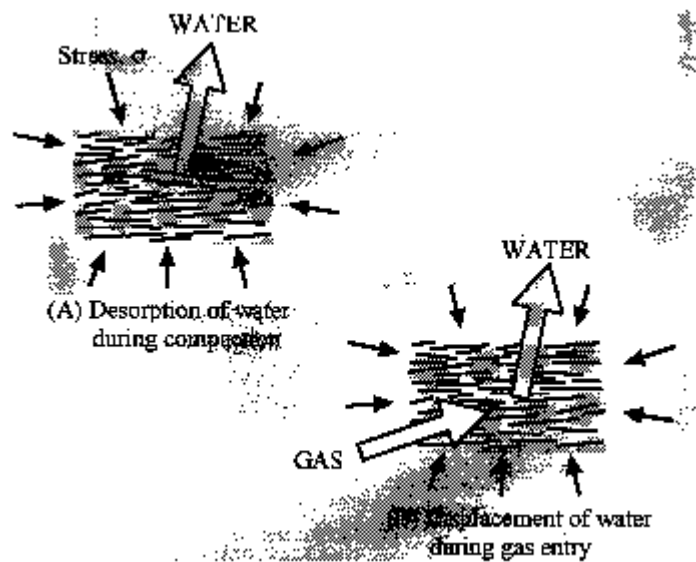


Figure 3.3 Desorption of water from compact clays (after Rodwell et al., 1999).

Harrington and Horseman (1999) performed experiments on the behaviour of hydraulic seals. Peak gas pressure responses illustrated crack propagation in the clay samples,

leading to gas movement through the newly formed, or dilated interconnected network of discontinuities. These peak responses were a result of strong coupling between the gas pressure and the porewater pressure, characteristic of gas migration in initially water-saturated, clay-rich media. The experiments illustrated relatively quick gas breakthrough through preferential pathways, leading to minimum desaturation of the sample. Following the seal failure and the gas breakthrough, changes in wettability were found, as partially filled gas voids remained in the rock matrix. This was evident from the lower gas breakthrough pressure in subsequent tests. However, increasing the total stress or re-introducing water into the clay specimen removed the gas-filled voids again.

The desaturation of clay materials can be very local; large amounts of gas migration were observed in the absence of significant desaturation (Harrington and Horseman, 1999). Increases in gas content exhibited insignificant changes in water content, which was explained by an overall increase in the total volume. Nonlinearity of fluid flow shown by Bolton and Maltman (1998) also illustrates the non-darcian flow behaviour of flow, and implies that shear zone walls are flexible.

Mitchell (1993) suggested the following reasons for deviations from Darcy's law:

- non-Newtonian water flow properties
- blocking and unblocking of flow as a result of particle migration
- local consolidation and swelling (due to compressibility of soil after the application of a hydraulic gradient).

Further investigation is required, but the belief is increasing that compact clays and mudrocks do not behave according to the traditional two-phase flow theory (Harrington and Horseman, 1999). Darcy flow models should be used with care for identifying potential gas migration in clay-rich materials, especially when they are heavily overconsolidated. Gas migration models illustrating independent flow paths are useful in describing other potential mechanisms of gas flow (Brown, 1999).

### **3.2 Gas-Bubble Ascent Theory**

Brown (2000) summarized the mechanism of gas transport through microfractures of low permeability materials which is known as Bubble Ascent Theory. This mechanism of gas transport does not follow Darcy's law since the relative saturations of the porefluids and the gas phases are not defined, because the gas phase is discontinuous. The rate of gas migration is controlled by the gas and the porefluid properties, the effects of the pore walls, the gas bubble concentration relative to the porefluid, and the gas bubble concentration effect of a mass of bubbles entrained in the porefluid. Discrete gas bubbles moving upwards displace the porefluid into a more narrow cross sectional area between the fracture wall and the particle. Closer to the wall the bubble velocity is smaller. This is known as the wall effect (Figure 3.4). The ratio of the size of bubble to the fracture width will also affect the viscous drag, and will have a similar effect. An increase in concentration will affect the velocity of gas ascent due to particle interactions, and thus decrease the velocity relative to the surrounding porefluid.

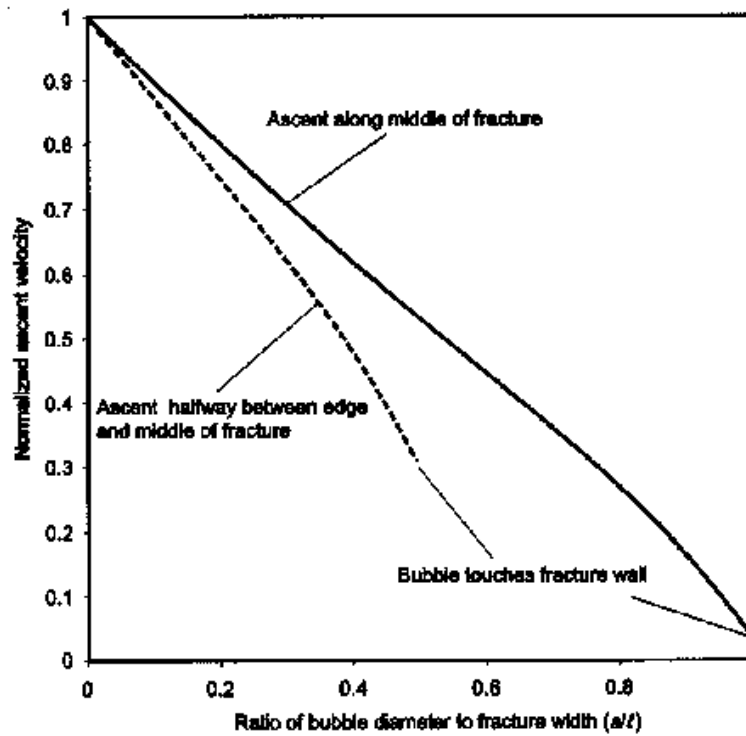


Figure 3.4 Wall effects on bubble velocity (after Brown, 2000).

Brown (2000) reports the work of Price (1986) and MacElvain (1969), suggesting that colloidal size gas bubbles migrate upwards due to Brownian motion, resulting in relatively low gas fluxes at rapid vertical velocities consistent with microseepage phenomena. This transport mechanism with a discontinuous gas phase is believed to occur within microfractures that are too small for significant bulk flow. The resulting transport rate will be significantly larger than transport by diffusion.

### 3.3 Unsaturated Soil Mechanics

Migration of gases into clay-rich materials due to desiccation is described by unsaturated soil mechanics (Fredland and Rahardjo, 1993). The entry of gases is then due to negative porewater pressures. Harrington and Horseman (1999) postulated that a link exists between the mechanism of clay desiccation and gas entry into water saturated clay media. Clay materials under the compressive boundary stresses of deep caprocks, which are initially water saturated, exhibit positive porewater pressures; however, their desaturation may be similar to the mechanisms of gas migration into clay cracks and porous space due to desiccation, shrinkage and negative porewater pressures.

### 3.4 Diffusion Dominated Transport

In the absence of open discontinuities acting as fluid conduits, diffusion will always provide a means of gas transport as long as a chemical concentration gradient exists. In the petroleum industry, the effectiveness of diffusive migration of immiscible hydrocarbons through water saturated shales has been heavily debated. More specifically, the debate was about the assumptions for the seal thickness, porosity, reservoir size, and geometry, which affect the calculation of the effective diffusion coefficient (Krooss et al., 1998; Nelson and Simmons, 1995; 1997; Krooss and

Leythaeuser, 1997). In the past, this has led to great discussions about the sealing capabilities of caprocks. For example, the diffusive losses of hydrocarbons through the overlying caprock of the Harlingen gasfield in the Netherlands has been calculated by various authors. Leythaeuser et al. (1982) suggested that diffusion was an effective process of primary migration for methane gas, and concluded that diffusive losses through 400m of shale caprock could result in the reduction of one half over a period of 4.5 million years. Reducing the caprock thickness resulted in the reduction of half the initial amount of methane being lost due to diffusion in 2.7, 1.3 and 0.4 million years for 300m, 200m, and 100m respectively. However, a recalculation on the Harlingen gas field revealed that assumptions about the boundary conditions at the caprock/reservoir interface were too simplistic, and that physio-chemical properties of the gas-liquid equilibrium between the reservoir gas and the aqueous phase in the water saturated caprock had not been accounted for (Krooss et al., 1992). The time required to lose half of the initial amount of methane in the reservoir through a 400m thick caprock was recalculated to be 70 million years. Calculations by Nelson and Simmons (1992) of the same reservoir yielded a half time of 11.5 million years through a 400m thick caprock.

Diffusion of gases across low-permeability clay-rich sediments is described by Fick's Law. Gas diffusion in saturated porous media depends on the properties of the gas, the pore fluid, and the porous matrix.

The porosity of the matrix, and the dissolution of the gas into the porous space are thought to be controlling factors in gas diffusion (Katsube and Walsh, 1987). An increase in the porosity causes an increase in the diffusion rate, (Krooss et al., 1998). However, no general correlation between the diffusion coefficient and the rock porosity exists. Reductions in the diffusive flux are caused by decreased pore throat diameters, which create an increase in the molecule-wall resistance due to the increased number of collisions (Cunningham and Williams, 1980). As the available porosity approaches unity, the diffusion rates approach that of diffusion in water at the same temperature, as illustrated by the work of Krooss and Leythaeuser (1988) performed with methane gas. More importantly, however, the total porosity in tight, clay-rich sediments is not effective for diffusion as it is in coarser-grained rocks, since clays exhibit smaller interconnected pore spaces relative to fluid molecule sizes and other dissolved species (Pearson, 1999). Diffusion takes place along tortuous pathways, and electrostatic and size exclusion processes along the media walls, that can be affected by interactions between the water and clay minerals play a role as well (Rebour et al., 1997). Thus, the available porosity can be a fraction of the total porosity, resulting in a restriction of ion diffusion rates into the available pore space. The term diffusive porosity refers to the porosity available for diffusive processes to occur. The porous network, and the tortuosity have a greater influence than the total porous volume.

An increase in effective stress will decrease the effective diffusion coefficient. This was shown to be the case for both  $N_2$  and  $CH_4$  (Krooss and Leythaeuser, 1988). Increasing the effective stress results in an increase in pathway tortuosity, decrease in total porosity, and thus reduces the mobility of the gas phase in the water wet pore space.

Restrictions in the pore space also affect the rate of diffusion in relation with the size of the diffusing molecule. Krooss and Leythaeuser (1988) observed a decrease in diffusion with decreasing molecular mass of C1-C5 hydrocarbons. It was suggested that this trend was due to restrictions within the pore space, acting as a sieve inhibiting movement of

larger molecules. A similar effect as described by ion exclusion effects of clay barriers used in landfills etc.

The property of the pore fluid which has the largest affect on diffusion is its salinity. Diffusion is closely linked to the solubility of the gas into the pore fluid: the greater the solubility the greater the diffusion. Increasing the salinity of the pore fluid results in smaller solubility of CO<sub>2</sub>, and therefore lowers the diffusion rates (Krooss and Leythaeuser, 1988). A decrease in the diffusion coefficient was thought to be a result of increased viscosity of the brine solution in comparison to the water. Solubility of CO<sub>2</sub> into the aquifer also affects the concentration at the aquifer/caprock boundary. This concentration and the caprock thickness determine the concentration gradient, which directly influence diffusive fluxes. The true thickness of the caprock is often difficult to assess, resulting in inaccuracies for the estimated diffusive flux. The prediction of diffusion was shown to be unrelated to the permeability of water-saturated rocks (Krooss and Leythaeuser, 1988). In general, diffusion of hydrocarbons through seals is thought to be dependent on the type of hydrocarbon, characteristics of the water-filled porous space in the caprock, and the time available for diffusion.

### **3.5 Concluding Remarks**

The mechanisms of multi-phase fluid transport in clay-rich low porosity materials require additional study to assess the dominant transport phenomena. Various migration models have been investigated, including Darcy's law for multiple phase compressible fluid flow. Due to the complex behaviour of clay-rich materials, the mechanism of advective flow through intact, low-porosity indurated clays is unlikely. However, in the presence of discontinuities, porosity and permeability can increase by orders of magnitude. Current consensus suggests that two phase models such as extended Darcy's, are inadequate for representing clay systems (Rodwell, 1999). These models fail to represent the development of gas pathways through saturated rock, entrainment of water in gas flow, and the effect of permeability as a function of pressure and stress. Whether the dominating transport mechanism is diffusion or gas bubble ascent through microfissures may depend on the actual circumstances. It is often difficult to make a quantitative judgement.

## 4 Solubility

Geochemical reactions involving CO<sub>2</sub> and diffusion of CO<sub>2</sub> in both the aquifer and the caprock are influenced by its solubility in the pore fluid. Duan and Sun (2003) summarized a number of experimental results on the solubility of CO<sub>2</sub> in pure water and in aqueous NaCl solutions, and also provided a model that honors the experimental data. The solubility of CO<sub>2</sub> is defined as the maximum amount that can be dissolved in water (in mol/kg, in g/100g, or in mmol/mol). The solubility into the aquifer pore fluid will determine the CO<sub>2</sub> concentration at the lower boundary of the caprock. Thus, the greater the solubility, the lower the concentration gradient, which influences the diffusion across the caprock (section 3.4). A larger solubility into the porefluid of the caprock results in a larger CO<sub>2</sub> concentration, all other parameters being equal. The reaction rates between minerals and CO<sub>2</sub> are increased when CO<sub>2</sub> is in the dissolved state (section 6.1). These phenomena demonstrate the importance of CO<sub>2</sub> solubility for geological storage.

### 4.1 Pure Water

Henry's law states that the solubility of a gas in liquid is proportional to the partial pressure of the gas at a constant temperature (Langmuir, 1997), and is valid as long as the liquid phase does not dissociate, ionize, or react with itself (Felder and Rousseau, 1986). It is pertinent to low solubility gases such as CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S (Freeze and Cherry, 1979), and is dependent on the system temperature and pressure. Solubility of CO<sub>2</sub> in water tends to decrease with increases in temperature, and increase with increases in pressure. Pressure is the dominant factor as shown in Table 4.1.

Table 4.1 Carbon dioxide solubility in water (g / 100 g) (Perry et al., 1997).

Total Pressure (atm)	T=35°C	T=40°C	T=50°C	T=75°C
25	2.56	2.3	1.92	1.35
50	4.39	4.02	3.41	2.49
75	5.51	5.1	4.45	3.37
100	5.76	5.5	5.07	4.07
150	6.03	5.81	5.47	4.86
200	6.29	6.28	5.76	5.27
300	-	-	6.2	5.83
400	7.06	6.89	6.58	6.3
500	7.51	7.26	-	-
700	-	-	7.58	7.43

### 4.2 Electrolytic Solutions

General conclusions from previous experimental work determined that solubility of nonpolar substances like CO<sub>2</sub> in aqueous electrolytic solutions will always be lower than its solubility in pure water under the same conditions. This is known as the salting

out effect (Markham and Kobe, 1941; Ellis and Golding, 1963; Takenouchi and Kennedy, 1965; Wiebe and Gaddy, 1941; Malinin and Savelyeva, 1972). The salting out effect of molecular species with no charge can be explained by the changes in the activity coefficient. Increasing the electrolyte concentration reduces the hydration of the ions, and increases the competition between the electrolyte and nonelectrolyte for the water molecule (Malinin and Kurovskaya, 1975), which results in an increase in the activity coefficient, as illustrated in Figure 4.1. Increases in activity coefficient with increasing ionic strength are common, not only for  $\text{CO}_2$ , but also for other uncharged species (Freeze and Cherry, 1979). The salting out effect is more pronounced at total dissolved solids greater than 5000mg/L, below which it can be disregarded (Freeze and Cherry, 1979; Langmuir, 1997). Therefore, increasing the concentration of the salt solution will decrease the solubility of  $\text{CO}_2$ . In addition, activity coefficients are affected by the electrolyte type, therefore solubility of  $\text{CO}_2$  in electrolyte solutions exhibiting lower activity coefficients will result in higher solubility. The solubilities of different molecules are a function of their size; decreasing solubility with increasing molecule size. Figure 4.1 illustrates the differences in activity at various ionic strengths for two different chloride solutions.

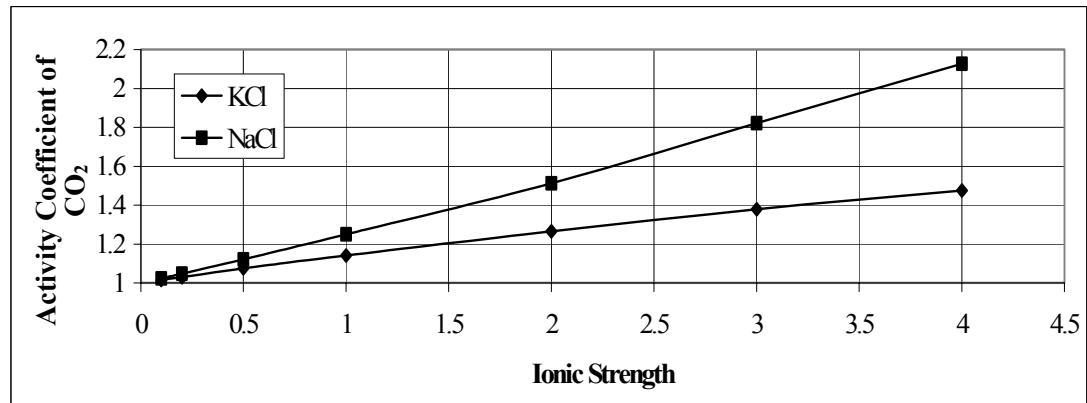


Figure 4.1 Effect of activity coefficient with ionic strength (based on data from Markham and Kobe, 1941).

The trends for  $\text{CO}_2$  solubility in electrolytic solutions are similar to those in pure water (Figure 4.2). At constant pressure, solubility will pass through a minimum with increasing temperature (Ellis and Golding, 1963). Pressure did not have a significant effect on the salting out factor between the pressures of 98.1 – 4905 kPa. Increasing pressures result in increasing solubilities (Malinin and Savelyeva, 1972; Duan and Sun, 2003).



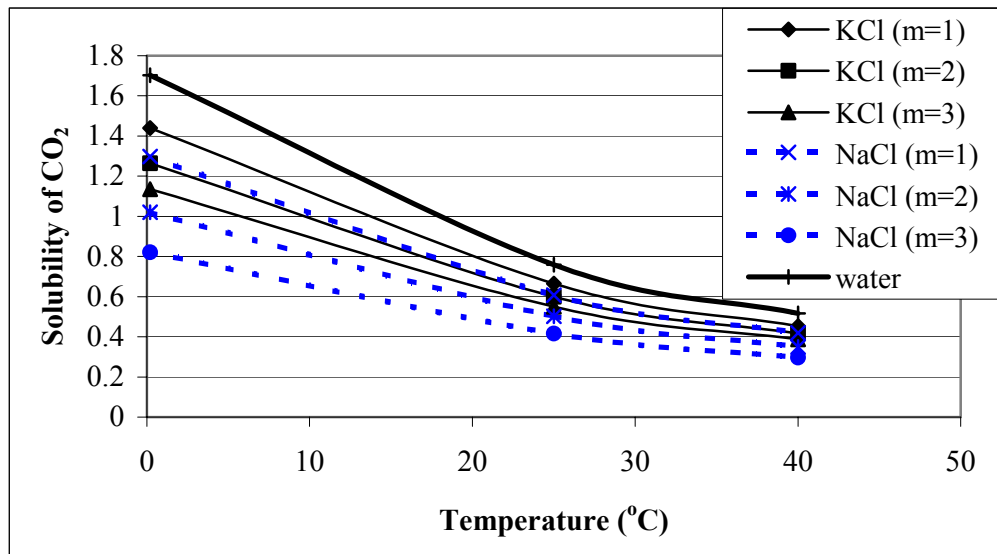


Figure 4.2 Effect of temperature on solubility (mmol/mol) (based on data from Markham and Kobe, 1941).

### 4.3 Supercritical Conditions

Solubility in the supercritical realm have not been extensively tested. As part of the Joule II project (Holloway et al, 1996), de-ionised and synthetic seawater were used to determine the solubility and the rate of dissolution of CO<sub>2</sub> under supercritical conditions, 80°C and 200 bar. It was determined that the amount of CO<sub>2</sub> which dissolved in de-ionized water and synthetic sea water, after density correction, was 1.158 mol kg<sup>-1</sup> (or 5.10g CO<sub>2</sub> per 100g water) and 0.977 mol kg<sup>-1</sup> (or 4.30g CO<sub>2</sub> per 100g water) respectively (Fig. 4.3). The buildup of the CO<sub>2</sub> concentration in the water was relatively fast, equilibrium was reached in less than 60 minutes. Measurements on shorter timescales revealed a value for the initial dissolution rate of 6.55x10<sup>-3</sup> mol cm<sup>-2</sup>s<sup>-1</sup>.

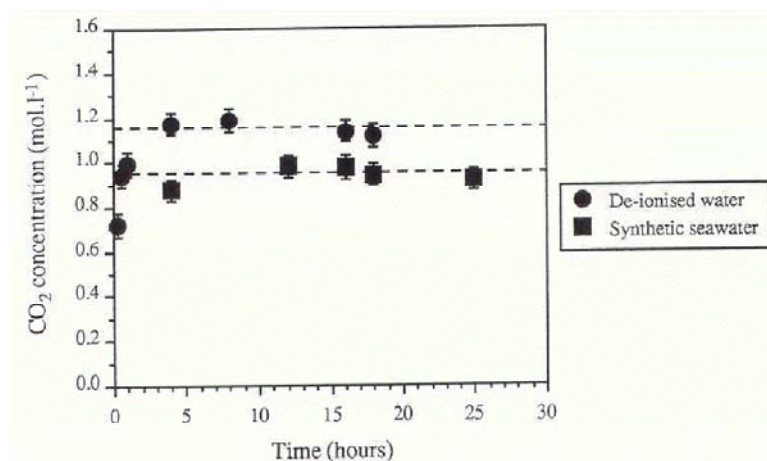


Figure 4.3 CO<sub>2</sub> concentration in water and synthetic seawater (Holloway et al., 1996).

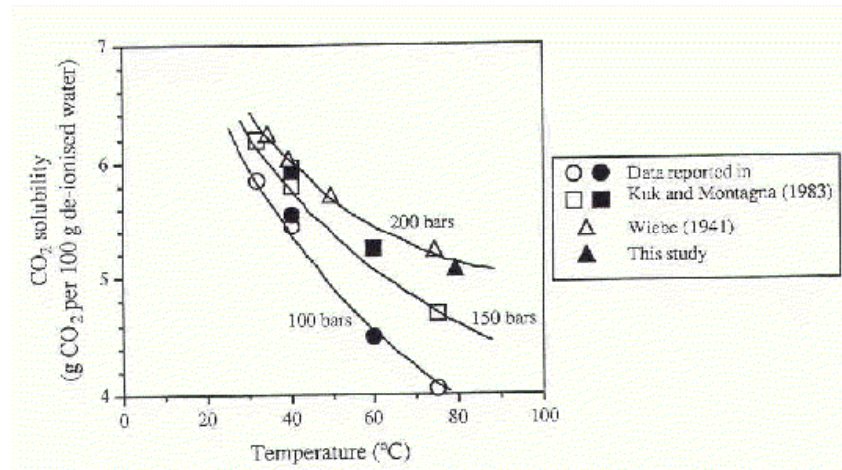


Figure 4.4 Effect of CO<sub>2</sub> solubility at supercritical conditions (Holloway et al., 1996).

Solubility measurements of CO<sub>2</sub> in synthetic Utsira porewater and distilled de-ionised water have been investigated (Rochelle and Moore, 2002). It was concluded that under supercritical conditions experienced within the Utsira formation solubility of CO<sub>2</sub> is in the order of 4.5g of CO<sub>2</sub> per 100g of synthetic porefluid solution. Data on supercritical CO<sub>2</sub> solubility in electrolyte solutions are not widely available, however the measurements obtained here are broadly in line with previous literature values. Solubility of de-ionised water under these conditions resulted in an approximate 10% reduction in solubility. The reason for the reduction in solubility was not entirely clear.

#### 4.4 Influence on Groundwater

Carbonic acid is responsible for the majority of rock weathering in natural systems. It is formed from the dissolution of CO<sub>2(g)</sub> in water (equation 4.1), however not all dissolved CO<sub>2</sub> becomes carbonic acid. Only 0.26% of the dissolved gas is converted to H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, despite common notation of all dissolved CO<sub>2</sub> as H<sub>2</sub>CO<sub>3</sub><sup>o</sup> (equation 4.2). Carbonic acid is a polyprotic acid, and therefore is prone to the loss of hydrogen ions depending on the pH of the water. Thus, which carbonate species is dominating depends on the pH of the formation, as illustrated in Figure 4.5. Changes in pH are also dependent on the minerals present in the formation, and their capacity to buffer changes in pH as CO<sub>2</sub> is added.



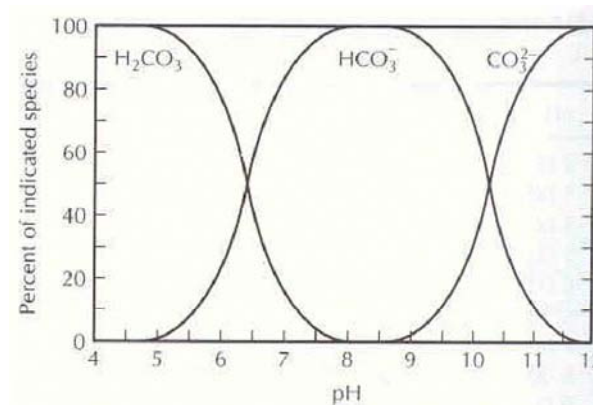


Figure 4.5 Carbonate species at various pHs and 20°C (Fetter, 1994).

Dissolution of minerals and precipitation of secondary minerals occur as a result of decreasing pH. Chemical reactions are dependent on the mineralogy of the aquifer and caprock, salinity of the pore fluid, and thermodynamic stability of these reactions (Section 6.0). The most important relationship is the formation of aqueous CO<sub>2</sub> (equation 4.1), which acidifies the pore fluid, and initiates the changes in chemistry within the aquifer and caprock. Dissolved CO<sub>2</sub> has been found to be far more effective in attacking caprock minerals than dry supercritical CO<sub>2</sub> (Holloway et al., 1996).

#### 4.5 Concluding Remarks

Solubility plays a large role in the migration properties of CO<sub>2</sub> in the subsurface. It will influence the rate of diffusion and the chemical reactions in the aquifer and caprock. Temperature, pressure, and ionic strength are the main factors in determining the solubility of nonelectrolyte ions in electrolytic solutions, as demonstrated by previous laboratory studies. Experiments conducted under supercritical conditions have been consistent with observations at lower temperatures and pressures. Increasing temperature, decreasing pressure, and increasing salinity all lead to a lower solubility. However, laboratory measurements describe the maximum solubility at given conditions, other factors may influence the amount of dissolved CO<sub>2</sub> in field conditions. The amount of CO<sub>2</sub> solved in the aquifer will likely be influenced by the shape of the reservoir, the presence of low-permeability interlayers, and other factors affecting mixing. The rate of advective, buoyancy-driven CO<sub>2</sub> migration to the top of the aquifer compared to the rate of CO<sub>2</sub> dissolution into the porefluid will influence the amount of CO<sub>2</sub> dissolved, and may result in a stratified layering of dissolved CO<sub>2</sub> in the formation waters. On its turn, the CO<sub>2</sub> concentration will affect potential geochemical reactions within the aquifer, and therefore geochemical trapping mechanisms. Geochemical aspects will be discussed in more detail in Chapter 6. A schematic diagram of in-situ CO<sub>2</sub> behaviour is presented in Figure 4.6.

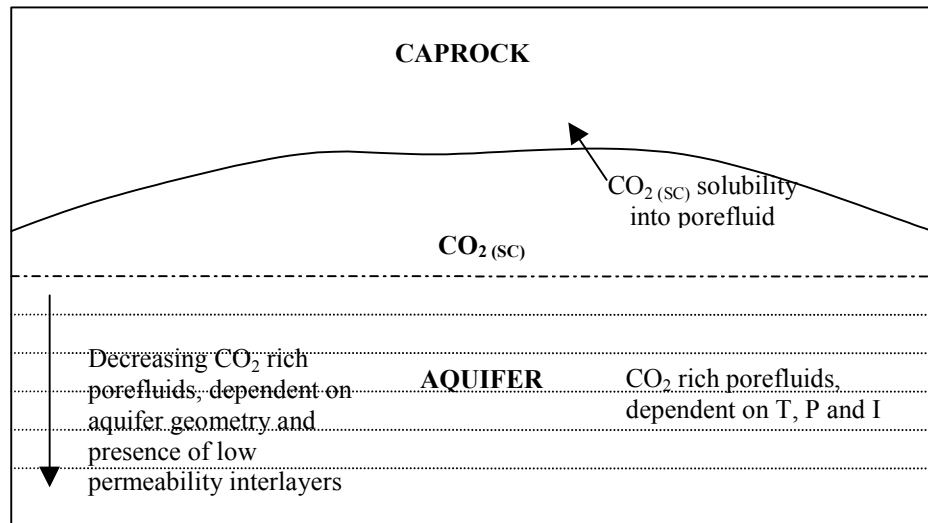


Figure 4.6 Schematic representation of possible in situ  $\text{CO}_2$  distribution.

## 5 Geomechanical Characteristics

Mudstones, clays and shales exhibit complex physical and mechanical behaviour, dependent on specific characteristics of its structure. Depositional factors, stress history (this chapter), diagenetic processes and weathering (Chapter 6) will govern the deformation behaviour of the material. The presence or the likely formation of discontinuities significantly influence the physical properties of low-permeability rocks. Deformation behaviour of argillaceous rocks has been described under the framework of critical state soil mechanics.

### 5.1 Structure

Mitchell (1993) described the structure of a soil as both fabric, determined by particle associations and arrangements, and interparticle forces. The structure of a soil will change from its natural state to a remoulded state, as controlled by its history. The structure will initially be determined by depositional and sedimentation processes, but exposure to physical (consolidation, shearing, unloading) and chemical (cementation, weathering) processes will lead to changes. Understanding the processes experienced by the formation will aid in the development of models to simulate its behaviour in-situ. Intact material fabric, both structure and material, define the microstructure, whereas the macrostructure refers to the presence of fissures, joints and discontinuities.

#### 5.1.1 *Microstructure*

The fabric or arrangement of particles in rocks and soils is defined by its lithology, porosity and pore size distribution, as developed from the geological processes which it has undergone. The initial porosity is affected by the mineralogy, the rate of deposition, the porefluid chemistry and other conditions during deposition. Slow deposition leads to a more open random fabric structure with a high porosity, whereas more rapid depositions result in a more densely packed fabric structure with a low porosity (Burland, 1990). The porosity is also a function of compressibility. Silt-rich materials are less compressible than clay-rich sediments, due to the greater physical interaction between silt-grade quartz grains (Dewhurst et al., 1998). The grain size distribution and the mineralogy of the formation affect the degree of mechanical compaction (Bjørlykke, 1999). Such compaction, described by the compressibility of clay minerals, will typically result in porosities not smaller than 25%. However, additional losses in porosity can result from chemical processes as dissolution and precipitation of minerals (Bjørlykke, 1999). The clay compressibility is a function of the clay mineral: increasing compressibilities are found when comparing kaolinite, illite and smectite (Mitchell, 1993). Further, time and temperature greatly affect the extent of chemical compaction. The chemistry of the depositional waters influences the early stages of fabric development, leading to a variety of flocculated or dispersed particle arrangements (Horseman et al., 1996).

Further post-depositional stresses subjected to the rock fabric will result in further porosity reduction through the reorientation and breakage of grains during compaction and/or consolidation processes. Typically, clay minerals are strongly aligned in the plane normal to the maximum compaction stress. Increasing the total stress results in the increase in effective stresses, which lead to a collapse of larger pores, and thus a reduction in porosity. Increasing consolidation (at greater burial depths or effective stresses) also results in a stronger rock matrix due to stronger interparticle contacts, and

decreased porosity. The correlation between increasing effective stresses and decreasing porosity is pertinent regardless of the lithology, but the pore throat collapse is more dramatic with silt-rich materials. However, in materials which have significant cementation, increased consolidation beyond a critical point can have the reverse effect, resulting in a breakdown of cements and weakening of the rock matrix (Mitchell, 1993). Clay-rich media exhibit lower permeabilities at equal porosities than silt-rich media, suggesting a relationship between lithology and porosity.

The determination of the porosity and the pore size distribution has traditionally been performed with mercury intrusion porosimetry. The usefulness of this method has been demonstrated on sandstones and other high porosity materials. However, in the case of clay-rich materials, the value of mercury intrusion techniques is questionable. In the preparation of mercury intrusion techniques, clay samples are dried at a maximum temperature of 105°C. During the drying phase, the clay structure will be prone to shrinkage, resulting in the decrease of porous spaces. On the other hand, the introduction of mercury under high pressures may result in hydrofracturing and lead to larger porosities. Interaction between clay minerals and adsorbed water significantly affects the results of mercury intrusion techniques in determining porosity distribution.

Definitions of total porosity assume that all available water is found in the pore space. However, as already mentioned in Section 3.1.1 and Figure 3.2, there are four types of water in relation to clay minerals: free water, typically found in the porous space of all sediments and water at three different levels of adsorbed structures on or in the clay mineral: [interlayer water, structured water, and loosely-held water in the diffuse layer (Horseman et al., 1996)]. Much of the water associated in compact mudrocks and shales is thought to be so strongly bonded to the clay minerals that it does not participate in advective transport (Horseman et al., 1996). Structured water is believed to have a larger density than the surrounding pore fluid. Pore size distribution can be determined by imbibition data if the interfacial tension and wetting angle of the water and gas phases are well known. Hildenbrand et al. (2002) illustrated the strong dependence on both interfacial tension and wetting angle in their experiments. A capillary bundle model can be used to calculate the pore-size distribution of rocks, as performed on fine-grained sedimentary rocks.

### 5.1.2 *Macrostructure*

The intact structure of deeply buried argillaceous rocks is thought to be impermeable in the absence of discontinuities. However, the combined effects of burial diagenesis and overpressuring makes these materials susceptible to brittle deformation, leading to the development of discontinuities. The presence of joints, fractures and fissures in a rock mass have a significant influence on its strength, permeability, and flow patterns. Discontinuities control the behaviour of stiff argillaceous materials through rapid, overall loss of strength and increasing susceptibility to weathering and other chemical reactions (Botts, 1998). Discontinuities are areas of inherent planes of weakness for shear failure to occur, and can lead to softening and rapid loss of strength of the formation. Increasing the fissure density increases the chemical reaction area, thus increasing the extent of reaction, and the likelihood of dissolution. The rate and extent of softening are believed to be highly dependent on the presence of fissures, irregardless of the mechanism which causes it (Botts, 1998). Generally the strength of the discontinuity is much lower than the strength of the intact material.

### 5.1.3 Influence on Permeability

A decrease in porosity results in a decrease of the permeability; however a reliable relationship between the two parameters is often not available (Bolton and Maltman, 1998). Different lithologies will result in different ranges of permeabilities at equal porosity. The permeability range at a given porosity was suggested to be a result of the grain size distribution (Dewhurst et al., 1998). A relatively large amount of loss of larger pore sizes was found in silt-rich materials when compared to clay-rich materials, thus explaining the greater loss of permeability with porosity in silt-rich materials (Dewhurst, 1998). The permeability is controlled more by the pore size distribution than it is by the total porosity, and is influenced by the lithology, degree of compaction, and diagenesis (Tavenas et al., 1983).

Discontinuities can significantly affect the permeability and transport through low-permeability material. The permeability through fissures can be several orders of magnitude greater than in the intact rock matrix.

The importance of the lithology is exhibited in Figure 5.1, which shows greater permeability in clay-rich materials at the same porosity than in samples with a lower clay fraction. The broad distribution of pore throat sizes in siltier samples is thought to be responsible for the higher permeabilities exhibited at similar or lower porosities than that of clay-rich samples (Dewhurst et al., 1998). However, the permeability values converge at very low porosities, indicating that lithology is not so important at very low porosities (Dewhurst et al., 1999). It is believed that lithology and porosity jointly exert major controls on the pore throat radii of mudstones. Mathematical relationships describing the proportional changes of permeability due to changes in porosity, Figure 5.2, are clearly unable to provide an adequate representation of the complexities which affect the permeability of tight porous structures.

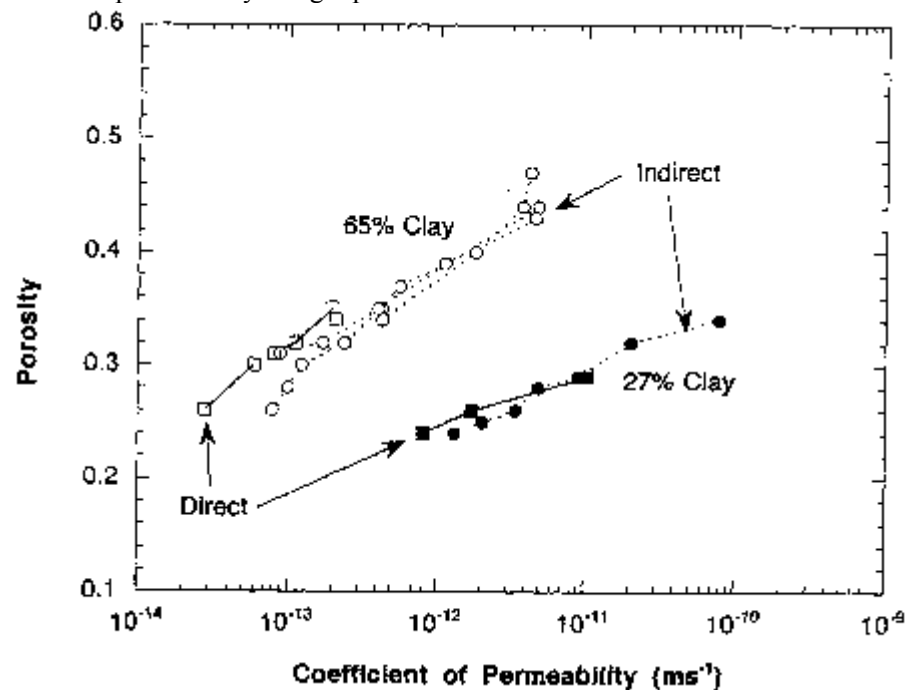


Figure 5.1 Relationship between porosity and permeability for London Clay (after Dewhurst et al., 1998).

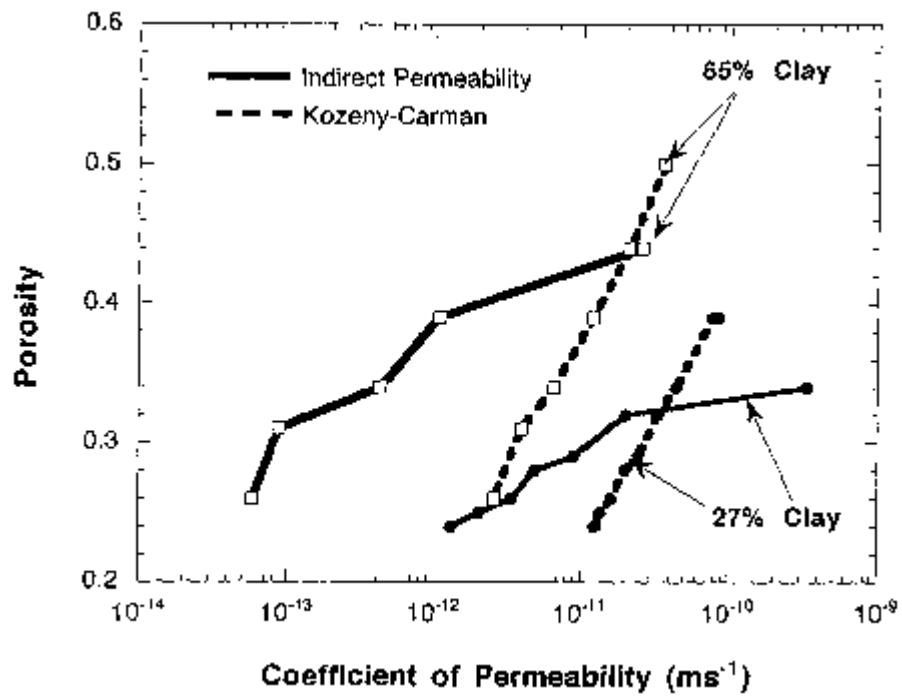


Figure 5.2 Comparison between experimentally measured and calculated relationship between porosity and permeability (after Dewhurst et al., 1999).

Increasing the effective stress leads to a decrease in porosity (see also Section 3.4), and ultimately to a decrease in the permeability. This trend is present for all lithologies, as illustrated in Figure 5.3. Studies provided by Dewhurst et al. (1998, 1999) were performed with water, not with nonpolar substances. Therefore, behaviour of CO<sub>2</sub> may differ from these findings.

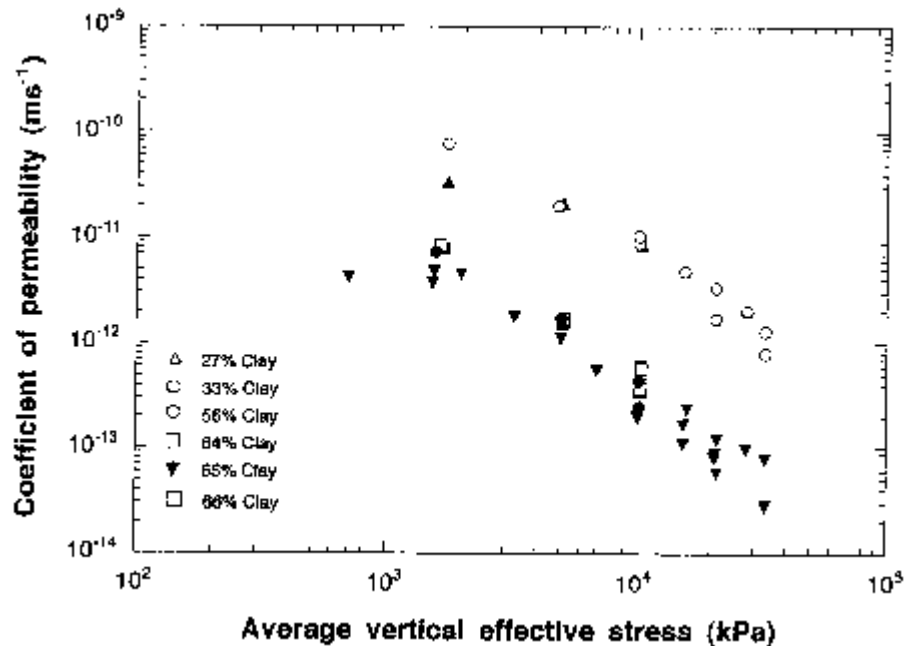


Figure 5.3 Relationship between permeability and effective stress (after Dewhurst et al., 1999).

In two-phase flow, the total porosity is not available to the incoming gas phase, and the permeability is a function of the available porosity. The effective porosity commonly



refers to the porosity available in transport processes. Since advective flow takes place only in interconnected pores, the transport porosity does not include isolated or dead-end pores. Hildenbrand et al. (2002) express transport porosity as the “nominal fraction of the rock volume corresponding to gas-saturated flow pathways after breakthrough”. In that study, the maximum effective permeability occurred at a transport porosity in the order of  $10^{-2}$  to  $10^{-5}\%$ , suggesting that very small transport porosities may allow gas flow through water saturated clay-rich rocks (see Section 3.1 and Figure 3.1).

Mudrocks and other clay-rich sediments possess very low permeabilities, therefore advective flow on a regional level is thought to occur only through discontinuities (Pearson, 1999). The virtually impermeable status of deeply buried shales is owed to the very small interparticle spaces of this class of materials. However, indurated rocks are capable of undergoing brittle fracturing (Horseman et al., 1996).

## 5.2 Fracture Development

Fractures can occur due to tensile failure, when the pore pressure is increased above the minimum in situ stress. For example, hydrofracturing, which is a technology developed to increase the well bore permeability and production, involves injection of the fluid into reservoir rock until the formation opens and tensile fractures occur. As the pore pressure increases, the effective stresses decrease towards zero and even become tensile. At zero effective stresses existing discontinuities will open up, while at tensile stresses that exceed the cohesion of the intact rock, the new fractures will be generated. Obviously, it is necessary to avoid fracturing through the caprock when fracturing the reservoir rock..

Fractures can be also generated by shear failure. The shear failure mechanism and the volumetric changes of the rock subjected to loading can be explained by the concepts of critical state soil mechanics. Critical state soil mechanics was developed from the application of the theory of plasticity to soil mechanics and it provides a complete theoretical framework for describing the mechanical behaviour of soils and other geomaterials that behave in a similar way (Horseman et al., 1993; Botts, 1998; Bolton and Maltman, 1998). Our further presentation of the critical state theory relevant to seal integrity will be limited to a short explanation of soil behaviour in undrained and drained triaxial tests. For a comprehensive examination of critical state soil mechanics Atkinson (1993), Atkinson and Bransby (1978), and Wood (1990) are recommended.

During undrained triaxial tests, axial loading of the sample is carried out in undrained conditions. Neither the dissipation of the excess pore pressure nor volumetric changes of the sample are allowed. As the total stress due to loading increases, the excess pore pressure develops without the possibility to dissipate. Consequently, the effective shear stresses increase to a point where shear failure is initiated. The onset of shear failure is dependent on the previous stress history of the sediments, and its position with respect to the Critical State Line (CSL), as illustrated in Figure 5.4.

During drained triaxial tests, axial loading of the sample is carried out in drained conditions. Both the dissipation of the excess pore pressure and the volumetric changes of the sample are allowed. As the sample is loaded, the excess pore pressure dissipates and effective stresses change at the same rate as the total stresses. Ultimately, the shear failure of the sample is initiated.

Heavily overconsolidated sediments are said to be *dry of the critical state line* (point D in Figure 5.4), whereas lightly overconsolidated or normally consolidated sediments are said to be *wet of the critical state line* (point W in Figure 5.4). As the materials are fully saturated, the terms wet and dry are relative and refer to the water content with respect to the water content of the material at critical state.

Normally consolidated materials will compress in shear and develop positive pore water pressures during undrained tests or release the pore water (i.e dewater, hence the name wet) in drained tests. Overconsolidated sediments, however, will dilate in shear and develop negative pore water pressures, i.e stay dry. Upon shear failure under drained conditions, the grains of normally consolidated sediments (wet side of critical) move into void spaces (compress), whereas grains of overconsolidated sediments (dry side of critical) must move apart (expand) during shearing, as described in Figure 5.4.

Dilation of overconsolidated materials results in the development of discrete brittle shear zones and discontinuities as the material accommodates the additional strain (Bolton and Maltman, 1998). In contrast, normally consolidated materials will accommodate the additional strain without the formation of brittle shear zones, but rather through more ductile deformation mechanisms (Rodwell et al., 1999; Bolton and Maltman, 1998; Atkinson, 1993).

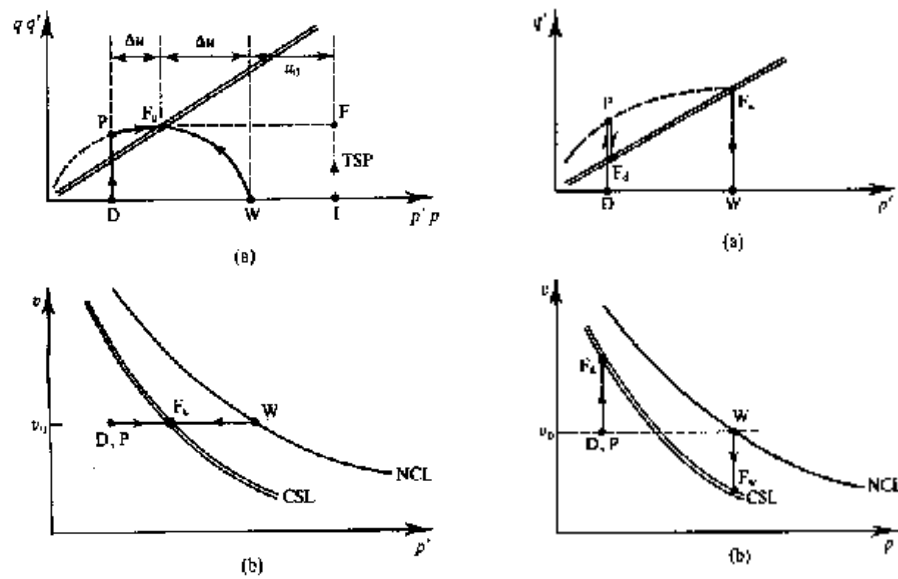


Figure 5.4 Undrained (left) and drained (right) behaviour of soils in the  $p':q$  space (top diagrams) and in the  $v:p'$  space (bottom diagrams)(after Atkinson, 1993). $p, q$  and  $v$  are the mean effective stress, deviatoric stress and specific volume, respectively

The magnitude of permeability enhancement during and after shear dilation is dependent on the amount of overconsolidation, and sediment stiffness at given stress conditions. Dilation will result in increases in porosity, and therefore increase in permeability. A direct relationship between porosity and permeability is not always clear, and it may be dependent on the state of drainage (Bolton and Maltman, 1998). The state of pre-existing fissures (open/close) is dependent on the effective normal stress on the fissure walls, and the porefluid pressure inside the fissure. The greater the porefluid pressures relative to the effective normal stresses, the more likely the fissure

will open, and vice versa. Overconsolidated sediments will dilate during shear deformation, and their permeability will increase. Gas migration in tight mudrocks requires developed dilated cracks, which are more likely to develop in overconsolidated mudrocks (Rodwell et al., 1999). Development of large strains can lead to the development of discontinuities or slip surfaces (Atkinson, 1993).

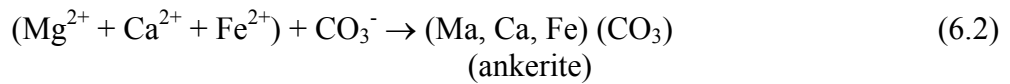
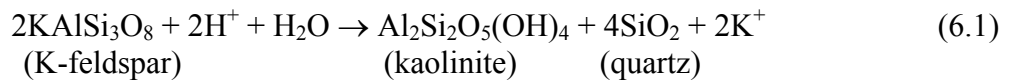
In conclusion, issues involving the continuity of the seal, fracture size and density are important in the development of faith that the seal will not fail under storage conditions. Understanding the geomechanical behaviour, and the mechanisms of deformation and failure are fundamental in identifying the potential processes which will result in or promote leakage through caprocks. The loading history of the sediments is one of the most important factors in determining its deformation behaviour. Using the framework of critical state soil mechanics to describe the potential behaviour of clays, mudrocks and shales will help to identify the potential dilatant or compressive behaviour of the caprock. It will provide a useful means of understanding the behaviour of fractures and fracture networks, both present, and newly created, when analysing caprock integrity. Based on critical state soil mechanics, it can be concluded that overconsolidated materials, i.e. sediments dry of critical state, will more likely undergo brittle deformation that will increase their porosity and permeability.

## 6 Geochemical Aspects

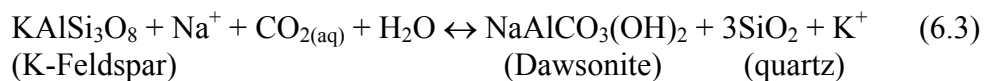
Carbon dioxide is an acidic reactive gas which partially dissolves in water, and it can cause mineral dissolution and precipitation. It lowers the pH of the formation waters which it enters, and can create large changes in the porosity and permeability of the aquifer and overlying aquitard. Changes in the formation properties are dependent on its mineralogy. The formation properties, the salinity of the porefluid, the rate of reactions, the mineral surface area, they are all factors influencing the effect of CO<sub>2</sub> on the surrounding formation.

### 6.1 Reactions

In the presence of aluminosilicates, in particular K-feldspar, several reactions are likely to occur upon the influx of CO<sub>2</sub>. Modeling work performed on the Magnus field (sandstone formation) in the North Sea by Worden and Barclay (2000) suggested that quartz, ankerite and kaolinite were likely products of four simultaneous reactions involving CO<sub>2</sub> and K-feldspar. A shift in equilibrium, caused by an influx of CO<sub>2</sub> and subsequent reduction in pH, results in favourable conditions for K-feldspar dissolution (Equation 6.1). This dissolution results in the formation of kaolinite and quartz. Ankerite formation (equation 6.2) occurs from the remaining carbonate ion reacting with ions present in the pore fluid. These chemical reactions maintain the equilibrium within the aquifer, therefore as long as an influx of CO<sub>2</sub> is present to sustain a low pH, dissolution of the aluminosilicates and precipitation of diagenetic cements will continue.



Under similar conditions that result in the formation of ankerite, an acidic environment, the presence of Na<sup>+</sup> ions, aluminosilicates (particularly K-feldspar) and CO<sub>2</sub> can react to form Dawsonite (NaAlCO<sub>3</sub>(OH)<sub>2</sub>) (equation 6.3). Other carbonatic cements are also common under these conditions including siderite, magnesite, and calcite. The precipitation of these cements is believed to decrease the overall porosity of the aquifer and caprock, despite the initial increase in porosity due to the dissolution of the aluminosilicates.



Little literature is available on reactions occurring in shale materials upon the influx of CO<sub>2</sub>. However, it appears that the magnesite precipitation would be the dominant carbonate reaction in the presence of Fe/Mg clays (Johnson et al., 2004).

## 6.2 Kinetics

The reaction rates between CO<sub>2</sub> and water are determined largely by the phase of the two substances. Gaseous CO<sub>2</sub> reactions with water are slow, being limited by the gas transfer. This slowness is also responsible for the nonequilibrium condition which exists between atmospheric CO<sub>2</sub> and surface waters. Aqueous CO<sub>2</sub> reactions with water, such as precipitation and dissolution reactions, are much quicker. Ionization reactions are established very quickly, quicker than hydration type reactions. The theory of chemical kinetics in groundwater has been well documented in the literature (Fetter, 1993; Langmuir, 1997; Stumm and Morgan, 1981; Faure, 1991).

In low-permeability materials, where the CO<sub>2</sub> influx is primarily due to diffusion, the reaction between CO<sub>2</sub> and aluminosilicates and/or ions in solution may be quicker than CO<sub>2</sub> diffusion itself. Under these circumstances the rate-limiting step in these reactions involving CO<sub>2</sub> becomes the rate of diffusion, which is referred to as diffusion controlled. The rate of diffusion of CO<sub>2</sub> into the pore space of the caprock is dependent on several factors (Section 3.4), including solubility of the CO<sub>2</sub> into the pore space. The solubility of CO<sub>2</sub> is dependent on the salinity of the porefluid, the pressure, and the temperature (Chapter 4). A larger CO<sub>2</sub> solubility results in a larger rate of diffusion, and thus a larger rate of reaction, all other parameters being equal.

The surface area available within a rock formation will affect the rate of reaction. With the exception of expanding clays (such as smectites), the BET method (christened BET after its authors: Brunauer, Emmett and Teller) can accurately determine the physical surface area. The reactive surface area, however, is more important for chemical reactions occurring in porous medium, and in particular in tight rock matrices. Differences between the reactive and the physical surface areas can range from 1 to 3 orders of magnitude. The reactive surface area refers to the surface area which contains chemically active sites. The rate of reaction is therefore a function of the reactive surface area density, as well as the defect density. Further, the porosity plays a significant role in chemical reactions within a tight porous medium. The reactive surface area, dislocation density and other factors that influence the rate of reactions are well described by White and Peterson (1990). The connection between the diffusion porosity and the geochemical porosity is particularly important in low-permeability clay-rich materials, where solute transport is likely to occur by diffusion (Pearson, 1999).

## 6.3 Laboratory Studies

Holloway et al (1996) reported experiments on the effect of supercritical CO<sub>2</sub> on anhydrite or mudstone caprocks. They had performed long-lasting (3 – 8 month) batch experiments, in which cores were subjected to CO<sub>2</sub> at 80°C and 200 bar. Both dry CO<sub>2</sub> was used and a 0.55 M NaCl solution saturated with supercritical CO<sub>2</sub>.

Concerning the anhydrite, the study revealed that CO<sub>2</sub> would not result in severe disintegration or loss of integrity. Some anhydrite dissolution was observed, and extensive precipitation of calcite. Only mudrock lenses or mudrock layers in the anhydrite samples experienced significant dissolution and increased porosities.

For the mudrock, there was a clear distinction between the dry CO<sub>2</sub> and the CO<sub>2</sub>-saturated brine. The experiments with the dry CO<sub>2</sub> did not result in damage to the cores,

while the experiments with the CO<sub>2</sub>-saturated brine yielded complete desintegration into several fragments or many small fragments. Significant dissolution of the dolomite present in the samples was observed, resulting in considerable increases in porosity. However, as the mudstones appeared inert when in contact with the dry CO<sub>2</sub>, it was suggested that in CO<sub>2</sub> storage scenarios the caprock would not be severely affected. Indeed, most of the CO<sub>2</sub> in the reservoir would be in the form of a gas cap. In that case, only at the edges of the reservoir, where the CO<sub>2</sub>-saturated waters are in direct contact with the caprock, corrosion would occur.

A comparison has been made with the natural CO<sub>2</sub> analogue, Bravo Dome in Northeastern New Mexico, USA. Some differences with the batch experiments were observed, like the presence of kaolinite, laumontite and gibbsite in the Bravo Dome. The occurrence of these minerals indicated reactions with acidic groundwater such as those that would develop following CO<sub>2</sub> injection. It has been speculated that the natural accumulation of CO<sub>2</sub> is in a more advanced stage than the laboratory experiments. It could be studied further to assess long-term reactions that are difficult to simulate in the laboratory.

#### **6.4 Effect of Geochemical Diagenesis**

Geochemical reactions discussed in the CO<sub>2</sub> storage literature generally refer to the conversion of gaseous CO<sub>2</sub> to mineral form. This conversion is thought to be more secure due to the formation of a less mobile product. Mineralization reactions have the added benefit of increasing the carbon storage capacity by sequestering in the more dense carbonate phase. However, geochemical reactions can have a different impact on the overlying caprock material. They can initiate changes in the aquitard, which can affect the permeability, and the physical strength of the caprock.

Cementation reactions and other forms of mechanical and chemical diagenesis can severely alter the rock matrix, resulting in plugging of the pore space and a reduction of the overall permeability. Although these pore-blocking cements can profoundly modify and impede reservoir fluid movement, it is rare that a continuous seal over an extensive area, such as an entire hydrocarbon accumulation, be formed as a result (Downey, 1984). Better understanding of the rate of reactions will determine the impact of dolomite and Fe/Mg bearing clay minerals, and the associated increase in porosity. Indeed, there is some evidence that the permeability increases due to the transformation of clay minerals: as the volume of clay minerals are decreased the grain size increases, resulting in an increase in permeability (Dewhurst et al., 1999).

Katsube and Williamson (1994) illustrated that the degree of cementation and dissolution can significantly affect the porosity and inter-connectivity of nanopores in shales at burial depths greater than 3.2km. Secondary dissolution reduced the ability of the shale skeleton to resist collapse during compaction and burial, thereby reducing its permeability. However, the significance of diagenesis at shallow depths was less. Diagenetic effects are more significant at greater depths when cementation and dissolution effects are larger than mechanical compaction. The influence of diagenesis is dependent on the depth of burial, but exactly how it changes with depth due to the influx of CO<sub>2</sub> is unknown.

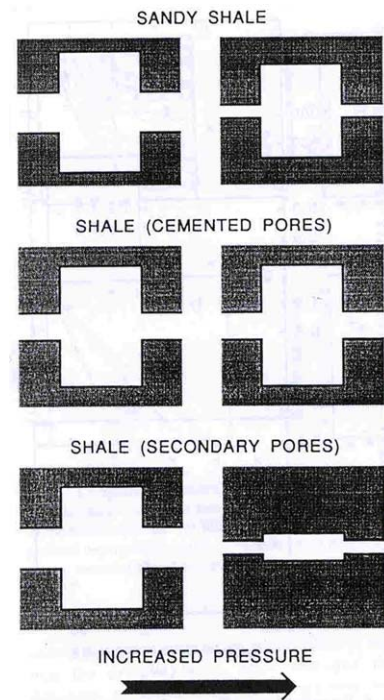


Figure 6.1 Effect of diagenesis on shale pores (Katsube and Williamson, 1994).

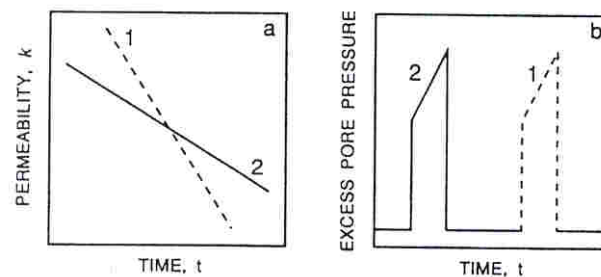


Figure 6.2 Changes in permeability with diagenesis (Katsube and Williamson, 1994)

Previous studies into the chemical diagenesis of siliclastic low-permeability materials suggested that chemical reactions decrease the permeability as a result of clay – mineral conversion. There is no direct evidence for a link between the effect of mudstones/shales and that of siliclastic materials (Dewhurst et al., 1999), but it has been suggested that similar diagenetic processes are likely (Bjørlykke, 1999). Data on chemical changes dominated by CO<sub>2</sub> addition in shales are not largely available in current literature.

Johnson et al. (2004) modeled reaction mechanisms under saline aquifer and shale caprock conditions available from the Sleipner field site (Chapter 8). It was concluded that under the modeled conditions the dominant carbonate reaction in shale caprocks was magnesite precipitation. It appeared that an aqueous phase of CO<sub>2</sub> moved slowly through the microfractures of the caprock in an advective nature, and diffused into the shale matrix blocks. This transport behaviour promoted the interaction between the CO<sub>2</sub> saturated plume and the clay minerals. The influx of CO<sub>2</sub> resulted in the dissolution of Fe/Mg bearing clay minerals. Rapid increase in Fe/Mg ion concentrations resulted, creating a much greater concentration in the caprock than in the underlying aquifer. This process is very conducive to Fe/Mg carbonate cementation. In the model illustrated by Johnson et al. (2004) the magnesite precipitation within the lower 5m of the shale

caprock accounted for 55% of the total CO<sub>2</sub> mass precipitated as carbonate. It is believed that the precipitation of magnesite will continue as long as an underlying immiscible CO<sub>2</sub> phase exists and some fracture porosity remains. It was concluded that a high concentration of Fe/Mg clays within the aquifer, and particularly in the main caprock itself, is beneficial in maximizing the local carbonate concentration, and reducing the risk of vertical migration of CO<sub>2</sub>.

The changes induced by chemical diagenesis require further investigation to determine the true effects of supercritical CO<sub>2</sub> under different saturations in brines and pore fluids representative of disposal in deep saline aquifers. The rate of dissolution in comparison to the rate of secondary precipitation must be quantified in order to identify the influence of each, and the changes in porosity. However, in shales and other low porosity, clay rich sediments, the more important parameter is the mechanical behaviour of such a class of materials. As chemical reactions occur, what is the change in its mechanical behaviour? Its changes in ductility resulting in the formation of dilatant or brittle fractures is important in assessing the true effect of chemical diagenesis, and its relation to changes in physical flow behaviour of caprock materials.



## 7 Natural Accumulations

Naturally occurring basins that contain large amounts of CO<sub>2</sub> have been found in various sedimentary basins. Identifying characteristics which are favourable sealing mechanisms in natural accumulations will provide an excellent basis for determining the suitability of an aquifer/caprock for its applicability in GHG storage. Despite the enormous value of investigating natural accumulations, little emphasis has been placed on its researching to date. In the status report on gas migration in radioactive waste storage issued by the European Union and the Nuclear Energy Agency in 1999, it was concluded that their review into natural analogue gas migration data was insufficiently detailed or quantitative to provide sufficient evidence for particular gas migration mechanisms, or to verify modeling parameters. Currently various research projects are underway worldwide to enhance the understanding of natural accumulations, and to incorporate these learnings into the selection of ideal geological recipients of greenhouse gases. These projects include the Natural Analogues for the Storage of CO<sub>2</sub> in the Geological Environment (NASCENT) project funded by the European Union, the Natural Analogs for Geologic CO<sub>2</sub> Sequestration (NACS) project in the United States, and the Geodisc project in Australia. An earlier study on the Bravo Dome reservoir was already mentioned earlier (Sections 2.2, 6.3, Pearce et al, 1996).

Recently, within the NASCENT project, the Montmiral (France), Vorderrhon (Germany), Florina (Greece), Milhalyi (Hungary), and Sesta (Italy) sites have been identified as appropriate research sites. The next stages in research of the caprock involve the identification of its properties, in particular their sealing capabilities through the analysis of caprock samples. This involves the evaluation of boundary conditions leading to failure of the reservoir seal during injection, and the potential for geochemical changes to occur. Descriptions of the resultant mineralogical changes and their effect on permeability, porosity, physical flow and geomechanical properties due to interaction of the caprock with CO<sub>2</sub> are target goals within NASCENT (Pearce, 2001).

## 8 CO<sub>2</sub> Storage – Field Study

The first and only field scale study of CO<sub>2</sub> injection into an aquifer started in 1996 offshore Norway in the North Sea. The Norwegian state oil company, Statoil, who owns and operates the Sleipner natural gas facility, has been injecting CO<sub>2</sub> back into the Utsira formation 2500m above the gas field. The Utsira aquifer is a flat lying reservoir structure (Chadwick, in press) bound by shale units on both the top and bottom, and lies approximately 800m below the seabed. It contains fine grained, homogeneous sand which exhibits little cementation (Baklid et al., 1996; Pearce et al., 2000). It has a porosity of 35-40%, a permeability of 1-8 darcys, (Baklid et al., 1996) and an estimated CO<sub>2</sub> storage capacity of 18 million metric tons over the operational lifespan of Sleipner (Korbøl and Kaddour, 1995). The overlying caprock is a Hordaland shale unit consisting of quartz, plagioclase, and between 40-60% clay minerals (mica/illite, mixed layers and kaolinite) (Pearce et al., 2000). Thin shale layers, 14 have been identified, exist within the Utsira formation. These thin layers are less than a meter in thickness, but have a large influence on the migration of CO<sub>2</sub> (Arts et al., 2000). Analysis of the Sleipner field is currently being conducted under the SACS (Saline Aquifer CO<sub>2</sub> Storage) project, funded by the European Union. Seismic monitoring and studies to map the Utsira, and to determine changes in its response as CO<sub>2</sub> enters the formation are on-going. Sufficient accuracy in the depth mapping of the Utsira can be difficult to obtain, due to the high level of accuracy required for flat lying reservoirs, where changes in depth by a few meters (less than 1%) can result in significant changes to the prediction of the migration direction (Chadwick, in press).

Evaluation of intact caprock samples was one of the objectives set out in SACS 2. Plans to perform laboratory tests to determine the sealing and transport capacity of the Nordland Shale caprock were hindered by the unavailability of samples. No full core material from the Nordland Shale was obtainable for caprock testing, and no suitable analogue was available (Lindgren, 2002), however efforts are being made to obtain caprock samples, as early as the summer of 2002 (Arts, 2002). Difficulties in obtaining intact caprock material have hindered the advance of caprock integrity research in the Sleipner field. In the meantime, seismic information, both 2D and 3D, and borehole information will be used to assess the extent and structure of the caprock (Chadwick, in press).

The forthcoming studies on caprock, subject to acquisition of samples from the Sleipner field, involve the following (Arts, 2002):

- characterisation of the petrography, mineralogy, and bulk chemistry
- characterisation of mechanical properties
- physical transport and sealing properties (single phase permeability and gas entry pressures)
- geochemical interactions between the CO<sub>2</sub> and the caprock
- regional extrapolation of core properties

It is intended that the framework of the work package be inclusive of all caprock properties at Sleipner, in order to gain a better appreciation of the overall sealing ability of the Nordland shale, and to assess the risk associated with caprock leakage.

## 9 Summary of the Coupled Processes; Caprock Evaluation

Caprock evaluation is a matter of closely taking into account the various processes, which may affect caprock integrity, and their couplings. In the Table 9.1 we have summarized the mechanisms playing a role, along with the relevant couplings. In the Table entries, processes are indicated identifying an influence of the row header process on the column header process. Couplings that may be of relevance to geological CO<sub>2</sub> storage are indicated in blue. Influence arrows between the table entries visualize these couplings.

Table 9.1 The processes and couplings relevant to the safety assessment of the geological CO<sub>2</sub> storage.

	<b>H</b> <b>Flow</b>	<b>T</b> <b>Thermal</b>	<b>M</b> <b>Mechanics</b>	<b>C</b> <b>Chemical</b>
<b>H</b> <b>Flow</b>	P – Q Mobility; porosity. Diffusion; Darcy flow	Convection. Adiabatic processes	Clay swelling. Poro-elasticity Compaction hydraulic fracturing	T-dependent reactions Concentration changes
<b>T</b> <b>Thermal</b>	Thermal stimulation (viscosity) Gas out of solution	T; thermal conduction coefficient; Heat capacity	Thermo-elasticity / Plasticity. Thermal fracturing	T-dependent reactions
<b>M</b> <b>Mechanics</b>	Compaction-driven production Permeability change Induced fractures	Frictional sliding. Geodynamics. Faulting	$\epsilon - \sigma$ Linear / non-linear Elasticity, Plasticity	Grain solution. Geodynamics. Diagenesis
<b>C</b> <b>Chemical</b>	Precipitation / Dissolution Permeability Volume / Pressure	Reaction heat	Diagenesis. Gips / Anhydrite.	Reaction Kinetics

The primary process of relevance to the safety assessment of geological CO<sub>2</sub> storage is physical transport of CO<sub>2</sub> by flow and mixing. Therefore all the processes should be assessed having in mind their influence on physical transport. The basic flow process is described by a relation between the pressure and the flow velocity; it is indicated in the H-H entry in the table. The relevant processes are described in Chapters 3 and 4.

The main risk for the seal integrity usually is a dramatic increase of the transmissivity through induced fractures, which is a result of coupling the flow with geomechanics. The mechanics plays a role through the influence of the pressure on hydraulic fracturing and back through the changed flow characteristics. Coupling between the flow and the mechanics is detailed in Chapter 5. For a depleted gas reservoir where the pressure is not increased above the original reservoir pressure, however, hydraulic fracturing without chemical interactions is unlikely. Indeed, if no gas chimney is present, the seal has proven to be a barrier to flow over geological timescales by the mere existence of the gas field. But there may be fracturing in layers interfacing between gas compartments.

Chemical reactions can be as important. The chemistry couples to both the flow and to the mechanics because the CO<sub>2</sub> transported to the seal may react with it. Chemical reactions may result in precipitation and dissolution of minerals, causing direct changes in the permeability of the caprock (coupling with the flow). On the other hand, chemical reactions may induce changes of stress and strain leading to fracturing of the caprock (coupling with the mechanics). We refer to Chapter 6 for more details.

Temperature can have some influence on the flow process. The CO<sub>2</sub> mobility is dependent on the temperature through the density and the viscosity. More importantly, however, when the injected CO<sub>2</sub> is much colder than the reservoir temperature, thermo-elastic effects will decrease the total stress. Combined with an increase in pore pressure, this may enhance the chance that fracturing occurs. Still, we expect that the coupling will be a one-way coupling, because the main driver is the temperature of the injected liquid. Convective heat transport would make the coupling a two-way coupling because the changed transport properties would on their turn influence the temperature distribution. However, the transport processes of relevance remain slow, making convective heat transport less important.

It is difficult at this point to provide comprehensive criteria for evaluation of the suitability of caprock seals for geological storage of CO<sub>2</sub> in deep saline aquifers. More research is required in order to understand the fundamentals behind caprock behaviour in the geochemical, geomechanical and physical flow sense. Specific attention needs to be given to coupled phenomena in clay-rich caprocks. However, some generic guidelines can be given:

- Thicker sequences are better due to a greater likelihood of intact seal properties over greater thicknesses (lower boundary of 50m in areas of low tectonic activity).
- Aquifers with multiple sequences of caprocks are superior.
- A low density of discontinuities is beneficial.
- Materials which exhibit ductile lithologies are better than brittle materials.
- The critical state soil mechanics provides an appropriate theoretical framework for geomechanical evaluation of caprocks
- Caprocks rich in K-feldspars in saline porefluids appear to form dawsonite upon influx of CO<sub>2</sub>. This mineralogy may be favoured if further research supports the current belief that dawsonite cementation will decrease the overall porosity despite an initial increase in porosity due to the dissolution of K-feldspar.

Some research has suggested that anhydrite seals are superior to clay-rich seals (Grunau, 1987), however, more recent research suggests that anhydrite and salt layers are not as impermeable as once believed (Lewis and Holness, 1996).

## 10 Current Research and Next Steps

Risk assessment of geological disposal of greenhouse gases is critical in determining the effectiveness and reliability of deep aquifer disposal. Research to date has not focused on the integrity of the aquifer seal, namely its caprock, and the ability of the caprock to prevent migration of greenhouse gases back to the atmosphere. Complex chemical, physical and geomechanical processes which affect the rock strength, integrity and ability to provide sufficient barrier to GHG are difficult to model, and require fundamental research in order to be effectively evaluated.

Apparent weaknesses in providing a comprehensive model to assess potential risks at selected geological disposal sites at present is the lack of fundamental understanding about the state of the caprock. The short and long-term changes in permeability due to the presence of faults and fissures in clay-rich media are poorly understood. The effect of discontinuities is difficult to predict and is exceedingly difficult to model realistically (Dewhurst et al., 1999). Models used to identify and describe the migration pathways of gases are often based on the conventional continuum approach to porous media, i.e. extended Darcy's law for two phase flow (Rodwell et al., 1999). However, it becomes clearer that gas migration in clay rich systems is different. Classical models are challenged by the difficulty in describing gas flow through complex materials, which exhibit coupled behaviour between clay minerals and water. Entrainment of water in gas flow can exhibit instabilities unaccounted for by simple models, and often the complexities of effective permeability as a function of pressure and stress variables are not addressed (Rodwell et al., 1999). Models must also incorporate stress-strain behaviour of clays, which is a function of desaturation. Current physio-chemical models for clay-rich low permeability materials have not been presented in this report. The general perception of models useful in analysis of caprock integrity is that a great deal of work is required for completeness. They should respond to very specific changes in caprock properties, based on its mineralogy, porefluid chemistry, changes in geochemical properties, geomechanical properties and coupled effects. Lawrence Livermore Laboratories in the United States is also currently involved in modeling of both the aquifer and caprock for geological storage (Johnson et al., 2004).

A major problem in caprock research appears to be the general lack of accurate caprock information. Lithology is generally known, but the caprock properties and thickness, and lateral and regional continuity are often hypothesized. Accurate caprock information remains difficult to obtain. Answers to other fundamental questions regarding dominant factors that control the direction of gas migration, fabric anisotropy or stress are often unknown (Harrington and Horseman, 1999).

Combination of the mineralogy, geological history and the critical state soil mechanics framework will improve the current understanding of caprock integrity. Further developments in such tools will enable a greater ability to properly select aquifer sites with sufficient sealing abilities to act as waste repositories for greenhouse gases. Effects of mineralogy on chemical diagenesis in clay-rich low permeability rocks, and thus changes in fluid flow require more indepth study. Rate and extent of precipitation of secondary minerals versus original mineral dissolution is of interest in determining the potential effects on fluid migration properties.

Investigations into natural accumulations which have shown significant evidence of leakage will be of interest to compare against securely stored accumulations. The state of caprock integrity at these sites is an important step in determining the viability of anthropogenic CO<sub>2</sub> storage. On-going research at Sleipner will result in numerous findings towards the viability of greenhouse gas storage in aquifers.

A comprehensive risk analysis remains to be done on the potential hazards of geological storage. The consequences of migration, both within the subsurface and at the surface, remain to be investigated.

## 11 Conclusions

Caprock integrity is one of the most, if not the most, important factor in determining the risk and reliability of deep saline aquifer disposal. Despite the fundamental importance of caprock, it has received little attention in past research efforts. Increasingly more focus is being paid to the state of the caprock in selected greenhouse gas disposal sites. Research is currently being conducted worldwide in an effort to gain a better understanding of caprock integrity using a combination of natural accumulations, field studies, laboratory experiments, and modeling.

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