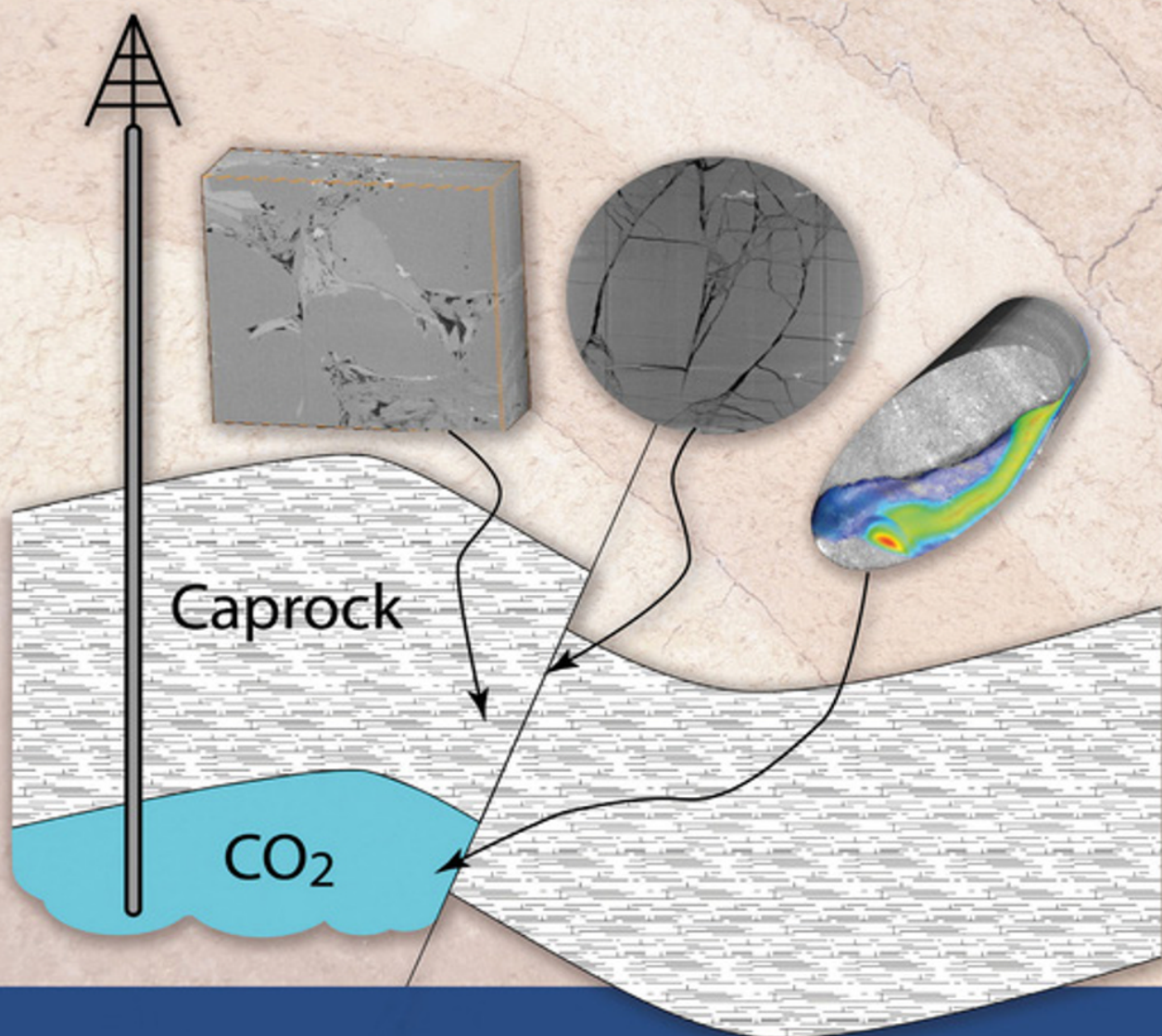


Geological Carbon Storage

Subsurface Seals and Caprock Integrity



Stéphanie Vialle, Jonathan Ajo-Franklin, and J. William Carey
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Stéphanie Vialle
Jonathan Ajo-Franklin
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Editors

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CONTENTS

Contributors.....	vii
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Preface.....	xi
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Part I: Caprock Characterization

1. Microstructural, Geomechanical, and Petrophysical Characterization of Shale Caprocks <i>David N. Dewhurst, Claudio Delle Piane, Lionel Esteban, Joel Sarout, Matthew Josh, Marina Pervukhina, and M. Ben Clennell</i>	3
2. Transport in Tight Rocks <i>Marc Fleury and Etienne Brosse</i>	31
3. Pore-to-Core Characterization of Shale Multiphysics <i>Thomas Dewers, Jason Heath, Hongkyu Yoon, Mathew Ingraham, Joseph Grigg, Peter Mozley, Enrico Quintana, and Zuleima Karpyn</i>	45
4. Analysis of the Pore Structures of Shale Using Neutron and X-Ray Small Angle Scattering <i>Lawrence M. Anovitz and David R. Cole</i>	71

Part II: Fracture Generation, Permeability, and Geochemical Reactions in Damaged Shale

5. Fracture Initiation, Propagation, and Permeability Evolution <i>Russell L. Detwiler and Joseph P. Morris</i>	121
6. Effect of Fracture Density on Effective Permeability of Matrix-Fracture System in Shale Formations <i>Li Chen, Jeffrey De'Haven Hyman, Zhou Lei, Ting Min, Qinjun Kang, Esteban Rougier, and Hari Viswanathan</i>	137
7. Gas-Water-Mineral Reactivity in Caprocks: Measurements, Estimates, and Observations <i>Julie K. Pearce and Grant K.W. Dawson</i>	147
8. Fluid-Rock Interactions in Clay-Rich Seals: Impact on Transport and Mechanical Properties <i>Elin Skurtveit, Rohaldin Miri, and Helge Hellevang</i>	167
9. Coupled Processes in a Fractured Reactive System: A Dolomite Dissolution Study with Relevance to GCS Caprock Integrity <i>Jonathan Ajo-Franklin, Marco Voltolini, Sergi Molins, and Li Yang</i>	187
10. Leakage Processes in Damaged Shale: In Situ Measurements of Permeability, CO₂ Sorption Behavior, and Acoustic Properties <i>J. William Carey, Ronny Pini, Manika Prasad, Luke P. Frash, and Sanyog Kumar</i>	207

Part III: Monitoring Caprock Failure

11. In-Zone and Above-Zone Pressure Monitoring Methods for CO₂ Geologic Storage <i>Seyyed A. Hosseini, Mahmood Shakiba, Alexander Sun, and Susan Hovorka</i>	227
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12. Monitoring and Modeling Caprock Integrity at the In Salah Carbon Dioxide Storage Site, Algeria <i>Donald W. Vasco, Robert C. Bissell, Bahman Bohloli, Thomas M. Daley, Alessandro Ferretti, William Foxall, Bettina P. Goertz-Allmann, Valeri Korneev, Joseph P. Morris, Volker Oye, Abe Ramirez, Antonio Pio Rinaldi, Alessio Rucci, Jonny Rutqvist, Josh White, and Rui Zhang</i>	243
13. Evaluation of Perfluorocarbons (PFCs) as Tracers for CO₂ Containment and Migration Monitoring <i>Matthew Myers and Cameron White</i>	271
Part IV: Environmental Impacts and Remediation Techniques	
14. Migration and Leakage of CO₂ From Deep Geological Storage Sites <i>Andreas Busch and Niko Kampman</i>	285
15. A Review of Studies Examining the Potential for Groundwater Contamination From CO₂ Sequestration <i>Charuleka Varadharajan, Ruth M. Tinnacher, Robert C. Trautz, Liange Zheng, Baptiste Dafflon, Yuxin Wu, Matthew T. Reagan, Jens T. Birkholzer, and J. William Carey</i>	305
16. Review of CO₂ Leakage Mitigation and Remediation Technologies <i>Cesar A. Castaneda-Herrera, Geoffrey W. Stevens, and Ralf R. Haese</i>	327
Index	339

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PREFACE

Caprocks or sealing units are an essential component of subsurface hydrogeological systems, controlling the migration and trapping of hydrocarbons over geological timescales. With the current need to find safe storage sites for various energy-related waste streams (CO_2 , the object of this monograph, but also nuclear waste), caprocks have recently received unprecedented attention, as an understanding of the integrity of such units, and their behavior over time, is crucial for the commercial deployment of storage technologies. Caprocks can be defined as a rock that prevents the flow of a given fluid at certain temperature, pressure, and chemical conditions; hence, the rock properties leading to sealing conditions may be distinct for different types of fluid. Caprocks encompass a broad range of rock types such as mudstones and shales (typically, clay mineral-rich rocks), evaporites such as anhydrite and halite, and tight carbonates (dolomite and marls). Although seals have been studied for decades by the oil and gas industry, a fundamental understanding of these units and of their evolution over time in the context of subsurface carbon storage is still lacking. Indeed new challenges have emerged with the case of CO_2 sequestration. First, sealing units contain minerals that are chemically reactive in the presence of CO_2 -rich fluids, and hence, fluid-rock interactions such as dissolution, precipitation, and adsorption can result in changes to the pore space and resulting alteration of transport and mechanical properties. Second, injection of CO_2 into the storage reservoir changes the state of stress of both the reservoir and the adjacent sealing units: the caprock can then be mechanically damaged via reactivation of preexisting sealing faults and fractures or creation of new fracture systems. Third, hydrological, mechanical, and geochemical processes are intricately coupled: the fundamental understanding of the coupling between these different processes is still poor, and current models often fail at describing large-scale tests. These chemical and mechanical changes may compromise the caprock, allowing fluid migration out of the storage reservoir, potentially impacting groundwater in overlying aquifers.

The important role of caprock in successful CO_2 storage operations has inspired us to gather in a single volume a review of the state-of-the-art scientific research on the integrity of sealing units in the context of carbon storage. The monograph is organized into four parts: caprock characterization; coupled hydrological, geochemical, and geomechanical processes; monitoring techniques

for caprock integrity; and environmental impacts of damaged caprock integrity alongside methods of remediating damaged caprock.

Part I of the monograph on caprock characterization begins with a review chapter presenting sample preservation methods and multiple mechanical and petrophysical characterization techniques (Dewhurst et al.). This is followed by a review and discussion paper on the transport properties of the caprock matrix at the core scale (Fleury and Brosse). A third chapter discusses characterization across pore-to-core-plug scales including both classical and recent cutting-edge technology aimed at development of constitutive laws that enable an unprecedented advance in the characterization of shale multiphysics (Dewers et al.). The last chapter of Part I focuses on a particular class of characterization techniques suitable for understanding the hierarchy of pore geometries down to the smallest scales, small and ultra small angle X-ray and neutron scattering methods (Anovitz and Cole).

Part II constitutes the core of the monograph and examines the coupling of geochemical, transport, and geochemical processes. Chapter 5 reviews processes associated with initiation, propagation, and reactivation of fractures and faults in caprock in light of changes to permeability and implications for developing an effective injection monitoring strategy (Detwiler and Morris). Chapter 6 considers the dynamic evolution of the effective permeability of matrix-fracture systems using 2D and 3D discrete fracture-matrix networks, combined finite discrete element methods to simulate fracture propagation processes, and a generalized Lattice Boltzmann model (Chen et al.). Chapter 7 is a review chapter on geochemical caprock reactivity covering observations from natural analogues worldwide, as well as experimental and modeling studies of caprock cores (Pearce and Dawson). Chapter 8 looks at the interdependency between fluid-rock interactions, fluid flow, and mechanical properties of seals, reviewing current theoretical models, experimental studies, and examples from sealing units in the North Sea (Skurtveit et al.). Chapter 9 describes a unique flow-through experiment conducted to image CO_2 -induced fracture evolution in a dolomite sample with dynamic synchrotron X-ray micro-CT at appropriate stress states, providing a unique data set to probe and validate the next generation of fully coupled fracture-scale simulators (Ajo-Franklin et al.). The last chapter of Part II reviews the permeability of fractured shale, the

potential for mitigation of CO₂ leakage by sorption to shale, and the detection by acoustic methods of CO₂ infiltration into shale (Carey et al.).

This leads to Part III of the monograph on monitoring techniques that can be used to assess CO₂ migration through caprocks. Chapter 11 reviews and discusses the most recent developments of in-zone and above-zone pressure monitoring techniques (Hosseini et al.). Chapter 12 describes the efforts made to monitor the fate of the injected carbon dioxide and the state of the caprock at the In Salah gas development project using a unique combination of wellbore, geophysical, and geochemical monitoring techniques (Vasco et al.). Chapter 13 presents a novel class of geochemical tracers, perfluorocarbon tracers, that provide a unique opportunity for monitoring caprock integrity for carbon storage and complements other geochemical and geophysical techniques (Myers and White).

Part IV of the monograph looks at environmental impacts and associated remediation techniques. Chapter 14 provides an overview of the physicochemical processes involved in fluid leakage from deep storage sites with a particular focus on the example of the Green River, Utah (Busch and Kampman). Chapter 15 reviews the literature on the primary concerns to groundwater quality from carbon sequestration and practices to mitigate or avoid impacts to water quality (Varadharajan et al.). Finally, Chapter 16 reviews the current research

related to CO₂ leakage mitigation and remediation techniques (Castaneda-Herrera et al.).

The research presented in this monograph constitutes an inclusive survey of the wealth of recent scientific work on caprock integrity in the context of carbon storage. The research also highlights that caprock integrity is more than simply a measure of permeability and lateral continuity: caprock resilience to induced chemical and mechanical stress is a key quality of a robust storage system. The assessment of potential damage to caprock is complex, as transport, chemical, and mechanical processes are coupled and time dependent. Nonetheless, tremendous progress has occurred through the collection of experimental data on shale characterization (from the pore to the core scale) and on shale chemical reactivity and mechanical strength at in situ conditions and exposure to CO₂-rich fluids. This monograph also identifies knowledge gaps that need to be filled, some appearing to be within reach: how to link the different scales of observations? Can we derive a set of constitutive relationships (most likely rock specific) to feed predictive computational models using all the required couplings? Can we image or detect a leak in the subsurface before it reaches the surface?

Stephanie Vialle
Jonathan Ajo-Franklin
J. William Carey

Part I

Caprock Characterization

Microstructural, Geomechanical, and Petrophysical Characterization of Shale Caprocks

David N. Dewhurst, Claudio Delle Piane, Lionel Esteban, Joel Sarout, Matthew Josh, Marina Pervukhina, and M. Ben Clennell

ABSTRACT

Geological storage of carbon dioxide requires extensive characterization of potential selected sites in terms of injectivity, storage capacity, and containment integrity. The latter item on that list requires a multi-scale evaluation of all aspects of the subsurface geology that can trap CO₂ underground and keep it there long term. One part of a containment integrity strategy includes characterization of the caprock at a given site. Many selected sites have clay-rich shales as caprocks, and this contribution will concentrate on workflows and methods for characterizing such rocks in the laboratory. Shale preservation is the most critical step in the process as dehydration from the native in situ water content significantly affects shale properties. Various mineralogical, microscopical, petrophysical, and geomechanical properties and associated testing methods are discussed, and where possible, examples are shown of the impact of lack of preservation. Results are discussed in the context of interaction of CO₂ with caprocks and trapping mechanisms. Finally, the discussion looks at a number of the uncertainties associated with laboratory testing of shales in terms of both results obtained to date and our limited understanding as yet of the behavior and interaction of supercritical CO₂ with clay-rich caprocks.

1.1. INTRODUCTION

Geological storage of carbon dioxide (CO₂) has been mooted as a greenhouse gas mitigation strategy for over 20 years. The practical mechanics of such a strategy have been tested out at small scale at sites such as the Otway Basin in Australia [Sharma *et al.*, 2009] and Frio in Texas [Doughty *et al.*, 2008] and during industrial-scale projects, for example, at Sleipner [Arts *et al.*, 2008] and In Salah [Ringrose *et al.*, 2013]. Many years of effort have been put into defining the critical parameters for potential CO₂ storage sites [e.g., IPCC, 2005], and these include depth, storage capacity of the site, injectivity of the reservoir, and the containment integrity of the structure into which the CO₂ is injected. Containment integrity is usually thought of in similar terms as traps and seals in

petroleum systems, and similar technologies can be used to evaluate the properties of the fault and/or top seals that provide the trapping mechanisms for keeping injected CO₂ in the deep subsurface. Fault seals usually result from the incorporation of material into the fault zone during fault movement, and this can comprise smearing out of ductile clay-rich units, abrasion of harder shales, cataclasis of rigid grains, and syn-/post-kinematic cementation of the fault rock products [e.g., Lindsay *et al.*, 1993; Yielding *et al.*, 1997; Fisher and Knipe, 1998; Dewhurst *et al.*, 2005]. Top seals are usually characterized in terms of their thickness (especially in relation to fault throw), areal extent, seal capacity (pore-scale capillary properties), and seal integrity (mechanical properties). There are multiple techniques for assessing the potential sealing capacity of faults [e.g., Watts, 1987; Lindsay *et al.*, 1993; Yielding *et al.*, 1997], and these will not be discussed further here. This paper will concentrate on methods that

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can be used to characterize caprocks in the laboratory and the relationship between these measurement techniques and the properties noted above. In this contribution, we will concentrate on shale-rich caprocks but acknowledge that other rocks such as anhydrites [e.g., *Hangx et al.*, 2010] are being evaluated as caprocks for CO₂ storage sites. However, it should be emphasized that any seal evaluation for a storage site or petroleum prospect should be fully integrated across both fault and top seals and for a wide range of scales.

Shale caprock properties are dependent on a number of factors, including depositional environment and resultant lithology, electrochemical conditions at deposition, mineralogy, the presence of organic matter, compaction, and diagenetic alteration. All of these processes have a significant impact on porosity and permeability, as well as the mechanical, capillary, and petrophysical properties of shales [e.g., *Bennett et al.*, 1991a,b; *Vernik and Liu*, 1997; *Dewhurst et al.*, 1998, 1999a, 1999b; *Clennell et al.*, 2006]. A number of these properties are also controlled by human intervention during and after the coring process, such as stress relief microfracture development and drying out and desiccation of recovered core, and care must be taken for certain properties that adequate sample preservation is undertaken [e.g., *Schmitt et al.*, 1994; *Dewhurst et al.*, 2012; *Ewy*, 2015]. This study will therefore review possible preservation methods and discuss multiple mechanical and petrophysical characterization techniques that can be used to either directly measure or estimate relevant properties required for shale caprocks.

1.2. SHALE PRESERVATION

The most critical stage for deriving high-quality laboratory results from shales is their immediate preservation on recovery. Loss of pore water from the in situ state can result in changing mechanical, physical, and petrophysical properties [*Schmitt et al.*, 1994] no matter whether the shale is soft, weak, and ductile or hard, strong, and brittle. Some pore fluid will always be lost from shales on recovery due to outgassing as cores are depressurized from the in situ conditions to the Earth's surface [*Schmitt et al.*, 1994]. However, most techniques that look to measure mechanical and rock physics properties, for example, would look to test the shale using a chemically compatible pore fluid under pressure, and this would generally drive any air into solution at fluid pressures >0.5 MPa. Running such tests under undrained conditions at low strain rates ($< 10^{-7} \text{ s}^{-1}$) allows monitoring of the pore pressure response either through Skempton B tests [*Skempton*, 1954] or during axial loading. Pore pressure increase under such conditions is indicative of full saturation. Hence, the slight loss of pore fluid during recovery can be alleviated for such tests. Equilibrating in relative

humidity (RH) environments equivalent to shale native water activity can also mitigate this effect [e.g., *Steiger and Leung*, 1991; *Ewy*, 2014]. Other tests such as composition via X-ray diffraction (XRD), cation exchange capacity (CEC), or specific surface area (SSA) measurements generally would not be significantly affected by core preservation, although one should be careful to verify whether the presence of salts (e.g., halite, sylvite) or gypsum is real or artifacts of core storage [e.g., *Milliken and Land*, 1994].

Ideally, fully saturated core samples should be preserved under a nonpolar mineral spirit (e.g., Ondina 15 or Ondina 68) such that the fluid does not interact with the clays present and prevents native pore fluids escaping from the sample. Oil cannot intrude fully water saturated nanopores in shale at ambient pressures due to immiscibility and wettability issues. Other potential fluids that can be used for shale preservation include decane [e.g., *Ewy et al.*, 2008; *Ewy*, 2014]. Core plugs subsampled from recovered core should also be sealed in glass vials immersed in an appropriate preservative solution. Should such materials not be available, a short-term solution would be to coat cores or plugs in cling film, tin foil, and wax as a short-period (weeks to months) stopgap and kept cool in a fridge (but not frozen). However, it would be preferable to immerse in the fluids suggested above as soon as possible as wax is slightly permeable to air and samples will eventually begin to desiccate.

In order to avoid sample desiccation and concomitant alteration of rock properties (see examples below), a workflow has been developed to maximize high-quality results from preserved shale cores (Fig. 1.1). Initially, a whole core is X-ray CT scanned in order to look for fractures, limestone stringers, nodules, and the like. This allows the development of a coring plan (Fig. 1.2) directly linked to the workflow which avoids such features and means that when core plugs are taken, exposure to air is minimized. While conventional rotary coring is sometimes used for harder and more isotropic shales, in general a Murg diamond wire bandsaw is used to take core plugs, and these plugs are finished off on a cylindrical grinder. This allows significantly increased core plug recovery and better quality of plugs taken in these notoriously difficult-to-prepare rocks. Shales are at their weakest in tension parallel to bedding [e.g., *Fjær et al.*, 2008], and rotary core plugs often lead to biscuiting due to closely spaced fracture development parallel to the fabric anisotropy. The lack of stress induced by torque in the case of the diamond wire bandsaw means that plugs can be taken in more difficult rocks without imposing stresses on the intrinsic planes of weakness in the shale and better plug condition and recovery is the result.

This paper will discuss the methods and application of a number of the tests shown in the workflow with a view

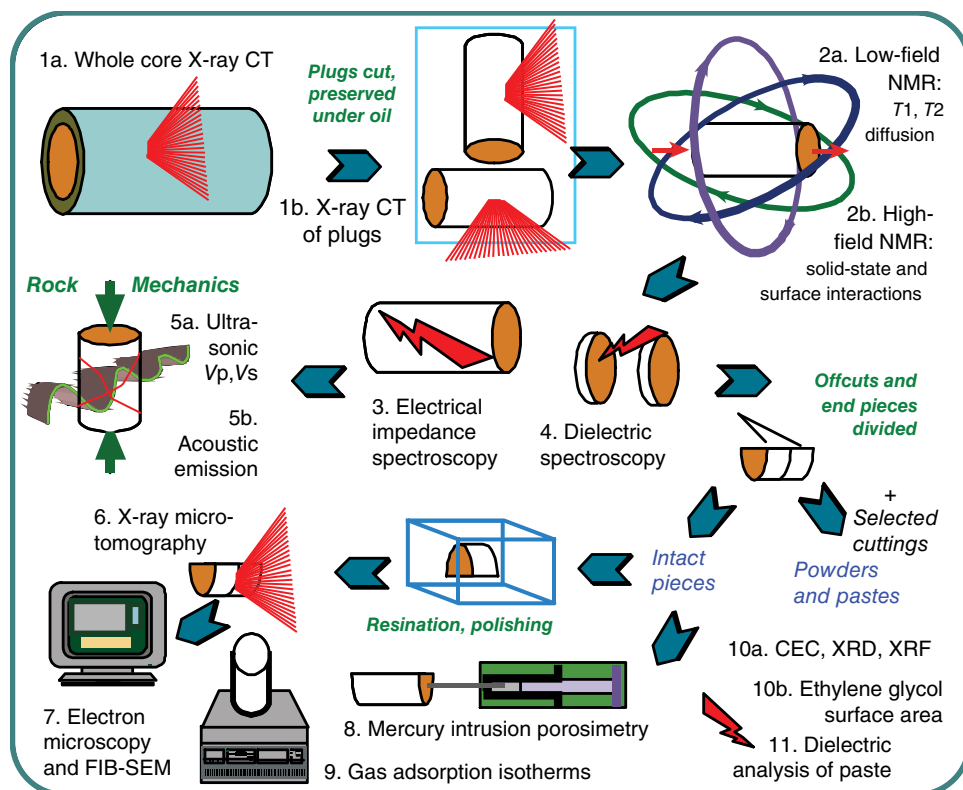


Figure 1.1 Schematic workflow for shale characterization. CT scanning of whole core and core plugs is followed by nondestructive petrophysical testing (NMR, electrical/dielectric properties) with plugs ending up in the rock mechanics laboratory for static and dynamic mechanical testing. Offcuts are sent for mineralogical, geochemical, and physicochemical properties testing, along with characterization of the shale microstructure and pore systems. Modified from *Clennell et al.* [2006]. Reprinted with permission of SPWLA.

to characterizing shale top seals for CO₂ storage and will also discuss the impact of poor preservation on results. Where possible, examples from CO₂ storage sites will be used; otherwise examples from top seals in petroleum systems will be shown.

1.3. MINERALOGY AND MICROSTRUCTURE

For a carbon capture and storage (CCS) project to be successful, it needs to guarantee the long-term trapping of the sequestered CO₂ underground. In this context, an important aspect to be considered is fluid-rock interaction which results from the contrast in physical properties between the injected CO₂ and the in situ pore fluids permeating the storage/sealing rocks and the potential reactivity between CO₂ as a free phase and as dissolved carbonic acid in the aqueous phase and the rock it comes in contact with. Through these physical and chemical interactions, the transport, elastic, and mechanical properties as well as the sealing effectiveness of shale caprocks could be changed, affecting the success of CO₂ geosequestration. A key factor to the understanding and

prediction of shale behavior is the proper characterization of the various elements that collectively constitute their microstructure. Here we regard the microstructure of shales in the context of CO₂ geosequestration as subdivided into two components: (i) the minerals and (ii) the pore space; specific techniques to characterize these two components are discussed below.

A detailed characterization of the mineral component of shales is desirable as a number of common minerals have been identified as being reactive in the presence of sCO₂ and water at temperature and pressure conditions relevant for subsurface carbon dioxide storage. Numerous studies indicate that CO₂ trapping via mineral carbonation can occur by dissolution of albite (NaAlSi₃O₈) and the precipitation of dawsonite [NaAlCO₃(OH)₂; e.g., *Romanov et al.*, 2015] as well as the dissolution of Mg, Fe-silicates and sulfides, with precipitation of Mg, Fe-carbonates such as siderite and magnesite [e.g., *Kaszuba et al.*, 2005]. Moreover, recent studies showed that electrical and capillary interactions can occur between clay minerals and CO₂ in the liquid and supercritical state. CO₂ diffusion into the clay layered structure

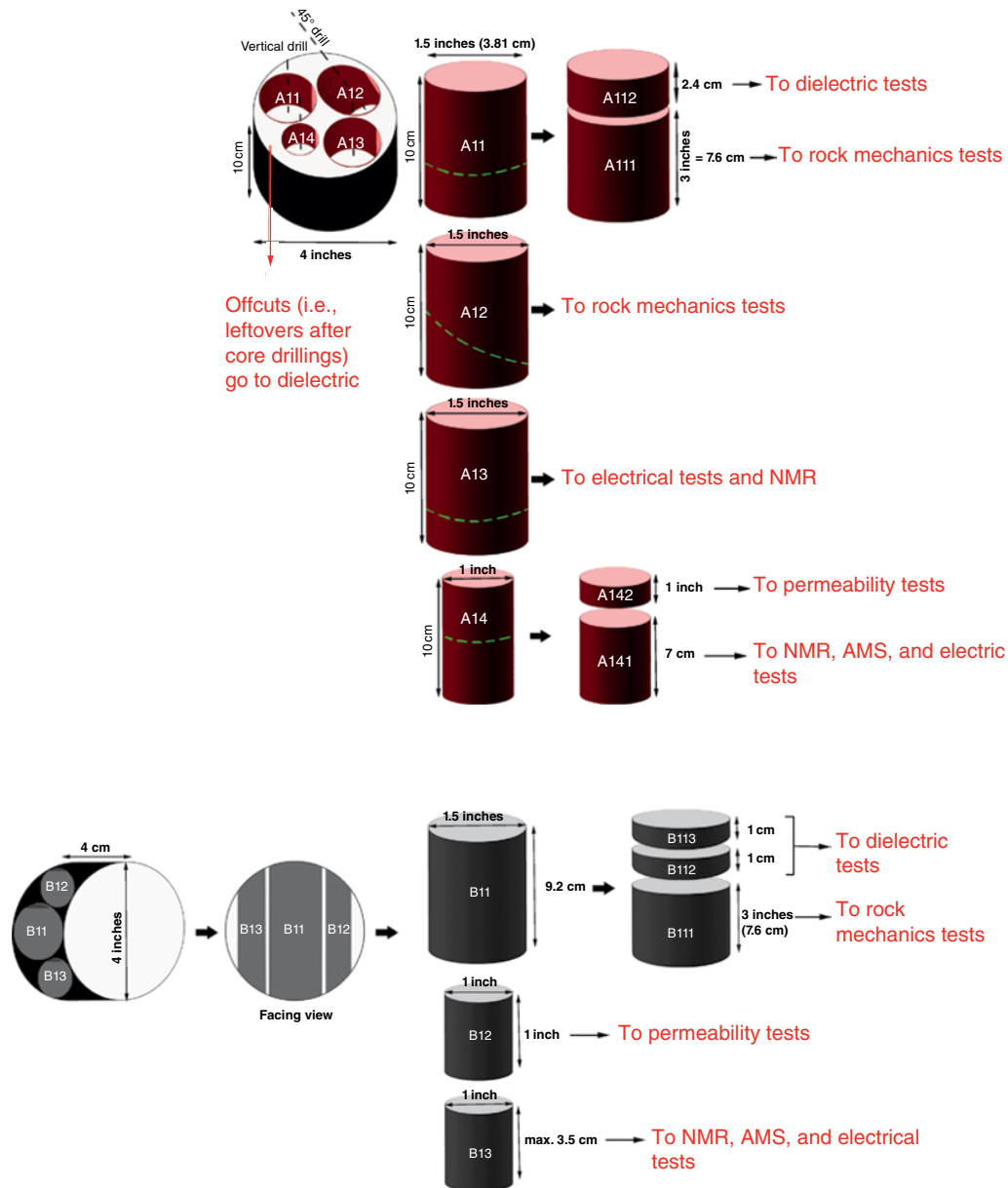


Figure 1.2 Example coring plan for subsampling whole cores normal to bedding (top) and parallel to bedding (bottom). Planning from medical CT scan images reduces exposure time to air, preventing further loss of shale pore fluids.

results in changes in the molecular clay-water chemistry leading to polarity changes in the internal electrical forces, eventually resulting in intraparticle/interparticle repulsion [e.g., Espinoza and Santamarina, 2012; Berrezueta *et al.*, 2013]. Electrical and capillary effects are modulated by the surface area of the particular clay minerals which in turn is known to be related to the type of clay [e.g., Josh, 2014]. Therefore, identification of the clay minerals in a shale caprock may help predict the potential fluid-rock interactions which could adversely affect the mechanical strength and seal capacity of the formation.

The importance of clay types has been shown, for example, by Busch *et al.* [2008] who indicated that the CO₂ sorption capacity of Muderong Shale (a regional seal in offshore Western Australia) could be attributed entirely to its clay mineral constituents.

Identification of clay minerals is traditionally achieved on powdered samples by XRD [Brindley, 1952; Moore and Reynolds, 1997], a well-established technique that only requires a few grams of material for quantification. This, however, is a destructive procedure, meaning that all spatial information on the arrangement of the identified

minerals is lost. Also, the technique is only sensitive to crystalline material such that any organic or amorphous matter will not be identified nor quantified; this could prove detrimental as organic matter is often found in shales and it is known to play a role in CO₂ sorption [Krooss *et al.*, 2002; Busch *et al.*, 2008]. Accurate determinations of grain size fractions (< 2 μm and < 0.2 μm) are critical for determination of important clay parameters and composition. The clay fraction is defined as the wt% of material < 2 μm in grain size and has been shown to be related to shale compaction and permeability [e.g., Aplin *et al.*, 1995; Yang and Aplin, 1998]. Accurate determination of wt% of clay minerals is also important as this defines the clay content parameter, which is directly linked to shale geomechanical and petrophysical properties [e.g., Clennell *et al.*, 2006; Josh *et al.*, 2012; Dewhurst *et al.*, 2015]. Finally, accurate determination of the composition and ordering of mixed layer clays, especially illite-smectites, requires analyses to be performed on the < 0.2 μm fraction to allow clear distinction of peaks, especially in the low reflection angle region [Moore and Reynolds, 1997].

Complementary methods that can preserve the spatial information regarding the arrangement of different mineral phases at the microscale and allow for their identification and quantification are normally based on petrographic analysis of polished rock samples. As a result of the fine-grained nature of shales, the use of scanning electron microscopy (SEM) is necessary to resolve many of the single components of the rock matrix. SEM allows the visualization of microstructural features down to a resolution of few tens of nanometers and, at its best, can be used to visualize areas on the order of cm². Additionally, the interaction between the incident electron beam and the analyzed material gives rise to the emission of X-rays which with the use of appropriate detectors can be analyzed in terms of energy or wavelength to infer chemical information of the emitting substance. Examples of the use of SEM-based automated mineral analysis for the quantification of shale mineralogy include Golab *et al.* [2012] and Timms *et al.* [2015]. In geological materials, electron bombardment also stimulates the emission of light at relatively low energy by cathodoluminescence (CL); spectral analysis of the CL emission in the UV to IR region offers the ability to measure trace ionic species with relatively short acquisition times enabling large areas to be mapped with detection limits orders of magnitude below elemental detections levels acquired using X-rays. This technique can be useful, for example, in mapping the distribution of authigenic quartz cement in shale formations to understand their diagenetic history and help evaluate their mechanical and elastic properties [Peltonen *et al.*, 2009; Thyberg *et al.*, 2010; MacRae *et al.*, 2014; Delle Piane *et al.*, 2015].

All of the above techniques are applicable to study small samples in great detail and provide high-quality reference points along a depth profile. There may be cases though where continuous depth profiling on recovered cores is desirable, and this can be achieved, for example, via hyperspectral logging [e.g., Haest *et al.*, 2012]. The technique has been recently used to assess the variation in clay mineral content in cores extracted from the Harvey 1 well in the clay-rich, Late Triassic unit known as the Yalgorup Member of the Lesueur Sandstone [Olierook *et al.*, 2014], in order to evaluate potential containment stratigraphic horizons for CO₂ injection in the Perth Basin, Western Australia, as part of the South West Hub Australian Flagship Carbon Capture and Storage Project [Stalker *et al.*, 2013].

The second component of shale microstructure to be characterized in the context of CO₂ geosequestration is pore space. Research on this topic has increased dramatically in recent years, particularly since shale gas systems have become commercial hydrocarbon production targets [e.g., Loucks *et al.*, 2009; Chalmers *et al.*, 2012]. SEM imaging is certainly the most direct approach to investigate porosity, but it is generally limited by (i) the poor quality of the mechanically prepared surfaces and (ii) the relatively low resolution achievable in a traditional filament instrument with respect to shale pore sizes. The introduction of field emission gun (FEG) SEMs has allowed the attainment of much higher resolution with images being acquired with pixel sizes down to a few nanometers. Also, traditional sample preparation for SEM imaging include several steps of mechanical grinding and polishing of the surface under investigation via the use of fine grits and diamond suspensions. While effective for most geological materials, these methods tend to produce topographic irregularities due to the differential hardness of the fine-grained components of shales. Loucks *et al.* [2009] showed that these irregularities greatly exceed the size of nanopores typical of shales. To eliminate these conventional preparation limitations, argon-ion milling has been introduced as a technique to produce a much flatter surface where the minor topographic variations are unrelated to differences in hardness of the sample forming minerals but, rather, to slight variations in the path of the Ar-ion beam. Both focused ion beam (FIB) and broad ion beam (BIB) [e.g., Holzer *et al.*, 2004; Desbois *et al.*, 2009, respectively] preparations have been used to establish a pore classification scheme based on the morphology of pores from representative sample areas. Desbois *et al.* [2009] defined three main types of pore morphology occurring at the interfaces between mineral particles: (i) *type I* (elongated pores between similarly oriented clay sheets), (ii) *type II* (crescent-shaped pores in saddle reefs of folded sheet of clay, and (iii) *type III* (large jagged pores surrounding clast grains). *Type III*

pores are typically larger than 1 μm , *type II* pores are between 1 μm and 100 nm, and *type I* pores are <100 nm. It should be noted that both FIB-SEM and BIB-SEM have relatively small areas/volumes of investigation, with the former on the scale of a few square microns and the latter around 1 mm².

Loucks et al. [2009], on the other hand, focused on the porosity observed within the organic matter defined as intraparticle organic nanopores and later introduced a simple classification scheme for the spectrum of pore types normally found in mudrocks, dividing them into mineral matrix pores (intraparticles and interparticles) and organic matter pores [*Loucks et al.*, 2012]. The classification follows the schemes normally adopted to describe pore space in sandstones and carbonates with the additional variable of pores contained within the organic matter. The classification is based on a ternary diagram populated via point counting of pores from SEM images. The authors concluded that interparticle and organic matter pores have generally better connectivity than intraparticle pores. The latter pores will provide storage and contribute to some permeability but will not have the same level of connectivity as the other pore types [*Loucks et al.*, 2012].

The 2D assessment of pore morphology has been complemented by the recent development of field emission microscopes coupled with ion milling (FIB) tools. This advance has allowed the production of in situ high-quality polished cross sections suitable for high-resolution SEM imaging of pores down to the nanoscale and the backstripping of the sample surface, in at best 5 nm steps, to visualize three-dimensional (3D) volumes of the specimen. Previous studies based on mercury injection highlighted that pore sizes of preserved shales are often well below the micron scale [e.g., *Dewhurst et al.*, 1998, 1999a, 1999b, 2002; *Yang and Aplin*, 1998]. FIB nanotomography is therefore ideal to describe porous networks in detail as it enables the 3D reconstruction of microstructural features on the 5–100 nm scale and can serve as a basis for quantitative microstructural analysis. *Keller et al.* [2011] used this approach on samples of Opalinus Clay considered as a candidate host rock formation for the disposal of radioactive waste. Their image acquisition and analysis workflow was adapted to the study of pores as small as about 10 nm, revealing preferential alignment of the pore paths along the bedding planes of the rock. *Heath et al.* [2011] investigated the properties of pore types and networks from a variety of geologic environments using core samples from continental and marine mudstones. They recognized seven dominant pore types distinguished by geometry and connectivity based on the quantitative and qualitative 3D observations. In particular, a dominant planar pore type was recognized in all investigated mudstones generally characterized by a

number of neighboring connected pores. The authors argued that connected networks of pores of this type likely control most matrix transport in these mudstones. Each sample was defined using cubes of 3D pore network reconstructions of 101.5 μm^3 obtained through the interpolation of 2D slices collected at a spacing of 25 nm. *Thyberg et al.* [2010] also noted planar geometrical bodies of diagenetic quartz cement in mudstones which may have precipitated in such pores and would serve to further impede fluid transport in materials already at nano-Darcy level permeability.

FIB nanotomography is a very powerful technique that allows imaging of porosity in situ; that is, the spatial relationships between pores and surrounding mineral matrix are preserved and constitute part of the visualization results. However, the technique has strong limitations in terms of sample volume and requires some image manipulation procedures in order to obtain quantitative information on the pore space. A novel approach is to complement the information provided by local high-resolution imaging with bulk measurements of pore size distribution (size ranging from nanometers to micrometers) obtained from small and ultra small angle neutron scattering (SANS/USANS) on cm-scale shale specimens [*Gu et al.*, 2015; *King et al.*, 2015] or small angle X-ray scattering (SAXS) [e.g., *Mildner et al.*, 1986; *North et al.*, 1990] to gain a more complete representation of the pore architecture and connectivity in shales (see below).

In terms of material preservation, mineralogical composition, CEC, and SSA are not significantly affected by desiccation, and indeed, generally the samples are dried out and powdered before such tests are made. However, microstructural imaging and pore size distribution measurements can be affected by lack of preservation. In soft and stiff clays, particle orientation can change on desiccation as can clay mineral shape, with resultant impacts on pore size distribution [*Diamond*, 1970; *Delage et al.*, 1982; *Griffiths and Joshi*, 1989, 1990]. Capillary threshold pressure and resultant seal capacity calculations for shales using mercury porosimetry can also be affected by drying method. *Dewhurst et al.* [2002] found that freeze-drying produced the most consistent seal capacity calculations, whereas air-drying and vacuum-drying results were more scattered.

1.4. GEOMECHANICAL PROPERTIES

Seal integrity for both hydrocarbons and CCS is usually assessed from geomechanical properties of the rocks in question. Laboratory properties of shales can be used to inform geomechanical models used to investigate the impact of injection on a prospective CCS site [e.g., *Rinaldi et al.*, 2015; *Zhang et al.*, 2015a] or as inputs for geomechanical techniques such as slip tendency [*Morris et al.*,

1996], critically stressed fractures [Barton *et al.*, 1995], or fracture stability [Mildren *et al.*, 2005]. These latter approaches have been used to assess potential CCS sites [e.g., Vidal-Gilbert *et al.*, 2010; Rasouli *et al.*, 2013; Tenthorey *et al.*, 2013, 2014; Zhang *et al.*, 2015b] in combination with magnitude and orientation of the situ stress field and pore pressure measurements. However, these field-scale approaches are beyond the scope of this paper which is reviewing laboratory measurements, and as such, we will concentrate on the latter in this section.

Standard triaxial testing and multistage triaxial testing are the best methods to obtain shale geomechanical properties [e.g., Marsden *et al.*, 1992; Horsrud *et al.*, 1998; Dewhurst and Hennig, 2003; Nygard *et al.*, 2004; Dewhurst *et al.*, 2015; Skurtveit *et al.*, 2015]. While unconfined compressive strength (UCS) testing and Brazilian testing are also standard tests, they are not recommended for shales as samples can dry out during testing and thus properties can be altered (see below). UCS can be calculated from standard triaxial tests anyway [e.g., Fjær *et al.*, 2008]. Standard triaxial testing involves placing samples in a cell surrounded by hydraulic oil at different confining pressures and loading axially until failure occurs and residual strength is reached. Best practice multistage triaxial testing involves axially loading samples to 80–90% of their failure strength at a given confining pressure, unloading to zero axial load, increasing confining pressure, allowing consolidation, and repeating axial loading [e.g., Fjær *et al.*, 2008; Dewhurst *et al.*, 2015]. To judge where individual axial loading stages should be terminated, assessment of proximity to failure can be determined through deviations

from linearity in the load-displacement curve (or stress-strain curve) or by monitoring volumetric strain and the onset of dilatancy [e.g., Fjær *et al.*, 2008; Youn and Tonon, 2010; Dewhurst *et al.*, 2015]. This train of events is then repeated multiple times, and the final stage is taken through to failure and residual strength. See Dewhurst *et al.* [2015] for a full description of the multistage methodology and associated limitations, plus Dewhurst and Siggins [2006] for definitions of geomechanical terminology used in this paper.

Geomechanical properties were required to evaluate the fault and top seal for the CO₂CRC Otway Project [Vidal-Gilbert *et al.*, 2010], a pilot-scale CO₂ storage site in Victoria, Australia. Standard triaxial testing was performed at varying confining pressures on seven 50 mm long × 25 mm diameter core plugs of preserved Belfast Mudstone plugged parallel to bedding. This orientation was necessary due to closely spaced stress relief fractures parallel to bedding which did not allow the recovery of long enough plugs normal to bedding. Two plugs failed early, splitting axially along the bedding, and were excluded from the analysis of rock strength, so results from five plugs are shown here (Fig. 1.3). The Belfast Mudstone is shown to be a weak rock with a cohesive strength of ~2 MPa and a friction coefficient <0.5 (Fig. 1.4). It should be remembered that these properties are measured parallel to bedding and that shales are significantly anisotropic in regard to strength and elastic properties [e.g., Niandou *et al.*, 1997; Ajalloeian and Lashkaripour, 2000]. In general, shales are stronger and stiffer normal and parallel to bedding and weaker at 30–60° to bedding,

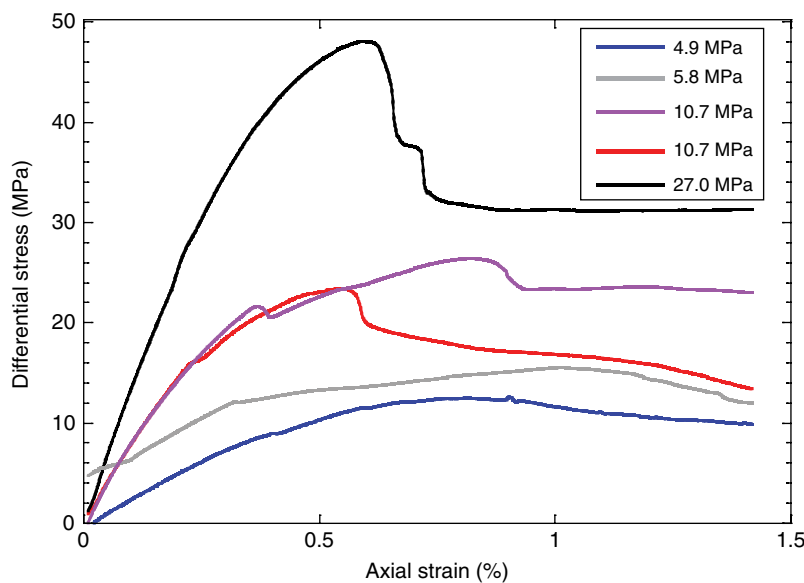


Figure 1.3 Stress-strain curves for Belfast Mudstone under increasing confining pressures with deformation parallel to bedding. The samples seem to become more brittle with increasing confining pressure, with the largest stress drop observed at the highest confining pressure used.

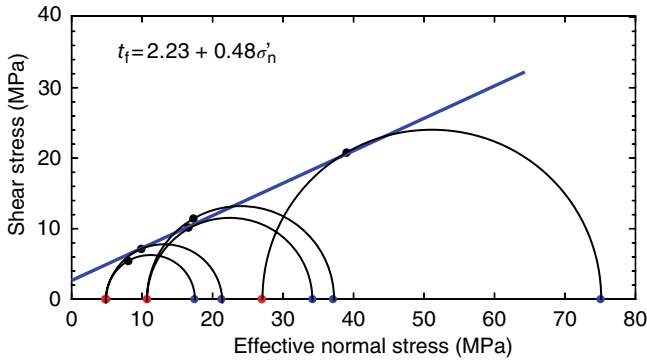


Figure 1.4 The Mohr circles derived from the peak strength takes from the stress-strain curves in Figure 1.3. The failure envelope appears to be linear with low cohesive strength and a friction coefficient lower than the standardly used values for non-shaly rocks.

usually weakest at $\sim 45^\circ$ [e.g., Valès *et al.*, 2004; Skurtveit *et al.*, 2015]. However, it is not clear whether shales are stronger normal to bedding or parallel to bedding or if the strengths in these orientations are similar as various past research shows contrasting results [e.g., Niandou *et al.*, 1997; Ajalloeian and Lashkaripour, 2000; Valès *et al.*, 2004; Skurtveit *et al.*, 2015]. The anisotropy of shale properties will be returned to in the discussion section below. These results were used in field-scale geomechanical assessments of the Otway site and the nearby Iona gas storage site by Tenthorey *et al.* [2013] and Vidal-Gilbert *et al.* [2010].

As noted above, preservation of shales for geomechanical testing is critical in terms of measurement of rock properties that would be applicable to in situ scenarios. Loss of in situ pore fluids from shales can completely change the rock properties being measured, and this is particularly the case in terms of parameters derived from triaxial testing such as strength and static/dynamic elastic properties such as Young's modulus or Poisson's ratio [e.g., Valès *et al.*, 2004; Dewhurst *et al.*, 2012; Pervukhina *et al.*, 2015]. An example of the change of properties on loss of water is shown in Figure 1.5. Here a preserved set of samples of Pierre Shale have been deformed at room temperature under different confining pressures to determine a failure envelope, which shows a cohesive strength of ~ 3 MPa and a friction coefficient of 0.39. A second set of Pierre Shale samples were equilibrated in a desiccator in a lower RH environment, resulting in a water saturation of 59%. Hence, these samples are no longer fully preserved and have lost some of their in situ water content. It should be noted that the 59% water saturation quoted is the value measured before shearing and that saturation will change during deformation due to porosity loss. These samples were deformed under the same effective stress and temperature

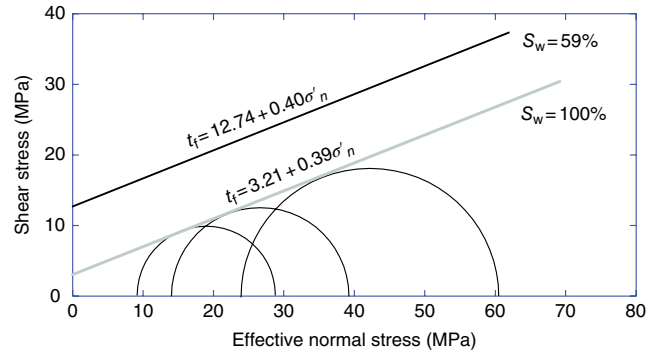


Figure 1.5 Failure envelopes for Pierre Shale deformed when fully water saturated (grey line) and partially water saturated (black line). S_w is the percentage of water-saturated porosity before samples were confined and axially loaded. The Mohr circles for the upper failure envelope have been omitted for clarity. Pierre Shale becomes substantially stronger as water saturation decreases although the friction coefficient does not change much.

conditions as the preserved samples. However, these partially saturated samples are significantly stronger than the preserved samples, with a cohesive strength of >12 MPa. The friction coefficient remains similar though for both sets of samples. Other examples of the effects of changing water saturation in shales can be found in Pervukhina *et al.* [2015]. Again, this shows the significant impact the lack of preservation can have on the results of rock properties tests on shales and why it is critical to preserve samples as soon as a shale core is recovered to the surface.

1.5. POROSITY AND PERMEABILITY

Transport properties and sealing capacity are two fundamental aspects for shale barriers when evaluating a site for CO_2 geosequestration. These parameters will control the volume and displacement velocity of fluid(s) able to move through the sealing layer. Other factors also affect flow properties, namely, (i) pore network tortuosity, (ii) pore network geometry (e.g., equant/tubular pores, planar microcracks) and grain surface, (iii) pore network connectivity, and (iv) wettability. Most of the characteristics of the pore network are affected by stress (nature and magnitude) to variable extents; for instance, microcracks are more prone to deformation and closure under compressive stress than equant pores [e.g., Paterson, 1977]. In addition, these characteristics of the pore network are not independent from each other, and in fact, a complex interaction between them is usually observed; as such, microcrack closure under increasing compressive stress affects pore network connectivity and hence fluid transport properties.

In clay-rich shales, porosity and permeability properties are linked by scale from nanometers to kilometers as illustrated by *Neuzil* [1994] and *Sondergeld et al.* [2010]. Over this wide range of scale, the notions of *free fluid* and *bound fluid* are fundamental as they affect the storage/sealing capacity and flow properties in different manner and intensity. At the reservoir scale, fractures can play a major role in the leakage risk and can be defined as the *free fluid* component of the shale formation. The fractures can have various origins such as overpressure, tectonic or induced during drilling and/or injection. In most cases, fractures, if preexisting, can be identified with logging tools and seismic exploration, and their scale and connectivity will govern the overall permeability (integrity) of the sealing barrier. The large-scale effects are beyond the scope of the paper however and will not be discussed further here [see, e.g., *Neuzil*, 1994; *Ingram and Urai*, 1999; *Dewhurst and Hennig*, 2003; *Lash*, 2006].

At the pore scale, the pore sizes generally range from sub-nanometer to micron scale in clay-bearing shale formations, making the notion of *free fluid* and effective porosity less applicable in the very small pores. Bound water is related to the interactions of the fluid(s) with minerals, mostly the clay minerals due to their strong affinity for water. As a result of the extreme surface area of clays, the water binds to clays over a large volume that is in most cases the dominant contribution to the total water content. Some clays, for example, smectites, can swell significantly by incorporating water (and ions) into interlayers in the mineral structure, which can complicate porosity determination [Brown and Ransom, 1996]. The various different types of water (free, clay-bound, capillary, and interlayer) make porosity determination in these materials rather more complex than it first appears [e.g., *Pearson*, 1999].

1.5.1. Porosity and Seal Capacity Determination

The recent interests in *shales* by the petroleum industry pushed development of new and existing technologies to investigate microscale and even nanoscale porosity in these rocks. Beyond the knowledge of porosity to estimate volumes and some fluid transport aspects, the small porosity scales occurring in shales have been found to have an impact on seismic-scale phenomena and rock physics modeling, for instance. Thorough porosity analysis in shales requires combined techniques to overlap all scales of investigations. The first rule to apply when investigating porosity in shales is to have preserved samples (i.e., original saturated water content) and handle samples with an extreme care to avoid dehydration and crack generation. Porosity can be assessed by various laboratory approaches: (i) 2D and 3D images, (ii) gas methods, and (iii) liquid methods. All of these approaches and methods have pros and cons.

1.5.1.1. Image Approaches

While assessment of nanopore scales and above have become easier and more accurate with the recent technologies such as SEM or X-ray micro-CT images, porosity determination remains challenging at the nanometer scale. Sample preparation can dry the samples that will change texture and potentially form some microcracks, although sometimes this can be mitigated by freeze-drying or critical point drying [Chiou et al., 1991; Dewhurst et al., 1998; Holzer et al., 2010]. However, such images are still useful to detect clay locations that could affect the flow properties (e.g., pore throat clogging, grain coating, pore/crack bridging) and will give essential insights about diagenetic processes. In all cases, image processing is not trivial, particularly the segmentation to separate pores from the various minerals composing the rock. Establishing representative elementary volumes for material property determination from images is also a non-trivial task [e.g., *Keller et al.*, 2013].

1.5.1.2. Gas Approaches

These methods are usually used on *unpreserved* samples with all the inherent risks on result quality (e.g., clay shrinkage, cracks, residual pore fluid), although again, such methods could use freeze-dried or critical point dried samples. Nitrogen or helium can be injected into solid plugs. The principle of gas methods is to invade the pore network with a high-diffusivity inert gas. Gas expansion is monitored, and the pore volume (i.e., porosity) of the rock sample is calculated from Boyle's law:

$$V_1 = \frac{P_2 \cdot V_2}{P_1}$$

where V_1 is the volume of gas permeating the rock sample, P_2 and V_2 are the pressure and the calibrated volume of gas before being released into the sample, and P_1 is the pressure of gas after sample infiltration. Overburden stress can be applied to close any potential microcracks. The low permeability of shales makes such measurements very time consuming to allow gas to permeate through the entire volume of the sample. Variations in temperature during the experiment will also affect the results. As a result of these limitations, such a method is rarely accurate and repeatable [e.g., *Sinha et al.*, 2013; *Wang et al.*, 2013; *Heller et al.*, 2014].

Helium pycnometry on granulated samples and powders is a good method to measure bulk and grain density in order to compute the total porosity. The best procedures involve granulation of preserved samples into 0.5–1 mm diameter size and immediately perform accurate mass and volume measurement by gas pycnometry to compute bulk density. The measurement is then repeated after drying the granulated samples in oven at 105°C for up to 2 weeks until mass stabilization occurs.

The bulk density and grain density of the sample are therefore accurately measured under the same conditions, and total porosity can be calculated (assuming negligible amounts of residual salts from pore fluid evaporation) from

$$\phi = \frac{(\rho_{\text{grain}} - \rho_{\text{bulk}})}{(\rho_{\text{grain}} - \rho_{\text{fluid}})} \times 100$$

where ϕ is the porosity in percent and densities (ρ) are in g/cm^3 . Gas pycnometry uses the same gas expansion principle described above but works at very low gas pressure (usually around 20 psi) to measure the sample volume with an accuracy usually around 0.0001 cm^3 . Most of the issues with grain density computations in laboratory come from the drying process. Many experiments have demonstrated that solid chunks/plugs cannot be fully dehydrated at 105°C due to isolated water-filled pores and clay-bound water that require time to dehydrate by diffusion transport, and this can result in lower than expected grain density measurements.

The molecular size of the gas used for the porosity measurement in the laboratory (N_2 , 0.421 nm equivalent spherical van der Waals radius; He, 0.356 nm) compared to the actual size of carbon dioxide (CO_2 , 0.454 nm) can affect the gas measurement results [Sondergeld *et al.*, 2010]. Helium is often used for porosity measurements, although its size is significantly smaller than carbon dioxide. As pore throats approach the molecular diameter of the gas used for testing, helium can pass into adjacent pores where CO_2 will not be able to pass. Layers of bound ions or water make the constriction filtration effect even more prominent. Therefore, helium determined porosity is potentially greater than the effective porosity to CO_2 . The magnitude of these porosity discrepancies is controlled by pore size distributions, which are poorly constrained and can reach up to a factor of 2.

1.5.1.3. Liquid Approaches

Several methods exist to access the porosity using injection of liquid (brine or mercury). Some of the techniques try to use the original water content without affecting the preservation state of the samples, and others push liquid through the pore network using dried samples (freeze-dried, critical point dried, or unpreserved).

Water immersion porosity (WIP) consists of saturating a solid plug or solid chunk of shale with water to invade all the pores. The wettability, fluid type, fluid composition, and pore pressure will affect the water mass intake of the sample during saturation, leading to considerable inconsistency. The saturation process can take a very long time as all fluids move at a diffusive speed and will only access the connected pores with a capillary force less or equal to the water injection pressure. In other words, it is virtually impossible to reach nanopores that require a large capillary force to invade, especially as the nanopores are water wet. However, it is fundamental to understand in the case of injecting water that any variation in the salinity and/or salt composition of the injected water from that in equilibrium with the shale will generate osmotic forces. Clay-water reactions and capillary forces in the case of partial saturation can quickly destroy the shale structure during water injection and re-saturation (Fig. 1.6) and is particularly significant in smectite-rich shales that can swell or shrink. However, the presence of organic matter and organic matter coatings can result in different wettability, and this may affect how clay minerals and shales as a whole respond to water injection.

If the sample is well preserved (i.e., approximately fully saturated), the sample can be dried under 105°C until mass stabilization and the difference in saturated and dry mass corresponds to the total water content. Assuming or knowing a pore fluid density allows the equivalent porosity to be computed from the sample volume [e.g.,



Figure 1.6 Opalinus Clay preserved (left) and the same sample after a few seconds in a non-appropriate brine solution (right); note the massive structural deterioration.

Head, 1980]. This is a relatively standard method and easy to use for well-preserved samples, and porosity calculated this way is directly related to the strength of overburden shales [Dewhurst *et al.*, 2015].

Mercury intrusion porosimetry (MIP) consists of recording the volume of injected non-wettable mercury at increasing injection pressures through a dry solid resin-coated shale cylindrical plug or, in a worst case scenario, cuttings [e.g., Vavra *et al.*, 1992; Dewhurst *et al.*, 2002; Esteban *et al.*, 2006]. Assuming cylindrical pores, the Laplace-Washburn equation [Washburn, 1921] can relate the pressure of mercury injection to an equivalent pore throat size. The cumulative pore throat volumes or total volume of injected mercury corresponds to the connected porosity. The typical maximum pressure of injection is ~400 MPa which is equivalent to a cylindrical pore throat diameter of ~4 nm. However, MIP is always lower than water or gas-derived porosity as mercury cannot access all pores. Some authors also demonstrated that pore orientations in shales can be anisotropic [e.g., Keller *et al.*, 2013], such that there is a strong orientation of pores in the foliation plane of shales resulting from grain shape and compaction, although MIP measurements performed parallel and normal to bedding in shales often show little difference in intrusion spectra [e.g., Dewhurst *et al.*, 2002; Sarout *et al.*, 2014].

MIP has also been used to estimate the capillary seal capacity of shales, that is, the height of a hydrocarbon or CO₂ column that can be retained by a given seal under in situ conditions before the non-wetting phase begins to move into and potentially breach the seal, assuming an idealized cylindrical tube pore morphology. Essentially, a capillary threshold pressure (P_{th}) for the air-Hg system can be calculated from a plot of pressure against cumulative intruded volume of mercury (or mercury saturation). This is considered to be the point where a continuous filament of non-wetting phase traverses the seal. There are a number of ways to pick P_{th} , including (i) the inflection point on the pressure-cumulative volume curve [e.g., Dewhurst *et al.*, 2002]; (ii) a percentage of mercury saturation, usually between 5 and 10% [e.g., Schowalter, 1979]; or (iii) by using the entry (or displacement) pressure where mercury first intrudes the seal sample [e.g., Vavra *et al.*, 1992]. None of these techniques has much rigor around them, and in the main, they are based on experimental results from Schowalter [1979] or from Katz and Thompson [1986] who evaluated mercury penetration through sandstones using MIP and electrical properties. Once an air-Hg threshold pressure has been calculated, this can be converted to an in situ capillary pressure for a given CO₂ column height through the use of air-Hg and brine-CO₂ contact angles and interfacial tensions; finally, a column height can be calculated from the seal and reservoir threshold pressures and the difference in brine and

CO₂ fluid densities. There are multiple publications that cover these methods in great detail [e.g., Schowalter, 1979; Watts, 1987; Vavra *et al.*, 1992]. It should be noted that estimated MIP threshold pressures for CO₂ do not often match CO₂ breakthrough pressures from laboratory experiments on shales [Hildenbrand *et al.*, 2002]. In addition, while it has long been known that surface conditions of samples need to be corrected for [so-called conformance; e.g., Vavra *et al.*, 1992], more recently, it has been suggested that for tight samples such as shales, parts of the MIP curve represent sample damage or compressibility and not intrusion of mercury [e.g., Clarkson *et al.*, 2012], and there is some concern that in tight shales, mercury might not even be entering the pores at all [Hildenbrand and Urai, 2003; Q. Fisher, *pers. comm.*, 2015]. As a final word of warning, MIP assumes that the shale system is water wet and there is some uncertainty around wettability in CO₂-mineral systems, although there is minimal research as yet on clay minerals which usually form the bulk (the load- and pore-bearing framework) of shaly caprocks [Iglauer *et al.*, 2015]. Capillary pressure techniques for measuring mudrock properties have been extensively examined by Busch and Amann-Hildenbrand [2013] and further discussed by Amann-Hildenbrand *et al.* [2013] in the context of CO₂ storage.

Ferrofluid injection combined with magnetic susceptibility consists of injection of a non-wettable ferrofluid into the pore network under high pressure. Ferrofluid is a liquid made of low-viscosity isoparaffin saturated with nanoparticles of magnetite. Such nanoparticles will be able to invade the small pores and will return a strong magnetic signal correlated to their amount [Pfleiderer and Halls, 1994]. Magnetic susceptometers can measure the intensity of the magnetic signal of the ferrofluid-saturated shales. The amount of ferrofluid in the shales (i.e., porosity, assuming full saturation) can be calibrated against the magnetic signal from a specific amount of ferrofluid. The use of an MIP apparatus with mercury replaced by ferrofluid was successfully applied on shales and provided information about porosity and pore shape/pore connectivity [Esteban *et al.*, 2006, 2007].

Low-field nuclear magnetic resonance (NMR) is probably the most promising tool for porosity and pore size distribution in shales. NMR is a nondestructive method that records the processing of protons occurring in liquid water for shales [Martinez and Davis, 2000; Dunn *et al.*, 2002]. The magnitude and time relationship of the magnetization decay signal after applying an external magnetic field (the so-called relaxation time) is directly proportional to the amount of protons and their interactions with the pore volumes and mineral surfaces. The water content measured by NMR can then be converted into equivalent porosity (assuming that water fully saturates the pore network) knowing the sample volume.

Beyond porosity measurements, NMR can provide details of the pore fluid distribution such as the clay-bound water, capillary water, and potential movable water in cracks. Models can be used to tentatively compute permeability [Coates *et al.*, 1991; Martinez and Davis, 2000; Hidajat *et al.*, 2003; Arns *et al.*, 2004; Minh and Sundararaman, 2006; Josh *et al.*, 2012; Rezaee *et al.*, 2012]. However, extreme care must be taken due to NMR machine resolution as a 2 MHz spectrometer (equivalent to NMR logging tool frequency) will not be able to resolve pores smaller than 10 nm [Nicot *et al.*, 2006]. Therefore, the total NMR porosity usually underestimates the real porosity by missing the part of the water signal from clay-bound and interlayer water. To overcome this limitation, a 20 MHz NMR spectrometer is more adapted to resolve nanopores, but the macroporosity will not be detected. A combination of 2 and 20 MHz NMR instruments is a good compromise to fully assess the pore size distribution and porosity of shales. In regard to the NMR technique and sample preservation, two spectra are shown in Figure 1.7, illustrating the impact of drying on NMR response in Opalinus Clay. The solid line shows the NMR spectrum for a preserved sample and clearly has a large peak at relaxation times between 0.4 and $\sim 3 \mu\text{s}$, which corresponds to capillary and clay-bound water. On dehydration, this water is mostly lost, and all that remains is water with relaxation times below $0.4 \mu\text{s}$ which is likely tightly bound and interlayer water in mixed layer illite-smectite.

Taken individually, each method will generate different results for porosity measurements [Howard, 1991]. Method combinations are necessary to overlap the different scales accessible by each method [Al Hinaï *et al.*, 2014] and for quality control in the overlap regions (Fig. 1.8). Repeatability of the measurements is the major laboratory issue due to difficult pore fluid accessibility related to the different sample treatment (grinding, sieving, drying, and partial re-saturation, same environmental conditions). Therefore, the best measurements are always achieved on preserved shales, particularly given the issues with crushing samples, limited pore access using MIP, or the clay-water reactions that can result from liquid re-saturation [Kuila, 2013]. Consistent sample treatment and environmental conditions (temperature, pressure, and RH) for each method, and ideally a combination of methods, can help overcome this repeatability limitation.

1.5.1.4. Radiation-based Approaches

In recent years, with the advent of gas shales, radiation-based approaches such as SAXS and SANS/USANS have come back into fashion after initial application to shales back in the 1980s [e.g., Hall *et al.*, 1986], and neutron-based methods have recently been applied to CO_2 storage research by Busch *et al.* [2014]. These methods use an incident beam of thermal neutrons or X-rays of known intensity and fixed wavelength impacting on the sample and then recording of the angle and intensity of scattering [e.g., Radlinski *et al.*, 2004]. These

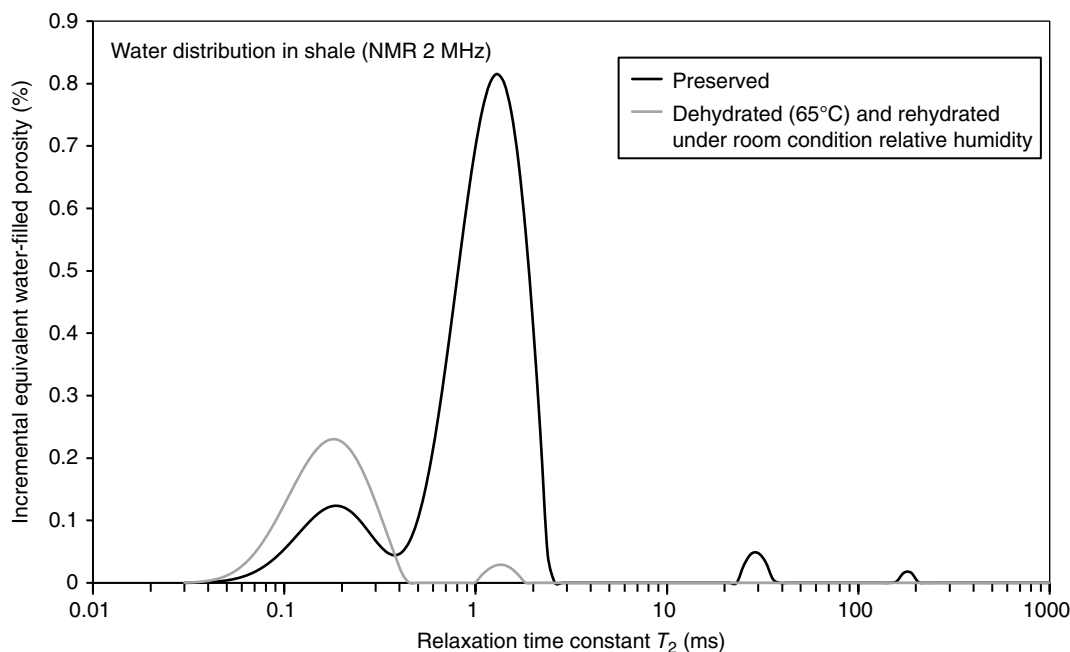


Figure 1.7 Nuclear magnetic resonance spectra for preserved and dehydrated Opalinus Clay showing significant differences in response due to dehydration. A clay-bound water peak is visible in the preserved sample but is almost gone in the dried-out sample.

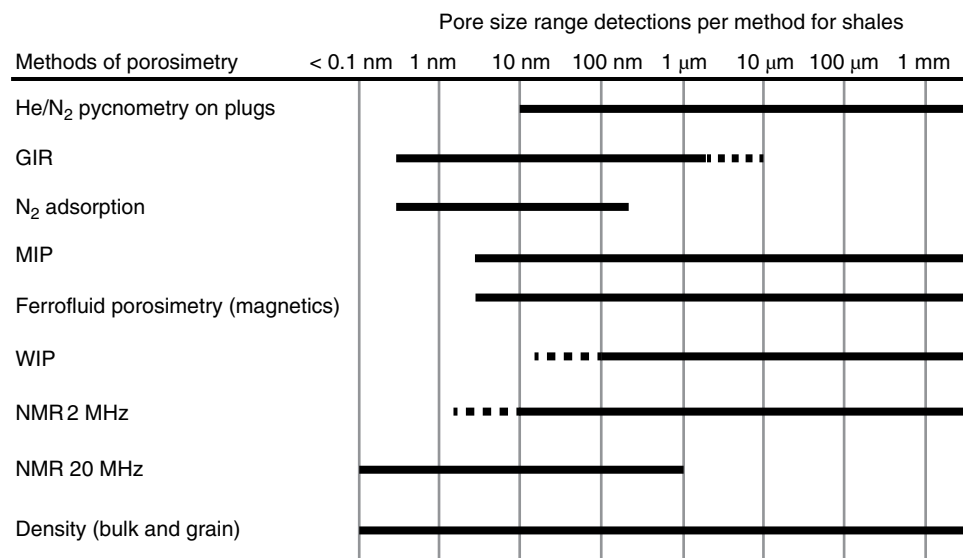


Figure 1.8 Overview of the pore size ranges detected by different methods of porosimetry for clay-bearing shales.

parameters are dependent on the geometry of the pore-matrix interface where scattering occurs [e.g., *Hall et al.*, 1986; *North and Dore*, 1993; *Radlinski et al.*, 2004]. Data obtained from such experiments can give information on total porosity, SSA, and pore size distribution (over a range from ~ 0.5 nm to ~ 10 μ m) as long as certain reasonable assumptions are made (e.g., spherical pore models). However, results can show significant anisotropy on sections normal to bedding due to preferred orientation of particles (especially clays), although isotropy is usually noted in the bedding plane [e.g., *Hall et al.*, 1986; *Gu et al.*, 2015]. Essentially, preferred orientation of particles resulting from compaction and diagenesis leads to preferred orientation and shape of pores, with strongly oriented slit and tube-shaped pores causing the observed anisotropy. This is observed in overburden shales as well as gas shales [e.g., *Keller et al.*, 2011]. This anisotropy gives different porosity and SSA in different orientations although this can be corrected for [e.g., *Gu et al.*, 2015].

Various studies have also compared the results of SAXS and SANS/USANS to pore size distribution and porosity determined through MICP and N₂ adsorption, for example. Differences are often noted between the results of these tests as they measure different properties, for example, total porosity and pore size distribution for the radiation-based methods and connected porosity and pore size distribution from MICP and N₂ adsorption [Hall et al., 1986; *Clarkson et al.*, 2013; *Gu et al.*, 2015]. The pore size distributions calculated from these methods also differ in that some measure pore bodies (N₂) and others pore throats (MICP), while the radiation-based methods do not distinguish between throats and bodies [e.g., *Clarkson et al.*, 2013]. SAXS and SANS/USANS usually give higher

porosities than N₂ adsorption which in turn is higher than MICP due to pore accessibility issues for the larger molecules, as well as different assumptions between scattering models, adsorption models, and MICP models used to estimate porosity and SSA [Gu et al., 2015].

SAXS and SANS/USANS have different sensitivities to water-filled pores, especially when pore sizes are < 2 nm and such pores are expected to hold water under ambient conditions [Hall et al., 1986]. For SANS/USANS, the contrast between hydrocarbon- or water-filled pores is strong compared to empty pores, but for SAXS the contrast is much less [e.g., *Hall et al.*, 1986]. While SANS/USANS, for example, nominally evaluates total porosity, *Clarkson et al.* [2013] used deuterated methane (CD₄) to look at connected porosity in gas shales with SANS/USANS and noted that not all micropores (< 2 nm) and surprisingly not all large pores (> 0.3 μ m) were accessible to CD₄.

Overall, radiation-based methods provide a further string to the bow in analyzing and evaluating shale properties, especially those that are porosity and pore size distribution based. In combination with other techniques which analyze different parts of the porosity spectrum, they can provide additional information useful in fully characterizing shale behavior at the nanometer to micron scale.

1.5.2. Permeability Techniques

Clay-rich caprocks are common in sites evaluated for geological storage of CO₂ due to high capillary seal capacity and often nano-Darcy level permeability. Additionally, it is known that CO₂ can be adsorbed onto clay minerals; as such, if capillary leakage occurred, this could result in extra storage capacity [e.g., *Busch et al.*,

2008]. Once capillary seal leakage occurs, then fluid transport properties such as water and effective CO_2 permeability become important [Hildenbrand *et al.*, 2002]. There are a number of methods for measuring water permeability of materials such as constant head tests, falling head tests, steady state flow, and transient pulse decay methods. The first two are generally unsuitable for clay-bearing materials, especially softer materials due to high hydraulic gradients which are imposed that can lead to sample deformation [Olsen *et al.*, 1985]. Pulse decay methods work well and have been used by Brace *et al.* [1968] and Kwon *et al.* [2004], for example, for testing of low-permeability materials as the technique is often held to be the most rapid of all the low-permeability testing techniques. However, in general, steady state methods have been used for the assessment of CO_2 -related caprocks in that this method can assure full saturation of a given caprock sample with brine under pressure as well as measuring permeability to said brine before CO_2 flooding through a sample is attempted [e.g., Hildenbrand *et al.*, 2002; Wollenweber *et al.*, 2010].

An example instrument for steady state flow testing by water injection and measurement of permeability is shown in Figure 1.9, along with some results on a cemented shale. Nominally, a disc of 25.4 mm in diameter and 10–15 mm in length is confined between two platens inside a Viton jacket and surrounded by pressurized hydraulic oil in a small steel cell. During a test, temperature and confining pressure are maintained at constant

values, typically 22°C and 20 MPa, respectively. Saturation with an appropriate brine composition (determined from petrophysical measurements) occurs through injection at the upstream side of the sample (bottom end) for several days while monitoring the downstream fluid pressure (top end) with the valve closed (Fig. 1.9). The downstream fluid circuit is initially flooded with brine at atmospheric pressure and then closed. During the saturation process, it shows an increase in pressure up to the desired value, equaling the pressure imposed at the upstream end (typically 10 MPa). The injection procedure helps us ensure that the specimen is saturated prior to the permeability test, although 100% water saturation is still an assumption, given there are almost no methods that can assess this properly in tight shales. The relatively high pore fluid pressure imposed (10 MPa) allows any residual air within the pore network to be dissolved in the brine. Following saturation, the downstream pressure is regulated at a specific pressure, typically 10 MPa. The upstream pressure is suddenly increased from 10 MPa to a higher pressure (15 MPa, for instance) and regulated at that value using a high-accuracy volumetric pump. The resolution of the upstream pump volume monitoring is 10^{-6} ml/min . The fluid pressure difference between the upstream and downstream circuits is then held constant at $\Delta P = 5\text{ MPa}$ throughout the test. Once a steady flow is achieved (straight line in Fig. 1.9), the constant fluid flow imposed by the pump is used to compute permeability using Darcy's law. Once this steady state flow regime is

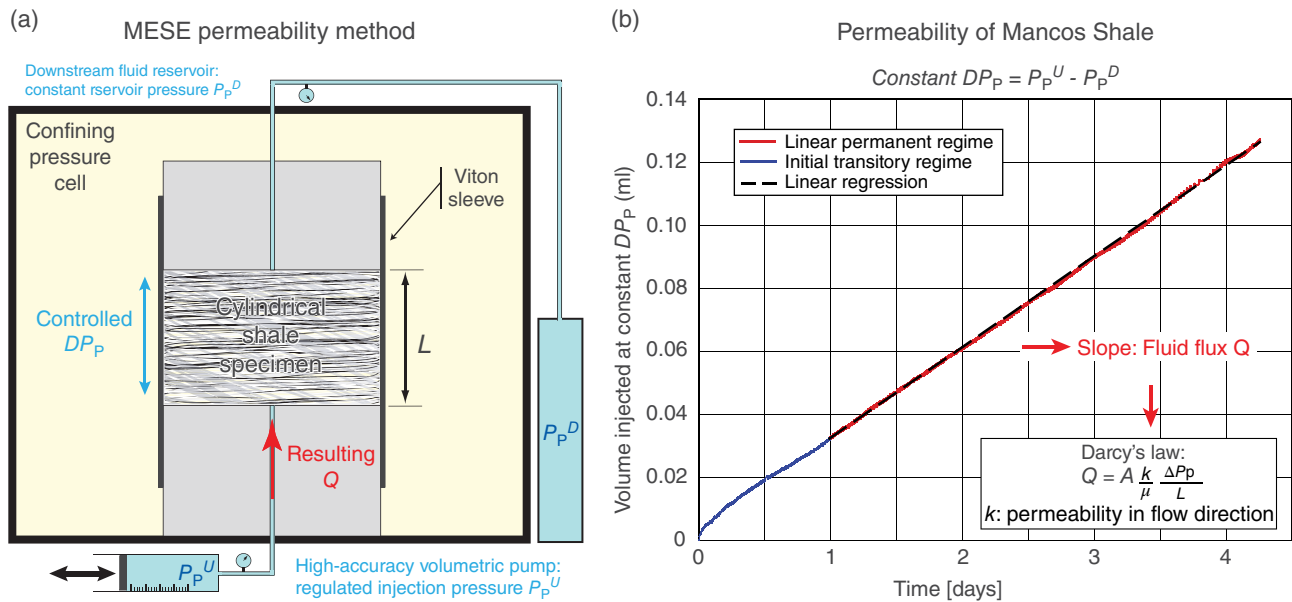


Figure 1.9 (a) Schematics of an experimental setup for permeability measurement of a cylindrical shale specimen. (b) Example of a permeability measurement for Mancos Shale, parallel to bedding, showing the fit of displaced water volume versus time during the permeability test.