

Theoretical and Experimental Study of Water Loss in Shale Matrix : A Nonequilibrium Thermodynamics-based Two-Phase Flow, Damage Chemo-poroelastic Investigation

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Theoretical and Experimental Study of Water Loss in Shale Matrix: A Nonequilibrium Thermodynamics-based Two-Phase Flow, Damage Chemo-poroelastic Investigation

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Supervisor: Dr. Hamid Roshan

A thesis in fulfilment of the requirements for the degree of

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Abstract 350 words maximum: (PLEASE TYPE)

Hydraulic fracturing (HF) is the most common technology in the development of shale reservoirs. It consumes large amounts of chemically treated water of which 60- 95% is often not recovered in flowback operations. This massive water loss can lead to significant environmental concerns and cause many economic and technical issues for operators. Despite past research, a comprehensive theoretical model coupling micro-scale mechanisms involved in the problem of water loss in shale is still lacking.

In this dissertation, a constitutive theory is developed using non-equilibrium thermodynamics and continuum mechanics which couples fluid flow with the mechanics of chemically active materials in the shale matrix. First, a micro-scale experimental investigation of damage behaviour in shale is performed under the coupled effect of stresses and fluid interactions. The observations are used to develop a novel two-phase flow, damage chemo-poroelastic constitutive model. Further experimental investigations are conducted to assess the extent to which these mechanisms contribute to the water loss phenomenon in the shale matrix and provide inputs to the model. To accomplish this objective, several techniques such as spontaneous imbibition, contact angle measurement, X-ray micro-computed tomography (micro-CT), neutron-CT, and pore pressure transmission tests are utilised.

Next, the COMSOL Multiphysics platform is used to numerically solve the coupled set of partial differential equations using the finite element method. Numerical results provide novel insights into the poromechanical behaviour of water and gas saturated shales. They indicate that, where chemical swelling stresses are negligible, shale's poroelastic and chemo-poroelastic responses are similar unless the micro-structural deterioration of the matrix with time is considered. This implies that, even when the swelling stress is low, the chemical effects – acting to lower the rock strength – induce significant changes in the stress distribution in the matrix and modify the fluid flow paths. The micro-structural deterioration occurs only in the water-saturated region increasing its storage capacity thus significantly contributing to the water loss.

The main contributions of this research are the theoretical development and modelling of two-phase flow, damage chemo-poroelastic behaviour of shale as well as the novel experimental investigation of involved physical and chemical processes. The research findings provide valuable insights into the chemo-poromechanics coupling in shale matrix and its important role in causing water loss.

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To my beloved family.....

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Abstract

Energy extraction from shale hydrocarbon resources using hydraulic fracturing (HF) has been marred with controversies mainly due to its presumed environmental impacts attributed to the fracturing fluid (mostly consisting of water). Among them, water use and water loss problems are critical issues especially in regions where water scarcity is a serious problem e.g., in Australia. A much serious repercussion is that 60 – 95% of the injected water is not recovered and hence cannot be recycled. Such huge amounts of water loss spanning many wells can have a significant impact on the local water supply. Although several micro-scale mechanisms have been found to cause such water loss in shales, a comprehensive theory coupling all such mechanisms is lacking which makes it hard to understand and predict water loss in shales.

The research presented in this dissertation is aimed at developing a constitutive theory using non-equilibrium thermodynamics and continuum mechanics for coupling fluid flow and micro-scale mechanisms with the mechanical behaviour of chemically active materials in the shale matrix. The research can be divided into four main parts. The first is the micro-scale experimental investigation of damage behaviour in shale rocks under the coupled effect of stresses and fluid interactions with the shale. The observations from this investigation are used as inspiration to develop the constitutive theory using principles of continuum damage mechanics (CDM) for chemically induced alteration and non-equilibrium thermodynamics. CDM is necessary as significant alteration to permeability and rock strength occurs under the combined influence of chemo-hydromechanical mechanisms. The second part details the development of the two-phase constitutive theory accounting for chemo-poromechanical interactions with associated chemically driven damage. This is a new development as two distinct continuity equations are used for water and gas phases instead of an average-pressure formulation and two separate damage variables for mechanical and chemical damage are utilized. This allows for observing unique poroelastic and damage behaviour (especially chemically driven) of water and gas saturated regions of the rock.

In the third part, different experimental techniques are utilized to simplify the highly nonlinear constitutive theory developed earlier i.e. shale samples from the Perth basin (Irwin River Coal Measures), Australia were used. Firstly, hydration-induced damage under varying stress conditions is studied in shale using X-ray micro-computed tomography (micro-CT). Here, the results indicate that under hydrostatic confinement there is minimal permeability evolution due to damage as the induced hydration stresses are much lower in magnitude than the in-situ stresses acting on the rock. Secondly, chemical osmosis and diffusion processes in shale are studied using pore pressure transmission tests (PPTT) and neutron-computed tomography (neutron-CT), respectively. It is found that chemical osmotic swelling is negligible in the specific shale used in this study and that pore-sizedependent heterogenous diffusion of water significantly contributes to shale water loss. Thirdly, a multi-scale study on shale wettability is performed explaining its role in shale water loss, and a fractal-based formulation of relative permeability is derived removing the need for tedious experiments to understand two-phase flow in shale. The three aspects are used as input into the constitutive theory as well as to study the extent of the coupling processes assisting in numerical simulation.

In the fourth part of the dissertation, numerical simulation of the two-phase, damage chemo-poroelastic constitutive theory is performed using the COMSOL Multiphysics finite element modelling (FEM) platform. The results indicate the importance of having a two-phase theory as clearly unique damage poroelastic behaviour was observed for water and gas saturated regions of the rock. It is found that for shales with negligible

chemical swelling effects, the poroelastic and chemo-poroelastic responses are similar implying chemical effects can be decoupled with poromechanics in the case of large-scale simulations. However, when the micro-structural deterioration of the matrix with time is considered, there is a significant alteration of matrix stresses for the water-saturated region. This suggests that even when swelling stress is trivial, the effect of chemical processes acting to weaken the rock is significant and must be accounted for in constitutive theories. The micro-structural deterioration occurs only in the watersaturated region which increases the storage capacity of the matrix contributing to water loss. This contribution can, however, be comparable to entrapment in natural or hydraulically-induced micro-fractures only when there is a manifold increase in permeability.

The main contributions of this research thus include the theoretical development and modelling of two-phase, damage chemo-poroelastic behaviour of shale along with unique experimental investigations to shed light on shale matrix water uptake processes. The research findings provide valuable insights to understand how poromechanics plays a role in causing water loss. The results indicate the developed theory is suitable for explaining water loss in shales during well shut-in periods.

List of publications

Journal articles

- Siddiqui, M. A. Q., Ueda, K., Komatsu, H., Shimamoto, T., & Roshan, H. (2020). <u>Caveats</u> of using fractal analysis for clay rich pore systems. Journal of Petroleum Science and Engineering. <u>https://doi.org/10.1016/j.petrol.2020.107622</u>
- Siddiqui, M. A. Q., Lv, A., Regenauer-Lieb, K., Roshan, H. (2020). <u>A novel experimental system for measurement of coupled multi-physics-induced surface alteration processes in geomaterials</u>. *Measurement*. <u>https://doi.org/10.1016/j.measurement.2020.108211</u>
- Siddiqui, M. A. Q., Chen, X., Iglauer, S., & Roshan, H. (2019). <u>A multiscale study on shale</u> wettability: Spontaneous imbibition vs contact angle. Water Resources Research. <u>https://doi.org/10.1029/2019WR024893</u>
- Siddiqui, M. A. Q., Ali, S., Fei, H., & Roshan, H. (2018). <u>Current understanding of shale</u> wettability: <u>A review on contact angle measurements</u>. *Earth-Science Reviews*. <u>https://doi.org/10.1016/j.earscirev.2018.04.002</u>
- Siddiqui, M. A. Q., Salvemini, F., Ramandi, H. L., Fitzgerald, P., & Roshan, H. (2020). <u>Configurational diffusion transport of water and oil in dual continuum shales</u>. *Scientific Reports*. <u>https://doi.org/10.1038/s41598-021-81004-1</u>
- Siddiqui, M. A. Q., & Roshan, H. (2020). <u>A non-equilibrium thermodynamics based two-phase, damage chemo-poroelastic constitutive theory for water swelling rocks</u>. *International Journal for Numerical and Analytical Methods in Geomechanics*. (Submitted)

Conference proceedings

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- Siddiqui, M. A. Q., Roshan, H. (2019). <u>Hydration-Induced and Stress-Restrained Coupled</u> <u>Alteration to Shale Permeability</u>. *Global Petroleum Show 2019*, Calgary, Alberta, Canada.
- Roshan, H., Siddiqui, M. A. Q., Lv, A., & Serati, M. (2018). <u>Digital Multiphysics</u> <u>Interferometry : A new approach to study chemo-thermo-hydro-mechanical interactions in</u> <u>geomaterials</u>. ARMA18 - 52nd US Rock Mechanics / Geomechanics Symposium.

Other contributions

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- Fauziah, C. A., Al-Yaseri, A. Z., Beloborodov, R., Siddiqui, M. A. Q., Lebedev, M., Parsons, D., Roshan, H., Barifcani, A., & Iglauer, S. (2019). Carbon Dioxide/Brine, Nitrogen/Brine, and Oil/Brine Wettability of Montmorillonite, Illite, and Kaolinite at Elevated Pressure and Temperature. *Energy and Fuels*. <u>https://doi.org/10.1021/acs.energyfuels.8b02845</u>

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List of Abbreviations

HF	Hydraulic fracturing
PSD	Pore size distribution
CEC	Cation exchange capacity
SI	Spontaneous imbibition
DI	De-ionized (water)
TOC	Total organic content
HRB	Horn River Basin
FS	Fort Simpson
OP	Otter Park
FEM	Finite element method
US	United States
EIA	Energy Information Administration
СТ	Computed tomography
SEM	Scanning electron microscopy
FIB	Focussed ion beam
SAXS	Small angle X-ray scattering
PPTT	Pore pressure transmission test
IRCM	Irwin River Coal Measures
MICP	Mercury intrusion capillary pressure
REV	Representative elementary volume
PRI	Poroelastic response interface
PDI	Poroelastic damage interface

Nomenclatures

σ_v	Vertical stress
σ_h	Minimum horizontal stress
σ_H	Maximum horizontal stress
σ_{ij}	Total stress tensor
σ'_{ij}	Poroelastic effective stress tensor
δ_{ij}	Kronecker delta
ζ	Variation of fluid content
υ	Poisson ratio
ω^0	Chemical swelling coefficient
R	Solute reflection coefficient
K _c	Inverse capillary pressure derivative
α_w	Biot's coefficient for water
α_g	Biot's coefficient for gas
G	Shear modulus
Ε	Young's modulus
\tilde{x}_{cur_i}	X-coordinate of image subset in the current configuration
\tilde{y}_{cur_i}	Y-coordinate of image subset in the current configuration
x _{refi}	X-coordinate of image subset in the reference configuration
y _{refi}	Y-coordinate of image subset in the reference configuration
V_p	Pore volume
V_B	Bulk volume
V_w	Imbibed water volume
k_{ϕ}	Rock matrix swelling constant
С‰	Percentage of radius coated with clay
κ^{-1}	Debye length
Na	Avogadro's number

Ι	Ionic strength
σ_{ow}	Oil/water interfacial tension
S_w	Water saturation
S_g	Gas saturation
$ au_w$	Water viscosity
$ au_g$	Gas viscosity
k _{rw}	Water relative permeability
k _{rg}	Gas relative permeability
u _i	Displacement field
Cc	Solute molar concentration
D _e	Solute diffusion coefficient
ϕ	Porosity
D_f	Fractal dimension
p_w	Water pore pressure
p_g	Gas pore pressure
p_c	Capillary pressure
p_{cmin}	Minimum (entry) capillary pressure
r _{min}	Minimum capillary pore radius
r _{max}	Maximum capillary pore radius
$K_{f,g}$	Gas bulk modulus
$M_{\alpha/\beta}$	Coupling coefficients between phases
We	Strain energy density
Y_D	Thermodynamic force causing damage
D _{mech}	Mechanical damage variable
D _{chem}	Chemical damage variable
E _{swell}	Swelling strain
α_D	Damage permeability coefficient

Chapter 1. Introduction

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1.1. Background

1.1.1. A brief description of shales

Clastic sedimentary rocks have several classifications based on their particle sizes. These particle size definitions especially for fine-grained rocks such as shale and mudstones (including both siltstone and claystone) have specific meanings in geology. In the petroleum industry, shale is recognized more by its characteristics (e.g. porosity, permeability, clay content, etc.) rather than by a precise geological definition [1]. A ubiquitous property of shales is that they contain a significant amount of clay minerals among other minerals such as quartz, feldspars, carbonates, and organic matter especially in organic-rich shales [2]. It is the clay minerals that cause shales to be of a typical greyish color tone [2].

Shale, as a source rock, contains organic matter and associated porosity which is called the organic matter porosity. Organic matter is the hydrocarbon that has been formed because of the degradation of ancient plants and planktons at high pressures and temperatures over millions of years [3]. Organic matter porosity is believed to have separate pore connectivity and a unique influence on fluid flow. The organic matter porosity, which can be higher than the inorganic porosity, is hydrophobic and tends to hinder water flow therein [4].

Shales can act as source rocks or cap rocks and hence overlie or underlie a conventional hydrocarbon reservoir. In fact, of all the geological sections drilled during any drilling

operation (oil or gas), almost 80% are shale [5]. As a cap rock (often an inorganic shale), they provide a seal due to their low permeability and small pores preventing the hydrocarbons to cross [1]. Since the commercial production of hydrocarbons from organic-rich mudstone, almost everyone today is cognizant of the term 'shale' which was not the case when it was first introduced almost three centuries ago. Shale was defined as a sedimentary rock that is fine-grained, fissile, and clayey with lamination [6].

Although conventionally, 'clays' and 'clay minerals' have been defined uniquely [7,8], both terms are used interchangeably in this thesis to refer only to clay minerals. Clay structures are hydrated phyllosilicates (sheets of silica (Si)) with aluminium (Al), magnesium (Mg), or iron (Fe) as vital constituents. The sheets can be either tetrahedral (T) or octahedral (O) in shape which are linked together consisting of stacked planes of silicon, oxygen, or hydroxyl groups [9–11]. Linking of T and O (e.g. 1:1 TO or 2:1 TOT) sheets results in exposed basal surfaces of oxygen atoms and hydroxyl groups [12]. Clay minerals of varying types are found in sedimentary rocks like shales; the most abundant of which are illite and chlorite followed by montmorillonite (smectite group) and kaolinite [9,13,14]. While illite and montmorillonite usually are 2:1 (TOT) type layered clays, kaolinite is 1:1 (TO) type layered. The readers are referred to previous classic and fundamental studies [9–12,15] for more details on clay types.

Most clay minerals generally adsorb water, of which the smectite group (e.g. montmorillonite) is the most significant. This water adsorption leads to swelling such that the clay layers are forced apart on contact with water. Illite also exhibits swelling although less than montmorillonite. Kaolinite is classified as non-swelling but dispersive clay [16]. The swelling has been known to be either crystalline (surface hydration) or osmotic [17]. Osmotic swelling occurs only in clays where exchangeable cations are present in the interlayer space and can lead to a significant increase in bulk volume compared to

crystalline swelling which is a short-range swelling not causing much increase in volumes [18–21]. Surface hydration (crystalline swelling) occurs due to surface layers of adsorbed water molecules whereas osmotic swelling occurs due to an existing concentration gradient between the surrounding water and interlayer cations [17,22].

In older and deeply buried shales, illite is the dominant clay mineral whereas in younger (Tertiary) shales swellable smectites are dominant [23]. The amount of clay minerals dictates the transport and petrophysical behavior of sedimentary rocks [1]. Clays are structurally present surrounding other minerals such as quartz, carbonates, mica, or felspars. The size of clay particles is typically less than 2 μ m with inter-platelet spacing in the range of few Angstroms. The microscale alignment of clay particles, on the other hand, dictates the macroscopic anisotropy of shales [5]. Due to their sheet-like structure, clay minerals tend to preferentially align along the (001) lattice plane [24]. During geological processes of sedimentation, compaction, and diagenesis, this alignment becomes parallel to the bedding plane [23]. It is worth mentioning that these bedding planes cause the shale to be fissile wherein it breaks easily along these planes [25].

Shale rocks contain a mixture of such clay minerals in variable amounts. The properties of clay minerals are hence of great importance to the oil and gas industry. The impact of clay swelling reduces the ability of fluids to flow (permeability) in hydrocarbon reservoirs [26]. Problems are encountered even during drilling (e.g. borehole instability, stuck-pipe, washouts) due to the presence of such clays that have been well studied and documented [21,27,28]. The economic losses associated with mitigating such problems have been known to be very severe [29].

1.1.2. Shale gas significance

The extraction of energy from organic-rich shale rocks in the form of natural gas has revolutionized the energy markets [30–35]. This was brought about by the advancement in technology such as horizontal drilling and hydraulic fracturing without which it would not be practical nor economical to produce natural gas from shales [36,37]. Shale gas has great potential to be a significant supplier of energy to the world. An estimated 6,867 trillion cubic feet of recoverable shale gas sits beneath various regions of the world [36–38]. The effect of the shale gas revolution is apparent in countries that have tapped the potential of shale gas. For instance, the US is now reported to possess a century's worth of natural gas supply at the present consumption rates. Also, fossil fuel-associated carbon dioxide (CO_2) emission fell by 7.7% (~0.4 billion ton) between 2006-2011 by shale gas production [39]. Moreover, by 2040 almost two-thirds of the US natural gas production is projected to come from shale and tight gas resources [40].

Shale gas is being increasingly used by many other countries to maintain their energy security and to reduce dependence on other fossil fuel resources such as coal and oil which are sources of high CO₂ emissions [40–44]. In Australia, the role of shale gas is significant as oil resources are limited and the conventional gas resources have been severely depleted [40]. The estimated natural gas reserves in Australia are around 133 trillion cubic feet (tcf) [45]. The major sources of shale gas are Cooper, Perth, Canning, Beetaloo, Georgina, and Maryborough basins [40]. Australia can use shale gas to suppress local demand, improve local energy security, and increase stock fuel storage. For instance, consumption of natural gas in Australia jumped from 0.3 tcf to 1.33 tcf between 1980 and 2010 [45] highlighting the increase in demand.

From the perspective of increasing concerns about air quality and CO_2 emissions around the world and particularly in Asia, Australia can also become a leader in the supply of natural gas. The geographical closeness to Asian markets such as Japan, South Korea, China, and India allows Australia to be a significant player in the natural gas supply market. It is also technically and economically feasible as it takes about a week to ship Australia's natural gas to North-East Asian markets [45]. Moreover, the lack of abundant energy resources in countries like Japan, Taiwan, and South Korea and their substantial reliance on energy imports can also play into Australia's advantage [45].

While Australia holds significant energy resources, even more than its local requirement, it is believed that Australia is not utilizing the full potential of its natural gas resources [45]. Tapping the shale gas resources can create tens of thousands of jobs in the Australian economy and create taxation revenue for the government. Proper planning is needed to overcome any hurdles related to the production and distribution of shale gas paving way for economical aspirations in the slowing Australian economy (as of 2019).

1.1.3. Hydraulic fracturing (HF)

Hydraulic fracturing (HF) or 'fracking ('fraccing') is a technique whereby high-pressure fluids (fracturing fluids) are injected to break the formation near the wellbore (Figure 1.1). The hydraulically created fracture network enhances the productivity of the well by increasing the formation permeability. These fractures are kept open using proppants (granular materials). The onset of HF dates back to 1947 where a limestone formation was hydraulically fractured in Kansas, United Sates (US) as a trial [46]. Fast forward to 2015, 67% of the natural gas production in the U.S. came from hydraulically fractured wells (Figure 1.2) [47]. As of 2016, of all oil or gas wells drilled in the US, 69% were hydraulically fractured accounting for almost half of the produced crude [48,49].

One of the most crucial components of HF treatments is the fracturing fluid. Water began to be used as a fracturing fluid in 1953 [46]. Before this development, HF was performed

using cheaper fluids such as kerosene, refined oils, or even crude oil [46]. Foams and alcohols have been added to water making it feasible to use in a wider range of formations. Acids, surfactants, and other chemicals are now integral parts of the water-based fracturing fluids [50]. This combination of water (base fluid), chemical additives, and proppants came to be known as 'slickwater fracturing' [50]. However, the concentration of additives is minimal i.e. 0.5 - 2%. Usually, components of the fracturing fluid are chosen by the operators depending on the type of formations [51,52]. Hence, each HF operation can utilize varying additives in the water-based fracturing fluid.



Figure 1.1 A schematic of hydraulic fracturing in a horizontal well (Source: Wikipedia

[53])



Figure 1.2 Marketed natural gas production in the U.S. (2000-2015) (Source: U.S. Energy Information Administration [47])

1.1.4. Environmental/technical problems of HF

The biggest concern related to HF, especially in shales, has been linked to the high volumes of chemically treated water used and lost in the operations. It is believed that such water loss can in turn potentially contaminate groundwater aquifers [54,55], in addition to technical issues associated with the inability to recover the HF fluids. A typical HF operation uses several thousand cubic meters of water per well. In the US, shale formations such as Eagle Ford, Barnett, Fayetteville, Woodford, Marcellus, Tuscaloosa, and Haynesville use on average >10000 m³ of water per well [56]. Such high volumes are mainly due to the horizontal orientation of the wells. Generally, higher water volumes used for HF reflect the length of the horizontal sections of the well [57].

The huge amounts of water used during HF translate into amounts of water lost to the matrix, amounts of wastewater produced, and usable water depletion. This is in addition to disposal problems and possible induced seismic earthquakes [56]. The large volumes of water used in HF can impact ground or surface freshwater sources disturbing the local ecology [56,58–60]. Where freshwater availability is scarce or its withdrawal is not

feasible due to droughts, regulatory water budgets, community concerns, agricultural activities, etc. saline or brackish waters are also used for HF operations [61]. Depending on the seasonal variations, a high rate of freshwater withdrawal for HF use can damage the aquatic habitat in a particular location [59].

There have also been reports of drinking water contamination by chemical additives used in HF as well as leaked gas migration into groundwater aquifers as a result of faulty well construction [62–64]. There is no strong evidence, yet, to suggest that fracturing fluid migration directly upward towards groundwater resources is the cause of such contamination [56]. Such contamination is mostly due to leaks, spills, leaked gas migration, or inadequate disposal of wastewater. The contentions associated with HF have pushed for stringent national standards and industry regulations in several countries including Australia. Thus, mandatory and extensive risk assessments are required before any HF operation can be carried out. Moreover, chemicals used in HF are government regulated inciting the operators to convince the local community of farmers and landowners about their unharmed nature [45].

Yet another issue is that approximately 60 - 95% of the fluid used for fracturing is not recovered during flowback operations [56]. It has been reported that water use per shalegas well ranges from 1400 to 33,900 m³ [56,65,66]. For example, the median water use for a shale-gas well in the Barnett play is around 10,600 m³ [57,67]. However, during flowback 70-80% of the fracturing fluid is unrecovered. In the Barnett play, an average water loss of 7500 m³ per well is common [67]. The (re)search for the cause of such high amounts of fluid loss in shales has caused immense curiosity among the community. This has inspired studies like "Where does the water go during hydraulic fracturing?" [67]. Thousands of cubic meters of fracturing fluid are simply 'lost' underground [67]. This loss of fracturing fluid aggravates the other issues associated with HF discussed above. The disappearance of the HF fluid will also have technical consequences such as permeability impairment [68–70]. Different mechanisms have been proposed in the literature to explain fracturing fluid loss in shales. These mechanisms can be broadly divided into two categories: entrapment in closed micro-fractures [71] (natural or hydraulically induced micro-fractures in the stimulated region) and uptake by shale matrix.

The uptake by shale matrix is further caused by several phenomena including imbibition [72,73], physio-electro-chemical forces including clay hydration and osmosis [74–80], micro-structural deterioration [81], and evaporation [82]. It is emphasized that shale water uptake in the matrix is the focus of this dissertation. Two of the main mechanisms, imbibition, and osmosis are briefly discussed here and are elaborated on in subsequent chapters.

1.1.4.1. Imbibition

Imbibition refers to a process wherein a fluid is displaced by another immiscible fluid. The displaced and displacing fluids can be both liquids and gases. Depending on the driving force of imbibition, it can be classified as either spontaneous or forced imbibition. Spontaneous imbibition refers to such a process where capillary forces dominate the driving process i.e. it is also called capillary imbibition. When other applied forces exist in addition to the capillary pressure, the process is referred to as forced imbibition. Since HF fluid is pumped at high pressures, at the main hydraulic fracture-shale matrix interface there exists a hydraulic pressure gradient initially. In the induced micro-cracks in the stimulated volume around the main fracture, the pressure is disconnected from that in the main fracture and hence capillarity gradient dominates initiating the spontaneous imbibition process of water into the shale matrix. The focus of this dissertation is this spontaneous imbibition process from the hydraulically induced micro-cracks into the

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shale matrix. Both forced and spontaneous imbibition play a role in causing water loss in shales. Based on the direction of flow of the displaced and displacing fluids, imbibition can be co-current or counter-current. Co-current imbibition is when both displaced and displacing fluids have the same flow direction as in a 1D piston-like displacement. On the other hand, counter-current imbibition refers to when the displaced and displacing fluids flow in opposite directions. Both co- and counter-current imbibition can occur simultaneously. At the HF fluid-shale matrix interface, both co- and counter-current imbibition are possible depending on the fracture and micro-fracture networks surrounding the matrix [83], however, mostly it is counter-current [84]. Shales usually have low porosities (<10%) and very low permeabilities exhibiting a sub-micron pore size distribution (PSD). Such low pore-radii results in high capillary pressures in shales which act as a suction force for water in the HF fluid contributing to the water loss in shales.

1.1.4.2. **Osmosis**

Osmosis refers to the transport of water molecules from a region of high solute concentration towards a region of lower solute concentration, both separated by a semipermeable membrane. The semi-permeable membrane only allows the water molecules to pass through blocking the solute molecules. Osmotic transport is equilibrated when concentrations on both sides of the membrane become equal [85]. Osmosis is also believed to contribute to water loss in shales because of the salinity difference between HF fluid and in-situ pore fluid [22]. Shales, however, due to being rich in clay minerals, behave as non-ideal semi-permeable membranes where complete blockade of solute molecules does not occur [86]. Passage of both water molecules and solutes (ions) brings in the concept of membrane efficiency of shales. If a shale can completely prevent the flow of ions, its membrane efficiency is said to be one. Contrarily, if all ions can pass
through the shale, then its membrane efficiency is zero. Different shales have varying membrane efficiencies depending on the porosity, permeability, clay mineral types, cation exchange capacity (CEC) among other factors [86].

1.1.5. Complexity of the water loss problem in shales

Although initially it was unclear if the lost fluid lies in the natural fractures or the matrix, there are now credible reports suggesting that the role of shale matrix in causing water loss cannot be ignored [67]. The uptake of the fracturing fluid by the shale matrix is characterized by the spontaneous imbibition (SI) process which is directly dependent on the wettability of the matrix [54,87–89]. However, the wettability of shales is complex and not yet fully understood with several reported inconsistencies and discrepancies [89]. Due to the tight (low permeable) and complex nature of the shale pore system, forced displacement techniques can hardly be applied to determine their wettability [90]. Therefore, contact angle (CA) measurements and SI experiments are widely used to characterize shale rock wettability. A review of shale rock wettability studies is followed which reveals the complexity associated with the water loss problem in shales.

1.1.5.1. Liquid/air wettability of shales

Bai et al. [91] and Elgmati et al. [92] measured the contact angles of air/deionized water (DI water) and several additives on the Haynesville, Utica (Indian Castle), Utica (Dolgeville), and organic-rich Fayetteville shale samples. Air/DI water contact angle was measured to be approximately 14°, 42.5°, 60-80°, and 47.8° for Haynesville, Utica (Indian Castle), Utica (Dolgeville), and Fayetteville shales, respectively. Some additives (polymers and surfactants) could bring down the contact angle to near zero, however, increased the contact angle from 14° to 20°-25° for Haynesville shale. Also, surfactants that resulted in zero contact angles for all shale samples including those of Utica (Dolgeville) from the depth of 1584 m, in fact, caused higher contact angles for shale samples from the depth of 1487 m of the same Utica shale. Utica (Dolgeville) shales from the two depths are almost identical in their mineralogy and TOC and yet have unexpectedly different wetting affinity to the same additives. Hence, the complex and unique wetting characteristics of shales cannot be solely explained based on mineralogical differences.

Engelder et al. [79] attempted to disprove the Warner-Myers [93,94] hypothesis of groundwater contamination due to brine leakage from shale reservoirs and measured contact angles of oil and water/brine in presence of air for Marcellus and Haynesville shale samples. Imbibition tests showed that despite being slightly water-wet (based on contact angles), Haynesville and Marcellus shales readily imbibe brine and water, respectively. A higher TOC Marcellus (Union Springs) sample imbibed water faster than the comparatively lower TOC Marcellus (Oatka Creek). In Haynesville shale imbibition tests, it was observed that the least saline brine (with a higher contact angle) was imbibed more rapidly than the most saline brine (with the lowest contact angle).

Dehghanpour et al. [81,95] studied water/brine and oil (kerosene) uptake of Horn River Basin (HRB) Fort Simpson (FS), Muskwa (M), and Otter Park (OP) shale samples using contact angle and spontaneous imbibition tests on intact shale samples. Air/water contact angles were measured to be 27° for FS, 38° and 45° for upper M and lower M, 46° and 50° for upper OP and lower OP, respectively. While oil completely spread on all shale surfaces (zero contact angle), their water/brine uptake was always higher than oil. Also, no consistent correlation was found between the rate of imbibition and brine concentration. Dehghanpour et al. [75] extended their study to investigate water/brine and oil uptake in the crushed samples of the same FS, M, and OP shales. It was observed that unsaturated crushed shale samples imbibe more oil than water in contrary to the prediction by Handy's model and imbibition front model. On the other hand, when the crushed packs were pre-saturated with oil/water, no water/oil uptake was observed. If the crushed packs were truly oil-wet as hypothesised, spontaneous expulsion of water from saturated shale packs should have been observed. This aberrant behaviour was attributed to the preferred affinity of the pore surface for the fluid it was initially covered with. Perhaps, contact angle measurements on saturated shale packs would have given more insights.

Later, Lan et al. [90] further investigated the pore connectivity influence on shale wettability. In their study Montney (MT) tight-gas shale samples and the HRB (M, OP, and Evie, EV) samples were used. Oil completely spread on the surfaces of these samples whereas air/water contact angles between 37° - 73° were observed for the shale samples. Oil spontaneously imbibed into intact MT core samples and oil uptake was higher than water uptake for all MT samples which corroborates the complete spreading of oil. Contrarily, water imbibition was higher for M, OP, and EV samples which were against the observation of complete spreading of oil on their surfaces. This was explained by the strong hydrophobicity and hydrophilicity of the connected pore network in MT and HRS samples, respectively. However, the same intact HRB with a hydrophilic pore network, when crushed created an artificially well-connected hydrophobic pore network resulting in higher oil uptake than water. Contact angles were not measured on crushed samples and the micro-structural alteration due to water exposure was not characterised for imbibition tests to explain the anomalous observations. In a similar study, while MT tightgas samples were found to be oil-wet, investigation on MT tight-oil samples [96] (taken from two different wells) found them to be mixed-wet imbibing both oil and water almost equally. Extending the above studies to the source rock Duvernay Formation in the Western Canadian Sedimentary Basin (WCSB), Yassin et al. [97] also found that the contact angle on crushed shale packs of samples from four different wells was much higher (127°-152°) than that on intact samples. This signified that the crushed shale was

highly repellent to water. Duvernay shale also imbibed more oil than water corroborating the complete spreading of oil on its surface.

Liang et al. [98] investigated the wettability of organic-rich shale samples from the Longmaxi Formation (LF) in China through contact angle and spontaneous imbibition tests. Air/water contact angles at normal temperature were 33.2°, 36.6°, and 32.5° for the three LF samples and oil exhibited a contact angle of zero. Similar to the American and Canadian shales, higher water uptake in LF shales was observed as compared to oil uptake which was also linked to good connectivity of hydrophilic pores.

Peng et al. [99] investigated multiphase fluid imbibition in Eagle Ford and Barnett shales using synchrotron-based dynamic micro-CT imaging. Measured contact angles for Eagle Ford, 81.5° (air/water) and 46.2° (air/oil), and for Barnett, 89.6° (air/water) and 40.9° (air/oil) indicated preferential wetting for oil for these shales, wherein the oil phase used was diiodomethane (CH₂I₂) and the water phase was a 10 wt. % KI solution. Complete spreading of oil was not observed like in the previous studies perhaps due to the nature of the oil used. However, during imbibition, water displaced oil from micro-fractures even in the supposed hydrophobic organic matter layer contradicting all previous contact angle measurements. It was hypothesized that the formation of a thin water film on the micro-fracture surface causes the actual contact angle at the micro-scale to be much smaller.

1.1.5.2. Liquid/liquid wettability of shales

Borysenko et al. [100] measured contact angles in water/hexadecane systems on quartz plates and shale samples using various techniques. The water/oil contact angles on shale samples ranged from 52° to 84°, which demonstrate water-wet toward intermediate wetting condition. It was also found that the rate of water adsorption into the sample was higher for more water-wet samples (lower contact angles). In a later study, Borysenko et al. [101] measured oil/water contact angles on two shale samples: one hydrophobic sample from the Bass Basin which has high quartz and kaolinite content, and one hydrophilic sample from the Officer Basin which contains abundant illite. The shale samples were treated with crude oil at 70°C for 24 hours. The water/oil contact angle was around 30° on the hydrophilic surface whereas it was between 140°-160° on the hydrophobic surface. It appeared that the crude oil did not form a continuous layer on the surface and the layer was readily destroyed when exposed to water on a hydrophilic surface. However, the crude oil layer on the hydrophobic surface increased its hydrophobicity. It is noted that these measurements gave contradictory conclusions to the air/water contact angle measurements.

Mirchi et al. [102] studied oil recovery mechanism from subsurface shales using surfactant flooding by measuring interfacial tension (IFT) and contact angle values of surfactant-in-brine/oil/shale systems. The contact angle for DI water/oil/rock at ambient conditions was measured as 72.64° indicating the rock is mildly water-wet. It was aptly pointed out that in such measurements where water is the bulk fluid it forms a thin layer on the rock surface before the oil drop is introduced which may prevent the oil to imbibe into oil-wet pores giving a higher contact angle.

Habibi et al. [96] measured liquid/liquid/rock contact angles on brine saturated samples with both oil-droplet-in-brine and brine-droplet-in-oil configurations. To measure the oil-droplet-in-brine contact angle field crude oil was used. However, to visualize the brine-droplet-in-oil, kerosene was used as the oil-phase due to the non-transparency of the crude oil. Brine-droplet-in-oil contact angles at equilibrium were between 30°-63° for all samples from wells 1 and 2. Oil-droplet-in-brine contact angles were not reported for all samples but were figuratively shown for a random sample. The results show that the rock

surface has a strong affinity for water than oil such that the brine drop tends to spread (making an acute angle) on the rock surface immersed in oil (kerosene) whereas the oil drop (crude oil) forms a high contact angle on the rock surface immersed in brine as pictorially depicted in their study. The results were completely, in contrast, to contact angle measurements in presence of air where oil (crude oil) was completely spread on the rock surface.

Pan et al. [103] carried out the contact angle measurements of methane/brine (5 wt. % NaCl/shale sample) on the Shengli shale sample. The CH₄/brine/shale advancing contact angle at atmospheric pressure stayed below 60° at temperatures ranging from 298 to 343 K emphasising that the shale is water-wet in methane/brine/shale systems.

1.1.5.3. **Open questions regarding shale wettability**

It is clear from the above review that the most noted inconsistency is that while oil completely spreads and water is repelled in presence of air on almost all shale samples during CA measurements, contrarily water spontaneously imbibes into samples equal or more than oil in many instances. Also, liquid/air and liquid/liquid wettability measurements give different conclusions. This prompts one to reminisce if shales are dominantly oil-wet or water-wet.

Delving further, can shales be classified as oil-wet based on CA measurements or waterwet based on SI experiments? If the same shale is classified as water-wet based on intact core SI test, is it then oil-wet based on crushed shale pack SI test? Can a shale sample from the same formation and the same well have different wetting affinities for a fluid at different depths despite having almost similar mineralogy and TOC e.g. Utica (Dolgeville) shale [92]. Is shale wettability characterization based on air/water or air/oil contact angle measurements more representative of in-situ reservoir wettability or is it the oil/water/rock contact angle measurements? Assuming oil/water/rock contact angle measurements are more representative indicators of actual reservoir wettability, then can it be reliable if it does not similarly behave as imbibition tests i.e. some HRB samples not imbibing any water in oil-saturated shale packs or any oil in water-saturated shale packs [75]. These and more intriguing questions regarding shale wettability have been answered in this dissertation.

1.1.6. Coupled flow and geomechanics

Shale formations can be subjected to various stress regimes based on local geological structures and regional tectonic forces (e.g. Figure 1.3). Shale gas is usually found at depths greater than 914 m [104]. According to data for the U.S., HF occurred between 1372 - 2743 m for Marcellus shale, 914 – 3962 m for Eagle Ford shale, and 1372 - 4267 m for Woodford shale [105]. At such depths, the vertical stress (σ_v) acting on the reservoir can be significant due to the weight of the overlying rock mass. A normal stress regime prevails in North America [106,107] where some of the world's largest shale gas formations are located. In such a stress regime, vertical hydraulic fractures are created. Both longitudinal and transverse hydraulic fractures can form depending on the orientation of the horizontal well in respect to the in-situ horizontal stress (e.g. both fracture types are common in the Bakken formation [108]). However, for consistency henceforth in the dissertation, unless otherwise stated, the discussion pertains to hydraulic fractures in the normal fault regime. It is obvious that horizontal drilling and HF operations disturb the in-situ equilibrium stress conditions inducing stress concentration around the wellbore.



Figure 1.3 Schematic of local stresses acting on shale reservoir [109]

When pore spaces of rock contain fluids, the fluid pore pressure acts in the opposite direction to the in-situ stresses resulting in effective stress acting on the rock being less than the total normal stress. Changes in fluid pore pressure and changes in stresses are coupled which forms the basis of the poroelasticity theory first developed by Biot for three-dimensional problems [110]. Basically, there are two forms of coupling in poroelastic behavior of rocks [111]. One is the rock-fluid coupling in which any change in the applied stress on the rock causes a change in the pore fluid pressure. Second is the fluid-rock coupling in which any change in pore fluid pressure causes rock deformation. Also, the two forms of coupling are assumed to occur instantaneously [110,111].

Karl Terzaghi [112] was perhaps the pioneer to introduce the concept of effective stress in the context of unconsolidated soils. His mathematical description was based on his one-dimensional laboratory experiments. Biot, however, extended the theory to threedimensional anisotropic space and considered Terzaghi's theory a special case of his theory [110]. The effective stress tensor is expressed as follows in indicial notations:

$$\sigma'_{ij} = \sigma_{ij} - \alpha p \delta_{ij} \tag{1.1}$$

In Eq. 1.1, σ_{ij} is the total stress tensor, σ'_{ij} the effective stress tensor, p is the pore pressure, and δ_{ij} is the Kronecker's delta ($\delta_{ij} = 1$ for i = j and $\delta_{ij} = 0$ for $i \neq j$ where i, j = 1, 2, 3). The coefficient of pore pressure, α , is known as the Biot's coefficient which has a value of one in Terzaghi's effective stress formulation [110,112].

Biot introduced the term 'variation of fluid content' defined as the change in fluid content (water in his work) per unit volume of soil represented by the symbol ζ [110]. This quantity must be viewed in the sense of fluid volume transported into or out of storage. The complete linear poroelastic response to volumetric deformation is characterized by three material constants [111]. The basic set is comprised of drained bulk modulus, poroelastic expansion coefficient, and unconstrained storage coefficient. Other constants can be derived using these three basic constants. A fourth constant called the Poisson's ratio (υ) is required when shear stresses are present [111]. Later, the concept of drained and undrained consolidation theory was introduced when Rice and Cleary [113] reformulated the equations of consolidation in terms of more easily measurable parameters.

In the original linear poroelastic theory, it was assumed that the pore volume was saturated with a single fluid type [114]. Biot's theory can be extended to account for thermal, inelastic, and anisotropic cases [115–117]. It is also possible to extend the theory for a porous medium saturated with two fluids each having distinct chemical interactions with the solid skeleton. There have been attempts to extend the theory to partially or variably saturated porous media. These studies have either considered the two-phase mixtures as one average fluid or have not considered chemical interactions of each fluid with the solid skeleton [118–120].

1.2. Scope of the study

As highlighted earlier, various mechanisms are potentially involved in the loss of such huge amounts of fracturing fluid. These mechanisms are divided into (i) entrapment in hydraulically induced micro-fractures, and (ii) water uptake by the shale matrix due to processes like clay hydration, osmosis, and capillary imbibition [71,73–77,80,82,121–124]. The focus of this dissertation is to ascertain the extent of water uptake by the shale matrix and not the entrapment in hydraulically induced micro-fractures. Most of these proposed mechanisms were identified in laboratory-scale experimental studies where their coupled effects were often neglected. It is, however, obvious that these phenomena are chemo-hydraulic and coupled. Taking such multi-physics couplings into account is necessary for gaining profound insights into the problem and developing predictive models for water loss in shales. Moreover, post-HF changes in the stress state cause the water loss problem in shales to be chemo-hydro-mechanical. The mechanical aspects of the problem require existing constitutive models to be extended.

The hydro-mechanical aspect of the constitutive models can be handled by the classical Biot's poroelasticity theory as discussed earlier [110]. However, the capillary influx of fracturing water into the shale gas matrix gives rise to the two-phase flow phenomenon. The redevelopment of the classical Biot's poroelasticity theory due to the presence of a flow of two fluids in the rock's pore space has been attempted from time to time [118,119] by considering the pore space to be occupied by a mixture with averaged properties. Very few studies have attempted to treat the two fluid phases (water, gas) separately [120], but without incorporating other multi-physics phenomena. It is known that in-situ water saturation in shale gas reservoirs can range from 15-50% [125–127]. The difference in chemistries between the fracturing and in-situ waters gives rise to several chemical phenomena (e.g. hydration of water molecules, osmotic flow of water, swelling of clay

minerals). Therefore, with the ever-increasing demand for more realistic models, there is a need to develop a two-phase flow chemo-poroelastic constitutive model to characterize the water loss problem more realistically especially in the shale matrix.

1.3. Objectives

The primary objective of this dissertation is to develop an advanced theoretical and experimental understanding of the water uptake by shale matrix. The shale matrix in this dissertation is defined as that part of the rock that is enclosed by hydraulically induced micro-fractures (or natural fractures) from one or more sides. As part of the objective, the aim is to propose a novel fully coupled two-phase chemo-poroelastic constitutive model. Such a model can help in predicting the role of in-situ stresses, clay-fluid interactions, and simultaneous water-gas flow in the micro-mechanical behavior of shale matrix post hydraulic fracturing. This overall objective is achieved by addressing the following:

- Significance of micro-scale measurements to facilitate constitutive modeling,
- Development of a non-equilibrium thermodynamics-based two-phase chemoporoelastic constitutive model,
- Extent of hydration induced damage in shale matrix under different stresses,
- Contribution of chemical osmosis and diffusion processes in shale matrix,
- Multi-scale shale wettability and fractal-based petrophysical properties of shales,
- Finite-element modeling (FEM) based solution to the developed chemoporoelastic constitutive model.

1.4. Structure of the dissertation

The dissertation is divided into five core chapters following this chapter. The first presents a micro-scale understanding of the chemo-mechanical processes occurring during hydraulic fracturing. The following chapter describes the development of a nonequilibrium thermodynamics-based fully coupled two-phase damage chemoporoelastic constitutive model. The next chapter describes the system characterization in detail wherein each of the sub-chapters presents a detailed study the outcomes of which help in simplifying the developed constitutive model allowing for simpler numerical implementation subsequently. Finally, a FEM-based solution to the coupled two-phase chemo-poroelastic model is presented in the last chapter before conclusions and future recommendations. The structure is summarized below:

1.4.1. Chapter 2: Micro-scale understanding of rock damage mechanisms post hydraulic fracturing

It is critical to understand the micro-macro link between hydraulic fracturing and the chemo-mechanical process occurring at a hydraulically induced micro-fracture-shale interface. In this chapter, a micro-scale understanding of the shale matrix water uptake has been perceived through a novel experimental and measurement system. Such understanding paves way for the further techniques adopted in the thesis to achieve the objectives.

1.4.2. Chapter 3: Fully coupled two-phase multi-physical model development

There is a critical need to understand the extent of water uptake by shale matrix to be able to decipher the water loss problem in shales. For this, it is incumbent to incorporate the different multi-physical processes occurring therein. In this chapter, a fully coupled twophase damage chemo-poroelastic constitutive model has been developed using the principles of non-equilibrium thermodynamics and continuum mechanics. A complete and detailed workflow arriving at the final field equations has been presented.

1.4.3. Chapter **4.1:** Hydration-induced and stress-restrained coupled damage evolution of shale

The role of varying stress states on hydration-induced micro-structural alteration (damage) in the shale matrix is delved into in detail in this chapter. With the use of the X-ray micro-computed-tomography (micro-CT) technique, hydration-induced micro-fractures have been characterized and the effect of different stresses thereof has been studied.

1.4.4. Chapter 4.2: Chemical osmosis and diffusion processes in organic-rich shales The presence of different types of clay minerals in shales causes it to behave as a semipermeable membrane. In this chapter, the membrane efficiency and swelling potential of the shale matrix have been investigated using the pore pressure transmission tests (PPTT). The results demonstrate that for the specific shale sample used in this dissertation, chemical osmosis (or swelling potential) is negligible. Further, to distinguish between water and oil diffusive behavior in shales, neutron-CT has been used to provide novel insights. Such insights highlight the subtle effect of configurational diffusion in dictating the diffusive behavior of water and oil based on pore accessibility.

1.4.5. Chapter 4.3: Two-phase flow characterization in clay-rich rocks: a fractalbased approach

Shale matrix petrophysical properties have been adversarial due to its low permeability and complex mineralogy and heterogeneity. In this chapter, the flow-inhibiting clay minerals that cause deviations from current fractal-based capillary pressure and relative permeability in shales was addressed and a correction was proposed based on sound physics. The correction showed significant potential by matching appreciably well with experimental data.

1.4.6. Chapter 5: Numerical simulation of the developed constitutive equation and sensitivity analysis

In this chapter, the judgements from the system characterization (Chapter-4) have been implemented and consequent adjustments have been made to the model. Next, a solution is obtained using the COMSOL Multiphysics FEM platform. Sensitivity analysis is also performed and discussed.

Chapter 2. Micro-scale understanding of rock damage mechanisms post hydraulic fracturing

The contents of this chapter are from "A novel experimental system for measurement of coupled multi-physics-induced surface alteration processes in geomaterials" in *Measurement*, DOI: 10.1016/j.measurement.2020.108211.

2.1. Introduction

2.1.1. The need for micro-scale investigations

As discussed in detail in Chapter 1, shale reservoirs are produced through horizontal wells with HF stimulation (Figure 2.1 (i)) [128] wherein a lot of water is used and lost [67]. Several contradictions were also highlighted in Chapter-1 relating to previous studies that investigated the shale water loss problem. The most notable reason for such uncertainty can be due to the failure to incorporate the in-situ stresses in laboratory investigations especially at micro-scale [129].

It is known that hydraulic fractures propagate along with the maximum in situ stress, hence open in the direction of minimum horizontal stress [130]. At the matrix-fracture interface (both main and secondary induced hydraulic fractures) (Figure 2.1 (ii)-(iii)), different chemo-mechanical phenomena occur such as water or ion-exchange reactions, clay swelling, and micro-cracking of the matrix, all of which contribute to the water uptake by the matrix [82,129]. In-situ stresses play a key role here; therefore simulating in-situ stresses on the sample is critical to understand the extent of such subsurface phenomena in the laboratory (Figure 2.1 (iv)-(vi)). We therefore designed and built the first generation of micro-shear cell interferometry to investigate water loss in shales under actual subsurface conditions – especially the in-situ stresses. Such investigations are also

significant in better guiding the development of constitutive models to represent the observed physical phenomena.



Figure 2.1 Schematic depicting (i) hydraulic fracturing in a shale reservoir under in-situ stresses, (ii)-(iii) zoomed versions of the phenomena occurring at shale-fluid interface,

(iv)-(v) simulation of subsurface phenomena in the shear cell, and (vi) capturing the

phenomena with an interferometer (Source: own work [131])

2.1.2. The micro-macro link in hydraulic fracturing

There has been significant research attention over the past few decades to the measurement of micro-scale processes controlling macro-scale phenomena in shales due to the pivotal role that energy-bearing shales play in fulfilling the global energy demand. This has pushed scientists to fervidly observe, characterize, model, and investigate such processes through new and innovative measurement designs, techniques, and procedures [132,133].

Micro-scale measurement techniques have been in practice for more than fifty years [134,135]. These measurements are often complemented by high-performance visualization equipment (e.g. microscopes) allowing for in-situ observation, quantification, and analysis of surface alteration processes e.g. fluid flow through porous surfaces and various fluid-geo-materials interactions [136]. Recent efforts to simulate subsurface conditions in micro-scale measurements include pore geometry employment based on Voronoi tessellations [137], new forms of etching [138,139], or use of true granular materials [140,141]. More recently, measurement systems capable of withstanding high flowing pressures and system temperatures [142,143] have been developed. However, despite such advancements, these measurement systems are limited to decoupled surface alteration investigations such as chemical (e.g. dissolution) and hydraulic (e.g. flow) phenomena [138,139,143,144]. The micro-scale investigations [129,145,146] lack in their implementation a critical parameter: the in-situ stress acting on subsurface geo-materials. According to a thorough literature search, there seems to be no micro-scale measurement design that integrates into its operation the simultaneous multi-physics coupling effect of mechanical, chemical, and thermal loading at high spatial/vertical resolution. This is significantly important for unconventional shale reservoirs where rock mechanics coupled with other physical processes (thermal, hydraulic, and chemical) is of particular importance.

A novel shear cell measurement setup coupled with interferometry was thus designed for observing actual geo-materials under in-situ isotropic or anisotropic (shearing) stress conditions while simultaneously being exposed to different fluids (gases and liquids). It can also be used for materials other than geo-materials such as metals, fibres, and chemical catalysts. Such a novel design capable of withstanding high pressures allows measuring coupled chemo-mechanical surface alteration phenomena. Examples of such phenomena include effects of fluid flow over a geo-material, crystalline, or osmotic swelling due to geo-material-fluid reaction, capillary imbibition of fluids into the geomaterial, and its consequence on micro-structure. The setup can be used to measure and visualize surface alteration (e.g. reaction kinetics) experiments under any type of microscopes depending on the application. To serve its purpose, we chose to visualize (with high spatial and vertical resolution using light interferometry) some critical chemomechanical surface alteration processes that occur in shales during hydraulic fracturing (HF). Several example applications have been performed in this study to show the versatility and applicability of the newly designed system and gain an understanding of the physical processes involved in shale water uptake for later constitutive modelling.

2.2. Materials and Methods

2.2.1. Sample preparation

The shale used in this thesis is an organic-rich shale extracted from a depth of 3012 m from the on-shore Phanerozoic sedimentary Perth Basin stretching for over 1000 km along the Western Australian coastline [147,148]. It is an extended rift with half of the basin onshore and covering around 100,000 km² in total [149]. The basin is shaped as series of echelon troughs due to faulting and rifting. The thickest sedimentary section of the basin exceeds 15,000m in thickness and belongs to an age range of Ordovician to Pleistocene [147]. The samples used in this Chapter and the rest of the dissertation were extracted from the Irwin River Coal Measures formation (Figure 2.2).



Figure 2.2 Northern Perth basin stratigraphy [148,150]

The organic carbon content was 2.85 wt. %, as measured by LECO CN analysis whereas the mean vitrinite reflectance (Ro), was 0.52 % with a standard deviation of 0.05 %. The major mineral phases of the sample were obtained through X-ray diffraction (XRD) analysis. The main clay minerals present in the shale were illite (28.2 wt. %), kaolinite (9.6 wt. %), and chlorite (9.6 wt. %). Other minerals included quartz (27.1 wt. %), muscovite (14.3 wt. %), albite (9.3 wt. %), and pyrite (1.9 wt. %). Pore size distribution (PSD), measured by mercury intrusion and nitrogen adsorption, along with other properties for this sample, have been reported previously [151].

In this study, the shale samples were exposed to deionized (DI) water and ionic (salt) solutions (NaCl and CaCl₂ at 0.1 and 0.5 M concentrations) at different stress states. Deionized (DI) water (18.2 M Ω ·cm resistivity at 25°C) was collected from the Millipore Milli-Q water purification system. The salts used to prepare the ionic solutions (NaCl, CaCl₂,) were procured in powder form from Chem-Supply Pty Ltd Australia (purity = 99.7 wt. %). All ionic solutions were prepared by adding known amounts of respective salts in one litre of de-aired DI water and magnetically stirring it for several hours.

The sample to be tested must exactly fit in the designed cell so that the hydraulic rams and platens are uniformly engaged against the sample edges and end surface effects can be minimised. The designed cell can accommodate samples with dimensions of 10 mm x 10 mm (length x breadth) and up to 5 mm thickness. The sample was cut into proper dimensions using the Gemini Apollo Ring Saw. The edges and surfaces were polished down to precise dimensions using a 3D-printed mould. Polishing was performed stepwise up to 1200 grit sandpaper with polishing time kept constant (3 mins) for all samples to ensure surface roughness consistency. After preparation, the sample was vacuumed and oven-dried at 105°C for 24 hours. It was then allowed to reach room temperature (25°C) in a desiccator before placement in the cell.

2.2.2. Interferometry

2.2.2.1. Sampling area and fluid exposure

A 2x lens was used in the interferometry microscope which allows scanning of a 2.4 x 1.8 mm^2 area lying in an x-y plane. The measured heights (z(x, y)) at each pixel hence produce a 3D representation of the scanned surface. The vertical resolution is 0.05 µm which allows identifying the surface changes precisely e.g. due to swelling at the

submicron level. The on-plane (x-y) resolution is $\sim 1.5 \ \mu m$ i.e. 20x lens is available for higher resolution.

Initial surface profile measurements were performed before fluid exposure. Here, the shale sample was exposed to de-ionized (DI) water and different ionic solutions. After exposing the sample to the fluid for the desired period, the difference in surface profiles before and after exposure to fluids was analysed. The same procedure was followed for measurement at both unconfined and confined states. Although the experiments were designed to measure static fluid-sample interactions, dynamic measurements can also be performed (at higher pressures) by allowing a continuous flow of fluid over the sample through the back-pressure regulator.

2.2.2.2. Surface profile parameters and data filtering

The three-dimensional surface profile measurements give an enhanced understanding of the in-situ surface profile changes which is not possible with 2D measurements (as in simple optical microscopes). Different areal parameters can be used, depending on the application, to characterize the changes occurring in the surface texture. Based on the focus of this study, we used the profile amplitude parameters S_a and S_z which were calculated after each measurement using the Bruker Vision64 software. Both are dimensionally equivalent to length. S_z on a sampling area (A) is the sum of the absolute values of the largest peak ($max{z(x, y)}$) and the lowest pit ($min{z(x, y)}$) heights measured from the mean plane. S_a on the sampling area is the arithmetic mean of the absolute value of the measured height and is given by:

$$S_{a} = \frac{1}{A} \iint |z(x,y)| dxdy$$
(2.1)

For appropriate analyses of surface profiles, it is necessary to remove any noise or outliers, if any, from the measured height data using appropriate mathematical filters. Visual inspection of the raw data was done for unrealistic spikes or for an intolerable percentage of missing data. Caution was taken before applying any filter as the unnecessary application of filters on measured data poses a risk of losing sensitive data related to the submicron changes in surface texture e.g. surface swelling due to clay.

2.3. Shear cell system

2.3.1. Design of the system

The shear-cell was fabricated out of stainless-steel grade 316 (Figure 2.3 (top)). The stainless-steel body ensures that the cell can withstand the high-pressure required for extreme testing conditions. The cell is essentially a cube shape box having space in the middle to host the sample. The cell has two hydraulic rams that pass through the sidewall of the cell into the cell body and push the respective steel platens against the in-sample using hydro-electric pumps. The opposite sides of the rams are fixed boundaries thus maintaining constant stress on the sample in the respective direction. Miniature-Viton Orings are installed between each of the hydraulic ram heads and steel platen to prevent the leak from the side of the rams' heads to outside the cell. To prevent corrosion and wearing of fittings, hydraulic oil is used as the confining fluid although other fluids can also be used. Hydraulic oil is pushed into the two hydraulic rams using two different highpressure pumps (Teledyne ISCO Series D) allowing for both isotropic and anisotropic (shearing) stress conditions. The in-place shale is sheared by maintaining different stresses in each direction through each of the two pumps. In other words, the sample is sheared in a particular direction by applying a higher pumping rate or pressure on one of the two hydraulic rams. It is noted that the pump can control the pressure rate meaning that constant load boundaries can be imposed on the sample. The connections between the pumps and the cell are made up of polyether ether ketone (PEEK) tubes (0.6 mm ID, 1.6 mm OD) for easy flexibility and corrosion resistance. Accessorial valves and fittings

are made up of high-pressure stainless steel (Swagelok). High-precision Keller digital pressure transducers are used to monitor the applied stresses which are connected to a computer for data recording purposes. Once the geo-material sample (shale herein) is in place, a scratch-proof sapphire glass with a flat O-ring is screwed against the sample top for visual observations by the optical measurement device through this window. Two other ports are fabricated in the body of the cell for fluid circulation i.e. injection and drainage. A third Teledyne ISCO Series D pump is used to pressurise and circulate the fluid over the shale sample in place. If low-pressure circulation is required; the downstream port is open to the atmosphere and fluid is injected from the upstream port into the sample. Otherwise, for high-pressure applications, the downstream valve is closed or if fluid circulation under high pressure is required, a back-pressure regulator (BPR) is installed on the downstream port to control the required pressure under circulating flow with a constant rate. Thus, the fluid is kept exposed to the sample under applied isotropic or anisotropic stresses for the desired period. If a corrosive fluid injection is of interest, a floating piston chamber (transfer cell) is placed in the injection line where corrosive fluid can be hosted and injected into the sample. All such details are highlighted in Figure 2.3. Spatial, vertical, or micro-structural changes to shale sample due to fluid exposure can then be analysed using any desired visualization equipment. In this study, a green light interferometer was used the details of which are discussed in the next section.



Figure 2.3 Schematic of the shear cell (top-left and top-right) and the complete measurement setup with interferometer (bottom)

2.3.2. Shear cell coupled with interferometry

The surface alteration measurement technique used in this study, interferometry, is a combination (interference) of two same-frequency waves (e.g. light or sound). In such measurements, the paths of two waves are interfered to create interference fringes. In the Bruker Contour GT-K VSI setup used in this study, the recombination of two light beams (which are generated from a single light source using a beam-splitter) is detected and interference patterns are created. Scanning vertically down, elevated points on the sample surface cause interference first. Hence, using these measurements, a surface map is built.

The combination of such height-sensitive interferometry technique with our novel shear cell allows measuring even the submicron-level surface changes e.g. clay mineral swelling on exposure to different fluids, or micro-structural alteration under different confining conditions and fluid exposure. This chapter presents the results of such a submicron process in shale. Moreover, it is emphasized here that any other submicron reactive phenomena especially in geo-materials can be studied under different confining conditions and high fluid pressures using this shear cell with interferometry technique. The complete design setup is shown in Figure 2.4.



Figure 2.4 Shear cell placed under the interferometer

For effective measurements of the surface topology through any transmissive medium covering the sample surface such as plastic or glass, a Through Transmissive Media (TTM) module is required. Measurements through a transmissive medium without the TTM module installed are inaccurate, dispersed, and aberrated. It is also highly challenging, without it, to find the location of best focus (high-intensity fringes) which serves as the starting point of surface height measurements. TTM module thus facilitates the insertion of a compensation glass of the same thickness and material as that covering the sample (Figure 2.5) which allows additional illumination on the sample surface.





Figure 2.5 (i), (ii) TTM module for light compensation, and (iii) schematic of the

compensation glass functioning

2.4. System assessments

2.4.1. Calibration and quality-check tests

The interferometer was calibrated with Bruker's provided atomic force microscopy (AFM) mirror chips which are highly reflective, smooth, and flat materials for which the locating of fringes can be readily identified. The measurement on the AFM chip confirmed the accuracy and reliability of the interferometer as the measured step heights matched well with the factory-configured heights. For illustration purposes, the step heights on the AFM chip are presented across two yellow lines drawn on Figure 2.6 (i) and (ii); each in x- and y- directions respectively. The measured height profiles are shown in Figure 2.6 (iii).



Figure 2.6 (i) Projected 2D profile of AFM chip with its (ii) respective 3D profile, and (iii) x- and y- profiles of yellow lines showing step-heights

To ensure that the interferometry measurements of the shale samples were also precise, the roughness parameter S_a values calculated from interferometry and atomic force microscopy (Bruker BioScope CatalystTM AFM) of the same shale sample substrate (polished up to 4000 grit for AFM compatibility) were compared. Bruker BioScope CatalystTM AFM can scan a maximum area of 90x90 μ m² with a maximum S_z of ~7.5 μ m. The shale sample substrate was first scanned at seven different 90x90 μ m² regions under the AFM followed by several scans under the interferometer for an area of 2.4x1.8 mm² which contained the seven AFM regions. Due to difference in measurement scales, surface roughness (S_a) from these techniques must be compared cautiously. It has been noted that as the vertical scan length increases (which gives the measure of S_z), the average surface roughness (S_a) increases [152]. This was also observed for the shale substrate (Figure 2.7). The seven smaller regions scanned by AFM gave varying S_z within those regions. Several scans of the substrate were made under the interferometer where the vertical scan length was varied from $4 \,\mu m$ to $10 \,\mu m$. As seen from Figure 2.7, within the vertical scanning range of the AFM (<7.5 μ m), the cluster of AFM S_a values (black squares) lay very close to the S_a values from the interferometer (red dots). The difference was obviously due to the different spatial scanning areas of the two techniques. Nonetheless, the accuracy of the non-contact interferometer technique to measure surface roughness could be confidently affirmed. An example of an AFM image and the shale sample interferometry image is shown in Figure 2.8. The other six AFM scans are shown separately in in Figure 2.9.



Figure 2.7 S_a vs. S_z for AFM and interferometry scans



Figure 2.8 (i) 3D surface profile of 4000 grit polished shale sample measured with interferometer, (ii) 3D surface projection of a 90x90 μ m² region on the same sample

with AFM



Figure 2.9 3D AFM surface projections of other six 90x90 μm^2 regions on the same sample

2.4.2. Fluid exposure and clay swelling at unconfined condition

The designed shear cell was used to measure surface swelling of shale on exposure to low and high concentrations of monovalent and divalent ionic solutions i.e. NaCl and CaCl₂ at unconfined stress conditions. Since the only minerals in the shale sample with a tendency to swell are clay minerals, the observed surface topology changes of the shale surface can be considerably assumed to be an effect of clay-fluid geo-chemical interaction. Different clay minerals exhibit different swelling characteristics. Illite, which is the dominant clay mineral in our shale, swells more than kaolinite, the second dominant clay mineral in this specific shale. Such clay swelling behaviour is of fundamental importance in the impairment of shale permeability when exposed to the hydraulic fracturing fluid. An example of 2D surface topology projections is shown in Figure 2.10 for before and after exposure to 0.1M NaCl. Different colours (see colour bar) show the height variation of the sample surface at each pixel. However, such 2D projections provide vague qualitative assessment and are inadequate for vertical surface swelling quantification although they can be useful for the realization of spatial micro-structural alteration. Thus, a quantitative statistical analysis of the measured surface height data was performed. As explained earlier, two important profile amplitude parameters S_a and S_z were used. Their definitions were discussed in Section 2.2.2.2. S_a is to be used in conjunction with S_z to comprehensively describe the changes in surface topography before, after, or during exposure to different fluids.



Figure 2.10 Example of surface profile (2D) of shale before (left) and after (right) exposure to 0.1M NaCl solution

It is seen from Figure 2.10 that the average surface roughness (S_a) changed after fluid exposure due to the swelling at certain places (which relate to the presence of clay minerals). It was already seen that exposure to 0.1M NaCl caused a significant alteration to the surface topology i.e. swollen regions were easily seen in the after-exposure image through increased heights of those regions (e.g. Figure 2.10 right column). Depending on the location of clay minerals, swelling can occur in pits or at peaks (at a nanometre level). Surface swelling causes an increase in height at the clay mineral regions relative to other non-swollen regions (no increase in heights) thus altering the average roughness (schematically explained in Figure 2.11). The change in average surface roughness corresponds to the average swelling of the surface (plotted in Figure 2.12(i)). For instance, the difference in before (11.56 µm) and after (6.46 µm) S_a values for 0.1M NaCl exposure resulted in an average surface swelling of 5.1µm. This is also affirmed by the increase in S_z value (Figure 2.12(ii)) from 123.93 µm to 134.62 µm which shows that distance between maximum peak and pit increased by 10.69 µm.



Figure 2.11 Conceptual schematic explaining change in average surface roughness (S_a) due to swelling of clay rich regions



Figure 2.12 (i) S_a and (ii) S_z values before and after exposure to 0.1, 0.5M NaCl and CaCl₂ solutions

The minuscule change in S_a (from 1.92 µm to 1.76 µm) did not imply any significant changes to surface topology after exposure to 0.5M NaCl solution. However, despite the insignificant change in S_a , a 14.2 µm increase in S_z (from 119.74 µm to 133.94 µm) was observed. This signified that some regions on the surface may have experienced swelling increasing the pixel height at that region. However, when complemented by overall roughness S_a it was concluded that no significant swelling of the overall surface occurred. Similarly, on exposure to 0.1M CaCl₂, S_a decreased by only 0.92 µm (from 10.78 µm to 9.86 µm). Also, there was no significant increase in S_z (from 126.66 µm to 126.92 µm) which implied that no significant swelling of the surface occurred. On exposure to 0.5M CaCl₂, however, a slight increase in S_a (from 16.04 µm to 17.27 µm) was observed. With the negligible increase in S_z (from 126.78 µm to 127.9 µm) it can be implied that change in S_a was due to both peak and pit height changes that increased the average roughness of the surface but cause no net change in the distance between the deepest pit and highest peak i.e. S_z .

The observed surface topology changes of the shale surface are an effect of clay-fluid geo-chemical reactions. Clay minerals possessing a net negative charge adsorb Na⁺ and Ca²⁺ cations giving rise to an electrical diffuse double layer (DDL) [153]. The DDL thickness is lower for divalent cations than for monovalent cations [22]. Also, a higher ionic concentration causes a reduction in DDL thickness due to the abating of the osmotic process [22]. Thus, the observed changes in surface topology were the highest for 0.1M NaCl exposure since it exhibits the highest DDL thickness as well as induces the highest osmotic uptake Na⁺ ions. This effect is reduced leading to lower swelling (due to reduction of DDL thickness) at higher concentration (i.e. 0.5M NaCl) and almost negligible for divalent ionic solution (0.1M and 0.5M CaCl₂) exposure. Such adsorption along with ion-exchange (with the clay inter-layer cations) phenomenon contribute to swelling. In addition to adsorption, ion-exchange processes are simultaneously prevalent both at the surface-exposed clay minerals as well as those present in the pores. The cations along with the associated water diffuse into the pores with time due to capillarity forces and react with the pore-coating clay minerals. Compared to Ca²⁺, lower hydration of Na⁺ implies less associated water molecules are transported with the ion [154]. In nonsmectite clays, such as in this study (illite), surface alteration due to associated water is less prevalent as compared to that caused by the specific cation-clay behaviour. Hence, in general higher surface alteration is seen for Na^+ than Ca^{2+} .

2.4.3. Fluid exposure and clay swelling at confined condition

The coupled effect of chemo-mechanical processes in clay-rich shale samples under stresses was studied by exposing the shale samples to DI water under unconfined and different stress conditions. Two stress scenarios were investigated i.e. isotropic confinement of 4.1x4.1 MPa (600x600 psi) and shearing stress of 6.2x4.1 MPa (900x600 psi). DI water exposure time was six hours for each of the tests. Micro-structural alteration due to fluid exposure is a spatial phenomenon rather than vertical and hence 2D-3D projections of the sample surface aids in identifying such alteration.

For unconfined DI water exposure on these tested shale samples, dynamic measurements conducted every 1.5 hours showed that average surface swelling was insignificant until after five hours of exposure e.g. S_a and S_z did not change significantly (Figure 2.13). Slightly decreasing S_a values and slightly increasing S_z values implied very little average swelling of the overall surface until approximately 5 hours of exposure.

Under isotropic confinement (4.1x4.1 MPa or 600x600 psi), it was observed that DI water caused a minimal micro-structural alteration to the shale sample even after 6 hours i.e. the acquired surface was identical before (left column, Figure 2.14(i)) and after exposure (right column, Figure 2.14(ii)). However, on exposure to DI water under shearing stress (6.2x4.1 MPa or 900x600 psi), a significant micro-structural alteration was evident in the shale within 6 hours i.e. the acquired surface before DI water exposure (left column, Figure 2.15(i)) changed significantly after exposure (right column, Figure 2.15(ii)) due to the combined effect of shearing and DI water-shale interaction. The exposure time of six

hours was sufficient under shearing conditions for DI water to cause rapid microstructural changes of the clay-rich shale [155].



Figure 2.13 Dynamic S_a and S_z measurements for DI water exposure



Figure 2.14 Surface profiles before (left) and after (right) exposure to DI water under isotropic confinement


Figure 2.15 Surface profiles before (left) and after (right) exposure to DI water under shearing confinement

2.5. Discussion

Clay minerals' hydration (adsorption of water) causes the generation of repulsive stresses that act against the applied (in-situ) stresses [136,156]. These repulsive hydration stresses are easily able to create new micro-fractures under unconfined conditions with the caveat of prolonged exposure [157,158]. This will also be corroborated in subsequent chapters (e.g. Chapter 4-1). However, at confined conditions, the hydration stresses must be strong enough to overcome the counter-acting external stresses to cause significant microstructural alteration i.e. an additional caveat of overcoming external stresses is necessary for the creation of micro-fractures. In addition, the external stresses cause the pre-existing micro-fractures (if any) to close thus reducing the water infiltration into the sample. The observed negligible alteration of the shale (at least at micro-scale) under isotropic confinement implies that the generated hydration stresses are less in magnitude than the applied 4.1 MPa (600 psi) confinement. This has been further confirmed in Chapter 4-1 by solving the linearized Poisson-Boltzmann equation [159] to give the repulsive stresses generated due to hydration of negatively charged surfaces like those of clay minerals.

The observed microstructural alteration of shale due to DI water exposure under shearing is explained with the help of the linear Mohr-Coulomb failure envelope [160,161] (Figure 2.16). The Mohr-Coulomb failure criterion is given by $\tau = c + \sigma' \tan \phi_a$, where τ is the shear stress, c is cohesion (rock's inherent shear strength), σ' is the effective normal stress, and ϕ_a is the angle of internal friction [162]. According to this criterion, rock failure occurs when the semicircle connecting the minimum (σ'_1) and maximum (σ'_3) effective stresses intersects the failure envelope (black line in Figure 2.16). However, the active minimum and maximum horizonal stresses before and after fluid exposure are not expected to change significantly due to hydration swelling. Hence, the only way the rock can fail (causing microstructural alteration) is due to the reduction in the rock's shear strength due to water adsorption [163]. This strength decrease is exhibited by the lowering of the failure envelope (red line in Figure 2.16) with reduced cohesion (c') where it intersects with the semicircle causing failure. This emphasises that reduction in rock strength by water is the predominant process in microstructural alteration. As explained before, the hydration-induced stresses are significantly smaller than in-situ stresses and therefore will not contribute to failure by modifying the local stresses. Reduction of strength on the other hand can readily cause failure [164,165]. This failure (creation of micro-fractures) entraps water and causes fracturing fluid loss in shales (schematically depicted in Figure 2.17). It is also noted that the effect of water uptake on internal friction is considered negligible [162,166]. These observations are significantly important as they can assist with the proper physical formulation of the constitutive equations.



Figure 2.16 Schematic of a representative Mohr-Coulomb failure envelope (Source:

Own work)



Figure 2.17 Schematic showing micro-structural alteration under shearing causing water loss in shales (Source: Own work)

An important point to consider is that for the acquisition of accurate interference images, fringes (interference patterns) become challenging to detect as the thickness of the cover glass or the liquid under it increases. There exist an optimum water thickness and cover glass thickness that generates strongly contrasting fringes making the data very accurate. This is inherent because no liquid compensation can be inserted into the TTM module. The thickness of the compensation optic inside the TTM module needs to be optimally chosen to compensate for both the cover glass and the liquid under it. In this study, the best fringes were observed for a 0.25 mm thickness sapphire cover glass. This thickness hinders the capability of the shear cell to operate at very high internal fluid pressures for injecting fluids. As mentioned, however, if the right combination of glass thickness and the fluid is found, then thicker glasses can be used for any specific system.

2.6. Conclusions

The focal objective of this study was to use the shear cell coupled with interferometry measurement design to understand the micro-scale damage mechanisms occurring in the shale matrix on exposure to HF fluid. Such understanding will aid in developing accurate and representative continuum-scale constitutive models. The application of the measurement system was demonstrated through surface alteration at a sub-micron scale due to clay-fluid exposure at unconfined and clay-fluid exposure at confined conditions. This gave insights into what exactly happens subsurface at the shale-fluid interface where in-situ stresses are acting.

Using the designed shear cell coupled with interferometry measurements, the following understanding was gained which will play a significant role in developing the constitutive model for the shale water loss problem (Chapter 3):

1) Hydration generated stresses in the specific sample are not significant to induce observable micro-fractures on their own even with highly clay-reactive fluids such as DIW.

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2) Isotropic stresses on the sample further suppress the hydration stresses and largely inhibit the creation of large (observable and detachable) micro-fractures.

3) The main cause of micro-structural alteration is the reduction of rock's shear strength due to fluid exposure mostly in presence of shear stress. This causes significant micro-structural alteration aided by the direction of shearing stresses.

Chapter 3. Fully coupled two-phase multi-physical model development

3.1. Introduction

3.1.1. Constitutive modelling

A mathematical relation between two or more physical quantities is defined as a constitutive equation [167]. For the formulation of such relations, material-specific coefficients are required which are also known as material constants. The first constitutive equation was established by Robert Hooke for elastic materials [168]. He observed that the elongation of different types of springs and the weight attached to them are directly proportionate. Such observation led to the establishment of Hooke's law for elastic materials which is a linear relationship between the stress and strain therein. More than a century later in 1807, Thomas Young defined a unique proportionality constant between the stress and strain which today is known as Young's modulus [169]. Similarly, viscosity is the proportionality constant for the constitutive relation between applied stress and rate of fluid shear strain, and permeability is the proportionality constant between applied pressure (or head) gradient and fluid flow, and so on. Often, such constitutive equations are combined with momentum, mass, and energy balance laws to investigate the physical response of materials under any perturbations. Such a combination is used to predict material responses which can be termed constitutive modelling. Constitutive equations are relevant in several engineering applications especially for the numerical modelling of underlying phenomena [120].

3.1.2. Approach to constitutive modelling

There are usually two approaches to constitutive modelling. One is the theoretical approach, which is based on first principles, and the other is the phenomenological approach based on phenomenology [170]. The first principles are usually established physical laws such as Maxwell's electromagnetic wave equations or the three laws of

Newton. The phenomenological approach, however, uses simple mathematics to relate an observed phenomenon (e.g. from experiments) to its cause without discerning the fundamentals [171]. Due to the underlying mechanisms of material responses not being fully understood or being complex to implement, a combination of theoretical and phenomenological approaches can lead to the efficient development of constitutive models.

It is believed that there is no sharp distinction between the two approaches and the boundary between them can be relative e.g. the Fourier's heat conduction law itself has an empirical basis [170]. Similarly, the problem of poroelasticity can be approached in either way. It can be assumed empirically that the deformation of a single-phase saturated porous medium is related to both stresses and pore pressure as observed. The constitutive equations can then be derived based on this assumption. This was the approach used by both Terzaghi [112] and Biot [110]. Alternatively, based on the thermodynamics laws, the underlying physics of fluid-solid interaction can be invoked to arrive at Terzaghi's or Biot's constitutive equations. The phenomenological approach was usually preferred for the convenience of numerical modelling. Both approaches result in the same final equations with proper simplifications to the theoretical basis. With the advancement in numerical discretization and modelling techniques, the criteria to choose between the two approaches lies in the ease with which more influencing coupled effects can be included in the constitutive model. In this regard, the theoretical approach has proven to be more robust [172].

3.1.3. Principles of continuum mechanics applied to poroelastic media

Stress is defined as the force acting on a unit area of a surface. Based on the concept of a continuum, this definition can be applied to a point in the interior of a body as a second-rank symmetric tensor which is known as the Cauchy stress tensor (σ_{ij}). The stress is

then a function of space and time within a solid body. This concept of stress at a point is more complex for porous media. Porous media are highly heterogeneous at the actual pore-scale where the solid is discontinued by void spaces (pores) within short distances leading to rapid variation of stresses [170]. To overcome this, it is more practical to interpret stresses and deformation averaged over a representative elementary volume (REV) which contains the point of interest. For smoothness and stability of the averaged quantities, a REV is typically chosen to be one to two orders of magnitude greater than the smallest pore size [170,172]. Due to the presence of fluid in pores, the total stress on a porous medium is divided into solid and fluid stress components. Fluid stress, however, is simply represented by a scalar called the pore pressure (p) based on Pascal's law and Newton's law of viscosity [170]. This leads to the relation:

$$\sigma_{ij} = (1 - \emptyset)\sigma_{ij}^s - \emptyset p \delta_{ij} \tag{3.1}$$

where σ_{ij}^{s} denotes the stress on the solid part, \emptyset is the porosity of the REV, and δ_{ij} is the Kronecker's delta. The term containing the pore pressure (*p*) is subtracted due to the sign convention that compressive stress is positive. It is apparent that σ_{ij}^{s} is not a measurable quantity, unlike the pore pressure. Similarly, the deformation of a porous medium is expressed in terms of strain or displacement. The deformation of a porous medium is defined by the displacement of the outer surface of the REV. As per the principles of solid mechanics, the displacement vector (\vec{u}) can be used to define the strain tensor (ε_{ij}) [170]. As is the case for stress, strain too has two components of a solid strain and a fluid strain. Since fluid strain is not an observable quantity, Biot introduced the variation in fluid content (ζ) defined as the amount of fluid entering the REV per unit volume of the REV [110]. If the fluid escapes from the REV, ζ becomes negative.

For a linear isotropic elastic material, stresses (σ_{ij}) and strains (ε_{ij}) are linearly related through specific material constants that serve as proportionality constants. As an example, Young's modulus (*E*) is the proportionality constant between uniaxial stress and strain and bulk modulus (*K*) is the proportionality constant between average normal stress and volumetric strain. Similarly, shear modulus (*G*) is the proportionality constant between torque and angle of twist. An interesting note is that such material constants are not all independent. In fact, an isotropic material can be defined by only two independent constants using which the rest can be derived [173–175]. Hence, based on Lamé's formulation it can be shown that for linear isotropic elastic materials the stress-strain relation is given by:

$$\sigma_{ij} = \lambda tr(\varepsilon) \delta_{ij} + 2\mu \varepsilon_{ij} \tag{3.2}$$

Where λ and μ are the two Lamé's material constants and tr is the trace function. It can be further shown that the following relations hold between Lamé's constants and other engineering constants (here v is the Poisson ratio):

$$\lambda = \frac{2Gv}{1 - 2v} = K - \frac{2G}{3} = \frac{Ev}{(1 + v)(1 - 2v)}$$
(3.3)

$$\mu = G = \frac{E}{2(1+v)} = \frac{3K(1-2v)}{2(1+v)}$$
(3.4)

Hence, the constitutive equation can be written in terms of any two material constants. For instance, in terms of *G* and *K* the constitutive equation becomes Eq. (3.5) and in terms of *E* and *v* becomes Eq. (3.6) respectively.

$$\sigma_{ij} = \left(K - \frac{2G}{3}\right)\varepsilon\delta_{ij} + 2G\varepsilon_{ij}$$
(3.5)

$$\sigma_{ij} = \left(\frac{Ev}{(1+v)(1-2v)}\right)\varepsilon\delta_{ij} + \frac{E}{(1+v)}\varepsilon_{ij}$$
(3.6)

In poroelasticity, stress (σ_{ij}) and pressure (p) are respectively related to solid (ε_{ij}) and fluid strains. Therefore, the isotropic elasticity equation is extended by realizing that the total (poroelastic) stress is now dependent on both strain (ε_{ij}) and variation of fluid content (ζ) resulting in the following two-way coupled constitutive equations (Eq. (3.7) and Eq. (3.8)).

$$\sigma_{ij} = \left(K - \frac{2G}{3}\right) tr(\varepsilon) \delta_{ij} + 2G\varepsilon_{ij} - A\zeta \delta_{ij}$$
(3.7)

$$p = -A'tr(\varepsilon) + M\zeta \tag{3.8}$$

where A, A', and M are additional material constants [110]. The meanings of these constants will become evident as the chemo-poroelastic constitutive model is derived in Section 3.4 where the concept of linear elasticity is derived from thermodynamics fundamentals and continuum mechanics concepts while simultaneously extending it to develop two-phase, damage chemo-poroelastic constitutive equations for the shale water loss problem. Prior to presenting the development of the constitutive model, a brief review of previous attempts to incorporate two-phase fluid in poroelastic constitutive equations is presented.

3.2. Modified mixture theory for two-phase chemo-poroelasticity

Mixture theories fundamentally describe the interaction of the constituents of a mixture [176–179]. In the jargon of continuum mechanics, a mixture exists when each point is co-occupied by two or more constituents [180]. Based on this assumption the conventional mixture theories exhibit challenges when applied to fluid-saturated porous media because when fluid is removed, a solid material is left instead of a dry porous solid skeleton [180]. The modified mixture theory was introduced to solve this problem. In this theory, dry and fluid-saturated porous solid skeletons were replaced by an equivalent homogenous solid

and an equivalent homogenous liquid [180]. The equivalent solid and liquid act as two unique continua occupying the same point.

The conventional Biot poroelasticity theory was developed for porous media where one fluid occupies all of the pore space [110]. This theory was widely used and extended for single fluid-saturated porous media accounting for chemical, thermal, and plasticity effects [163,172,181,182]. There is an abundance of literature available for single-phase poroelasticity and its extension for varied applications which will not be detailed here. However, a dearth of literature exists even for simple two-phase poroelasticity let alone its extension to other effects. There have been, nonetheless, attempts to generalize the theory to include partial saturation or two-fluid saturation of the pores. Such a realization was made considering the usual existence of two-phase mixtures (gas/water, water/oil, gas/oil) in deeper hydrocarbon-bearing rocks. Also, for shallow rocks close to the atmosphere, pore spaces are often partially saturated i.e. filled by air and water where a general two-phase poroelasticity theory can be useful.

Hassanizadeh and Gray [183–185] made an early attempt to develop constitutive equations for multiphase porous media systems using an averaging procedure. Though rigorous derivation was presented in a three-part series of articles, no solution was attempted for the complex field equations. Gray [186] presented a more rigorous thermodynamics-based constitutive framework for multiphase flow in porous media including interfacial and common line effects. This was, however, not coupled with poroelastic concepts. Schrefler et al. [187] also used the averaging principles to derive constitutive equations for partially saturated poroelastic media and presented a solution using the finite element modelling (FEM) framework. Safai and Pinder [188] formulated poroelastic constitutive equations for unconsolidated soils containing water and air where the air was considered to be at atmospheric pressure. It was reported that obtaining the

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model solution using finite element modelling (FEM) framework was difficult for low water saturations i.e. this solution cannot be used where two-phases have pressure. These constitutive models also did not have chemical coupling effects incorporated.

Heidug and Wong [172] were among some early researchers who derived the singlephase chemo-poroelastic theory based on non-equilibrium thermodynamics and continuum mechanics. Their detailed derivation starting from the first law of thermodynamics to the FEM-based solution of the constitutive equations served as the basis and starting point of countless more constitutive modelling studies. Their approach applied the concept of modified mixture theory to soil and rock problems. The classical mixture theory [176,189] maintains the individuality of the solid and fluid phases. However, it does not offer any information on the interaction between the phases. The method of Heidug and Wong [172], on the other hand, does not distinguish explicitly between solid and fluid phases. It rather assumes a fluid-filled porous rock to be a single continuum which came to be known as the modified mixture theory. Chen and Hicks [190] later extended the concept to develop constitutive equations for an unsaturated rock who also introduced chemical aspects to the modified mixture theory [191]. This approach (used by Heidug and Wong [172]) was different from other coupled modelling studies in rock mechanics which were based on consolidation theories of Terzaghi [112] and Biot [110]. Many complex constitutive models for real-world applications including unsaturated porous media were built based on consolidation theories [192–195]. The issue with consolidation theories is, however, that extending the constitutive equations to incorporate complex chemical fluid-solid interactions becomes challenging [191,196]. This drawback is easily overcome by the modified mixture theory approach [172].

Chemical effects represent an internal coupling phenomenon where the force transfer is not apparent. Although micro-level interactions could be captured with molecular dynamics modelling, such an approach is not feasible to extend the coupling effects to macro-scale [191]. Here, by macro-scale, it is implied that scale at which the hydromechanical coupling occurs. Using non-equilibrium thermodynamics concepts as in the modified mixture theory, the time-dependent chemical-hydraulic couplings effects can be easily incorporated using the concept of chemical potential [172]. The modified mixture theory [172] uses continuum mechanics along with non-equilibrium thermodynamics to establish a link between mechanical and chemical coupling by looking into energy dissipation mechanisms and the time evolution of state variables [172,190]. This approach was used lately to extend the unsaturated poroelastic constitutive equations to incorporate chemical (hydrational swelling, osmosis) and thermal effects [197–201]. The lacking in these studies and others [193,202] is that for unsaturated porous media, the gas phase (air) pressure was ignored, and average pore pressure was used for an averaged fluid mixture. Thus, such an approach again cannot be applied to the shale water loss problem required here. The issue with assuming gas phase pressure to be atmospheric is that it implies the gas phase can flow freely without any resistance. The results obtained without such simplification have been found to differ considerably from the assumption of a passive gas phase in fluid flow simulations [203]. This can be significant where a gas phase (especially for gases other than air) is present which can have a significant change in flow and adsorptive properties with changes in pressure and/or temperature. Therefore, a rigorous modelling framework where gas flow is considered is important especially for hydrocarbon-bearing rocks or for underground construction scenarios where water is displaced by compressed air [204]. Schrefler and Scotta [204] made progress in this regard where two continuity equations for the water and gas phases were used. Efficient numerical stability was portrayed in their study using the various fluid relationships between saturation, capillary pressure, and relative permeability. Most recently, Cheng

[120] developed phenomenological constitutive equations for unsaturated porous media and presented simplified observable relationships between fluid saturation (in the case of partial saturation) and laboratory-measurable constants (in the case of full saturation). For pure mechanical effects, consistency was found between the phenomenological micromechanical approach and the thermodynamics-based variational energy approach. No solution to the constitutive equations was presented but the developed model seemed robust. Although such an approach is appealing towards efficient numerical and engineering applications, it is not easy to extend it to couple other multi-physics phenomena including chemical, thermal, or reaction mechanisms [120]. Hence, there still is a dire need to extend the Biot poroelasticity theory to two-phase flow conditions and to address the shale water loss problem. Therefore, in this dissertation, a non-equilibrium thermodynamics-based framework along with continuum mechanics principles has been utilized to develop two-phase chemo-poroelastic constitutive equations addressing the shale water loss problem. The details of the derivations are presented later in this chapter.

3.3. Continuum damage mechanics

Damage mechanics was first introduced by Kachanov [205]. Since then, rapid progress has been made with damage characterized at all scales i.e. atomic, micro, and macroscales [206]. Any solid material is composed of a unique microstructure. The mechanical behaviour of the material such as strength, stiffness, etc. depends on this microstructure [207]. Observations have shown that a change in microstructure results in the reduction of the mechanical properties (e.g. strength) and can eventually lead to fracturing (failure) of the material. This microstructural change (e.g. micro-cracks or micro-voids) is referred to as damage. Such micro-cracks need not necessarily always cause measurable permanent deformation of the material but at the same time can lead to a significant loss in strength of the material (i.e. elasto-damage or brittle-damage [208–211]). It is the accumulation, growth, and localization of this damage that causes the material to fail.

In continuum mechanics, damage can simply be referred to as the reduction in stressbearing capacity of the material [205,212–215]. To incorporate the distributed microstructural alteration of the material through continuum mechanics, the mechanical effects of the micro-structure must be homogenized and represented as a continuous field macroscopically [211]. This is achieved by using the concept of the representative elementary volume (REV) [216]. This notion where micro-structural deterioration of material is discussed in the framework of continuum mechanics came to be known as continuum damage mechanics or damage mechanics [205,211,213,217]. Today, most continuum thermodynamics-based damage models are inspired by the work of Lemaitre [217] who introduced the concept of strain equivalence and 'effective stress'. He measured the critical damage (at which the material fails) using a direct tensile test and quantifying the reduction in elastic modulus. Later, Le Roy et al. [218] measured damage as the growth of the void area in a uniaxial tensile test which was a more consistent damage evolution law. Dhar et al. [219] further included void nucleation in these models making the evolution more consistent [220].

From a thermodynamics point of view, the principle of local state asserts that a point in a continuum can be described by specific state variables. As mentioned, damage refers to the deterioration of the material's micro-structure. This micro-structural deterioration at a point in the continuum is an internal state and can be represented by an internal variable called the damage variable, denoted by D [211,213]. The damage variable gives a quantitative description of damage at the macroscale. If the discontinuities in the micro-structure are assumed isotropic, then D is simply a scalar. In actuality, D refers to the loss in solid part of the material that bears the stress and hence is defined as:

$$D = \frac{\Delta A_v}{\Delta A} \tag{3.9}$$

where ΔA_{ν} is the void area (that does not contribute to stress-bearing) and ΔA is the planar area. This leads to the concept of effective stress (σ_{ij}^*) i.e. the stress acts on the effective solid part of the material $(\Delta A - \Delta A_{\nu})$:

$$\sigma_{ij}^* = \frac{\sigma_{ij}}{(1-D)} \tag{3.10}$$

It is noted that the effective stress definition herein (as defined by Lemaitre [217]) is linked to the effect of damage on overall stress and should not be confused with the poroelastic effective stress. The conjugate variable to *D* is the elastic strain energy release rate (Y_D) which is described in detail later in Section 3.4.4.3. Scalar damage models are simple as a single variable *D* describes the degradation of the microstructure [205,221]. The damage variable, *D* varies between 0 (for the virgin material) and 1 (for the material which has totally micro-structurally deteriorated). The Cauchy stress tensor for the microstructurally deteriorated material is thus represented by:

$$\sigma_{ij} = (1-D)\sigma_{ij}^* = (1-D)L_{ijkl}\varepsilon_{kl}$$
(3.11)

where L_{ijkl} is the elastic stiffness tensor of the virgin material. Thus, (1 - D) acts as a reduction factor that produces the transformation from the virgin equivalent space to the real damaged space [222]. Damage variable monotonically increases until the material fails such that its time derivative is always increasing ($\dot{D} \ge 0$).

The above-discussed concepts have been used as inspiration in developing the two-phase, damage chemo-poroelastic constitutive model to explain the shale water loss problem. Although the term damage and formulation of continuum damage have been used for chemical-induced damage in this dissertation, the conventional concept of damage is not inferred herein. In fact, micro-cracking is not of significant importance in chemical damage where the loss in material cohesion (strength) prevails. The development of the constitutive model presented subsequently is a thermodynamically consistent extension of previous chemo-poroelasticity models, such as that of Heidug and Wong [172], to two-phase porous media with consideration of chemically induced micro-structural alteration. As and when needed, concepts have been elaborated and detailed in subsequent sections.

3.4. Two-phase, damage chemo-poroelastic model development

The Helmholtz free energy (F) balance is used in the development of the constitutive equations for a two-phase chemo-poroelastic (hydro-chemo-mechanical) gas-water system. Consider a macroscopic region of volume V within the rock matrix having a boundary R. This region contains both solid (grains) and voids. The following simplifying assumptions are initially made:

(i) The rock is isotropic, the deformation of *R* is infinitesimally small, and the conditions are isothermal.

(ii) *V* is significantly larger than the largest pore size of the rock matrix.

(iii) R is attached to the external solid (grains) part of V such that the deformation of the solid matrix is governed by the evolution of R in space [172]. Thus, this boundary is closed to the flow of solid matter while fluid (and/or solute) inflow and outflow are allowed.

(iv) The water phase consists of only one type of solute where water and solute exhibit chemical potentials μ^w and μ^c respectively.

(v) The fluids can be electrolytes however the effect of ionic charge (or current) on their flow is not considered. Hence, chemical potentials instead of electrochemical potentials should suffice.

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(vi) The gas phase does not contain any solute and its adsorption to the matrix is trivial.

(vii) The bulk porous medium consists of two kinds of connected voids: a) pore space filled with freely diffusing water and gas and b) inter-layer surface space occupied with bounded water (e.g. in clays).

(viii) Considering the low amounts of total organic content (TOC) in organic-rich shales, the freely diffusing water and gas are assumed to be present uniformly in the two kinds of pores in organic-rich shales viz. organic pores and inorganic pores.

(ix) The damage is assumed to be only of chemical nature caused by clay swelling. Although the model is derived comprehensively to account for both mechanical and chemical damage, due to the quasi-constant states of stresses during the well shut-in period post hydraulic fracturing, mechanical damage is assumed negligible. Moreover, the water-clay interaction and consequent swelling are assumed to be instantaneous or very fast compared to the movement of fluids in the rock. Although this maintains the local physio-chemical equilibrium, the mechanical equilibrium assumption is not invoked i.e. the swelling stress evolves with time (and solute concentration). In other words, the micro-structural alteration is not instantaneous but rather a consequence of the timedependent stress field equation (more details will be elaborated later).

(x) There is no cyclic loading considered nor are there any drying-wetting cycles i.e. the theory is developed for strictly monotonic loading.

3.4.1. Balance laws

The balanced equation for Helmholtz free energy of a thermodynamically open system is given by [172,191]:

$$\frac{D}{Dt}\left(\int_{V} FdV\right) = -\int_{R} \boldsymbol{\sigma}\boldsymbol{n} \cdot \boldsymbol{\nu}_{s} dR - \int_{R} (\mu^{w}\boldsymbol{I}^{w} + \mu^{g}\boldsymbol{I}^{g} + \mu^{s}\boldsymbol{I}^{s}) \cdot \boldsymbol{n} dR$$

$$-T\int_{V} \gamma dV \qquad (3.12)$$

where the material time derivative of any argument *a* is given by:

$$\frac{D}{Dt}(a) = \frac{\partial a}{\partial t} + \boldsymbol{v}_s \cdot \nabla a \tag{3.13}$$

In Eq. (3.12), *F* is the Helmholtz free energy density, σ is the Cauchy stress tensor, *n* is the outward unit normal vector, v_s is the velocity of the solid, T is the temperature (constant), I^w , I^g and I^s are water, gas, and solute flux respectively, γ is the rate of entropy production density (i.e. the rate of entropy production per unit volume). It is noted that the bold font symbolizes either a vector or a matrix. The flux can be defined as:

$$I^{\beta} = \rho^{\beta} (\boldsymbol{v}^{\beta} - \boldsymbol{v}_{s}) \tag{3.14}$$

Where $\beta = w, g, c$ for water, gas, and solute respectively, ρ^{β} is the mass density of each component, and v^{β} is the velocity of each component (water, gas, or solute). The constituents of *V* in addition to the free energy are the fluid and solid masses which also need to be balanced for any change in time. Since, as already stated earlier, *V* is closed to solid matter influx and open to fluid (water, gas, and solute) flow, we have:

$$\frac{D}{Dt}\left(\int_{V}\rho^{s}dV\right) = 0 \tag{3.15}$$

$$\frac{D}{Dt}\left(\int_{V}\rho^{\beta}dV\right) = -\int_{R}\boldsymbol{I}^{\boldsymbol{\beta}}\cdot\boldsymbol{n}dR$$
(3.16)

Next, using Reynold's transport theorem and Gauss divergence theorem, we obtain the localized version of the balance equations for free energy, solid mass, and each fluid component mass respectively:

$$\dot{F} + F\nabla \cdot \boldsymbol{v}_s - \nabla \cdot (\boldsymbol{\sigma}\boldsymbol{v}_s) + \nabla \cdot (\mu^w \boldsymbol{I}^w + \mu^g \boldsymbol{I}^g + \mu^s \boldsymbol{I}^s) = -T\gamma \le 0$$
(3.17)

$$\dot{\rho}^s + \rho^s \nabla \cdot \boldsymbol{v}_s = 0 \tag{3.18}$$

$$\dot{\rho}^{\beta} + \rho^{\beta} \nabla \cdot \boldsymbol{v}_{s} + \nabla \cdot \boldsymbol{I}^{\beta} = 0 \tag{3.19}$$

The densities of each fluid component used heretofore were in respect to the unit volume of the bulk (fluid-solid mixture). They are related to their average individual mass densities shown by a top bar $(\bar{\rho}^{\beta})$ through:

$$\rho^{\beta} = \phi^{\beta} \bar{\rho}^{\beta} \tag{3.20}$$

where ϕ^{β} is the volume fraction of the respective fluid component, which is related to the total porosity (ϕ) of the medium through the fluid saturation (S^{f}) by:

$$\sum \phi^{\beta} = S^{f} \phi \tag{3.21}$$

3.4.2. Entropy production rate

The entropy production rate γ in Eq. (3.12) needs to be specified in order to quantify the dissipative mechanisms within the rock. It is assumed here that the cause for dissipation is the friction generated during flow at the solid/water interface and due to damage. We assume that the dissipation caused by inelastic deformation of the rock, chemical reactions of the fluid components with one another and with the rock are negligible. In other words, reversible elastic deformation and local interfacial chemical equilibrium are assumed. Hence, using standard arguments of non-equilibrium thermodynamics, we obtain the macroscopic expression for dissipation [172,223]:

$$0 \le T\gamma = -(\mathbf{I}^{w} \cdot \nabla \mu^{w} + \mathbf{I}^{g} \cdot \nabla \mu^{g} + \mathbf{I}^{c} \cdot \nabla \mu^{c}) - Y_{D}\dot{D}$$
(3.22)

where *D* is the damage variable (a scalar), \dot{D} its time evolution, and Y_D is the thermodynamic force causing damage. The fluxes heretofore were based on the velocity

of each component relative to the solid matrix velocity. It is more convenient to replace them with diffusion fluxes (J^{β}) that is relative to the mixture's barycentric velocity (v^{f}) :

$$J^{\beta} = \rho^{\beta} (\boldsymbol{v}^{\beta} - \boldsymbol{v}^{f}) \tag{3.23}$$

Where $\boldsymbol{v}^{f} = (\rho^{w}/\rho^{f})\boldsymbol{v}^{w} + (\rho^{g}/\rho^{f})\boldsymbol{v}^{g} + (\rho^{c}/\rho^{f})\boldsymbol{v}^{c}$ and $\rho^{f} = \rho^{g} + \rho^{w} + \rho^{c}$. It is thus obvious that the two types of fluxes are related through:

$$J^{\beta} = I^{\beta} - \rho^{\beta} (\boldsymbol{v}^{f} - \boldsymbol{v}_{s})$$
(3.24)

Rearranging Eq. (3.24) then substituting in Eq. (3.22) gives:

$$0 \leq T\gamma = -\left(\left(J^{w} + \rho^{w}(v^{f} - v_{s})\right) \cdot \nabla \mu^{w} + \left(J^{g} + \rho^{g}(v^{f} - v_{s})\right) \cdot \nabla \mu^{w} + \left(J^{c} + \rho^{c}(v^{f} - v_{s})\right) \cdot \nabla \mu^{c}\right) - Y_{D}\dot{D}$$
(3.25)

Here, Darcy velocity is introduced using:

$$\boldsymbol{u} = \phi S^f (\boldsymbol{v}^f - \boldsymbol{v}_s) \tag{3.26}$$

Also, recalling the Gibbs-Duhem equation for multicomponent multiphase systems [224]:

$$\bar{\rho}^{w}\nabla\mu^{w} + \bar{\rho}^{g}\nabla\mu^{g} + \bar{\rho}^{c}\nabla\mu^{c} = \nabla p_{pore}$$
(3.27)

Using Eqs. (3.26) and (3.27), Eq. (3.25) can be further simplified to:

$$0 \le T\gamma = -\boldsymbol{u} \cdot \nabla p_{pore} - (\boldsymbol{J}^{\boldsymbol{w}} \cdot \nabla \mu^{\boldsymbol{w}} + \boldsymbol{J}^{\boldsymbol{g}} \cdot \nabla \mu^{\boldsymbol{g}} + \boldsymbol{J}^{\boldsymbol{c}} \cdot \nabla \mu^{\boldsymbol{c}}) - Y_{\boldsymbol{D}} \dot{\boldsymbol{D}}$$
(3.28)

where p_{pore} is the pore pressure due to the total fluid (water-gas combined). It is noted that the diffusion fluxes are not all independent, and must satisfy:

$$J^{w} + J^{g} + J^{c} = 0 (3.29)$$

Hence, the entropy production can be written in terms of two independent diffusion fluxes:

$$0 \le T\gamma = -\boldsymbol{u} \cdot \nabla p_{pore} - \boldsymbol{J}^{\boldsymbol{g}} \nabla \cdot (\mu^{\boldsymbol{g}} - \mu^{\boldsymbol{w}}) - \boldsymbol{J}^{\boldsymbol{c}} \nabla \cdot (\mu^{\boldsymbol{c}} - \mu^{\boldsymbol{w}}) - Y_{\boldsymbol{D}} \dot{\boldsymbol{D}}$$
(3.30)

It is noted that in the above equation, the term $\nabla \cdot (\mu^g - \mu^w)$ can be neglected as water and gas movement is assumed piston-like and no interfacial exchange or mixing occurs between the two phases.

3.4.3. Equations of state

Using the entropy production (Eq. (3.30)) in Eq. (3.12) and assuming $\nabla \cdot \boldsymbol{\sigma} = 0$ (i.e. the rock maintains mechanical equilibrium during deformation), we arrive at:

$$\dot{F} + F\nabla \cdot \boldsymbol{v}_s - tr(\boldsymbol{\sigma}\nabla\boldsymbol{v}_s) + \mu^w \nabla \cdot \boldsymbol{I}^w + \mu^g \nabla \cdot \boldsymbol{I}^g + \mu^c \nabla \cdot \boldsymbol{I}^c + Y_D \dot{D} = 0$$
(3.31)

Next, it is necessary to characterize the rock's deformation state which is done using concepts from continuum mechanics. An arbitrary element in a reference configuration (\mathbf{x}) is mapped onto the deformed (current) configuration (\mathbf{X}) . For the mapping purpose, we utilize the Green strain (\mathbf{E}) for the measure of the rock's deformation state and the second Piola-Kirchhoff stress (\mathbf{T}) for the measure of the referential [172]. From continuum mechanics, the mapping gradient (deformation gradient) vector at any time (t) and Green strain (\mathbf{E}) are defined respectively as:

$$H = \frac{\partial x}{\partial X}(X, t) \tag{3.32}$$

$$\boldsymbol{E} = \frac{1}{2} \left(\boldsymbol{H}^T \boldsymbol{H} - 1 \right) \tag{3.33}$$

The second Piola-Kirchhoff stress is related to the Cauchy stress by $T = JH^{-1}\sigma H^{-T}$. Here, $J = |H| = dV/dV_0$ where dV is the deformed volume element (current) and dV_0 is the reference volume element (undeformed). It is also noted that [172]:

$$\dot{J} = J\nabla \cdot \boldsymbol{v}_s \tag{3.34}$$

Using these concepts and invoking the fluids mass conservation (Eq. 3.16), Eq. (3.31) becomes [172]:

$$\dot{\boldsymbol{F}} = tr(\boldsymbol{T}\dot{\boldsymbol{E}}) + \mu^{w}\dot{\boldsymbol{m}}^{w} + \mu^{g}\dot{\boldsymbol{m}}^{g} + \mu^{c}\dot{\boldsymbol{m}}^{c} + Y_{D}\dot{\boldsymbol{D}}$$
(3.35)

Where $\mathbf{F} = JF$ is the free energy in the reference configuration, $\dot{\mathbf{F}}$ is its time change, $m^w = J\rho^w = J\phi^w \rho^w$ is the mass density of water, $m^g = J\rho^g = J\phi^g \rho^g$ is the mass density of the gas, and $m^c = J\rho^c = J\phi^c \rho^c$ is the mass density of the solute. Substituting these definitions in Eq. (3.35) readily makes it the referential equivalent of Eq. (3.31) [172]. If we are concerned with small strains (which is the case here), we can substitute $\mathbf{E} = \boldsymbol{\varepsilon}$ and $\mathbf{T} = \boldsymbol{\sigma}$ where $\boldsymbol{\varepsilon}$ is the infinitesimal strain corresponding to the applied Cauchy stress $\boldsymbol{\sigma}$:

$$\dot{\boldsymbol{F}} = tr(\boldsymbol{\sigma}\dot{\boldsymbol{\varepsilon}}) + \mu^{w}\dot{\boldsymbol{m}}^{w} + \mu^{g}\dot{\boldsymbol{m}}^{g} + \mu^{c}\dot{\boldsymbol{m}}^{c} + Y_{D}\dot{\boldsymbol{D}}$$
(3.36)

Next, it is assumed that there is no gas residing in the interlayer pore space. The interlayer water (including solute) in the clay pores (m_{bound}^{β}) is influenced by intermolecular and surface forces that are not described by macroscopic thermodynamics. The free pore fluid (m_{pore}^{β}) , however, follows familiar thermodynamics. Therefore, assuming compressive pressure is positive, the free energy density of the fluid system in this free pore volume (containing water and gas) is:

$$F_{pore} = -\sum_{w,g} p_{w,g} + S_w \mu^w \bar{\rho}_{pore}^w + S_g \mu^g \bar{\rho}_{pore}^g + S_w \mu^c \bar{\rho}_{pore}^c$$
(3.37)

The above equation can also be written as:

$$F_{pore} = -\sum_{w,g} p_{w,g} + S_f \sum_{\beta} \mu^{\beta} \bar{\rho}_{pore}^{\beta}$$
(3.38)

Invoking the same continuum mechanics concepts as above, we can deduce the referential pore volume free energy density $(J\phi F_{pore})$:

$$J\phi \dot{F}_{pore} = -p_w \dot{v}_w - p_g \dot{v}_g + J\phi S_w \mu^w \bar{\rho}_{pore}^w + J\phi S_g \mu^g \bar{\rho}_{pore}^g$$

$$+ J\phi S_w \mu^c \bar{\rho}_{pore}^c$$
(3.39)

where $v_w = J\phi^w$ and $v_g = J\phi^g$ are the pore volume fractions of water and gas per unit referential volume, respectively. The total pore volume is $v_w + v_g$. Since $J\phi\bar{\rho}_{pore}^{\beta} = \bar{m}_{pore}^{\beta}$, we have:

$$J\phi \dot{F}_{pore} = -p_w \dot{v}_w - p_g \dot{v}_g + S_w \mu^w \bar{m}_{pore}^w + S_g \mu^g \bar{m}_{pore}^g + S_w \mu^c \bar{m}_{pore}^c$$
(3.40)

It is recalled that the bulk volume element (as characterized by Eq. (3.36)) consists of two types of pores in water-absorbing rocks. One is the pore space with freely flowing fluid (water/gas) while the other is the interlayer pore space between clay platelets which contains the bound water [116,172]. Therefore, the total water mass (m^w) within the porous material can then be defined as a summation of the pore water (m_{pore}^w) and the bound water (m_{bound}^w) [116]:

$$m^{w} = S_{w}(m^{w}_{pore} + m^{w}_{bound})$$
(3.41)

where, S_w is the water saturation defined based on the total water in the porous medium. Subtracting this from the combined shale/fluid bulk system, the free energy of the 'wetted' rock skeleton (i.e. solid part of the rock including the clay interlayer water) is obtained:

$$\dot{\boldsymbol{F}} - \left(J\phi\dot{F}_{pore}\right) = tr(\boldsymbol{\sigma}\dot{\boldsymbol{\varepsilon}}) + Y_D\dot{D} + p_w\dot{v}_w + p_g\dot{v}_g + S_w\sum_{\beta}\mu^{\beta}\dot{m}^{\beta}_{bound}$$
(3.42)

Here, $m_{bound}^{\beta} = m^{\beta} - J\phi \bar{\rho}_{pore}^{\beta}$ is the mass density of the $\beta = w, s$ fluid component in the interlayer pores in the reference volume. It is reiterated that there is no such 'bound'

gas in the interlayer pores or in the 'wetted' matrix which is consistent with our earlier assumption that gas adsorption is trivial (or negligible). Next, it is convenient to employ the following dual potential:

$$W = \left(F - J\phi F_{pore}\right) - \sum_{w,g} p_{w,g} - S_w \sum_{\beta} \mu^{\beta} m_{bound}^{\beta}$$
(3.43)

Taking $W = W(\boldsymbol{\varepsilon}, D, p_w, p_g, \mu^{\beta})$, we have:

$$\dot{W}(\boldsymbol{\varepsilon}, \boldsymbol{D}, \boldsymbol{p}_{w}, \boldsymbol{p}_{g}, \boldsymbol{\mu}^{\beta}) = tr(\boldsymbol{\sigma}\dot{\boldsymbol{\varepsilon}}) + Y_{D}\dot{\boldsymbol{D}} - v_{w}\dot{\boldsymbol{p}}_{w} - v_{g}\dot{\boldsymbol{p}}_{g} - \sum_{\beta} m_{bound}^{\beta} \dot{\boldsymbol{\mu}}^{\beta}$$
(3.44)

From Eq. (3.44), we have:

$$\sigma_{ij} = \left(\frac{\partial W}{\partial \varepsilon_{ij}}\right)_{D,p_w,p_g,\mu^\beta}, D = \left(\frac{\partial W}{\partial Y_D}\right)_{\varepsilon_{ij},p_w,p_g,\mu^\beta}, v_w = -\left(\frac{\partial W}{\partial p_w}\right)_{\varepsilon_{ij},D,p_g,\mu^\beta}, v_g = -\left(\frac{\partial W}{\partial p_g}\right)_{\varepsilon_{ij},D,p_w,\mu^\beta}, \text{ and } m^\beta_{bound} = -\left(\frac{\partial W}{\partial \mu^\beta}\right)_{\varepsilon_{ij},D,p_w,p_g,\mu'(\neq \mu^k)}$$
(3.45)

Where, using indicial notations, σ_{ij} is the second order stress tensor, ε_{ij} is the corresponding second-order strain tensor; both are based on a Cartesian coordinate system i.e. i, j = 1,2,3. Hence, Eq. (3.44) can be written as:

$$\dot{W} = \left(\frac{\partial W}{\partial \varepsilon_{ij}}\right)_{D,p_{w},p_{g},\mu^{\beta}} \dot{\varepsilon}_{ij} + \left(\frac{\partial W}{\partial D}\right)_{\varepsilon_{ij},p_{w},p_{g},\mu^{\beta}} \dot{D} + \left(\frac{\partial W}{\partial p_{w}}\right)_{\varepsilon_{ij},D,p_{g},\mu^{\beta}} \dot{p}_{w} + \left(\frac{\partial W}{\partial p_{g}}\right)_{\varepsilon_{ij},D,p_{w},\mu^{\beta}} \dot{p}_{g} + \sum_{\beta} \left(\frac{\partial W}{\partial \mu^{\beta}}\right)_{\varepsilon_{ij},D,p_{w},\mu'(\neq\mu^{k})} \dot{\mu}^{\beta}$$
(3.46)

Differentiating Eqn. (3.45) with respect to the time, the following constitutive equations for the evolution of stress, variation content of water phase, variation content of gas phase, variation in interlayer (bound) water, and damage evolution are obtained:

$$\dot{\sigma}_{ij} = L_{ijkl} \dot{\varepsilon}_{ij} + V_{ij} \dot{Y}_D - M_{ij} \dot{p}_w - N_{ij} \dot{p}_g + S_w \sum_{\beta} S_{ij}{}^{\beta} \dot{\mu}^{\beta}$$
(3.47)

$$\dot{v}_{w} = M_{ij}\dot{\varepsilon}_{ij} + W_{ij}\dot{Y}_{D} + \left(\frac{\dot{p}_{w}}{M_{w/w}} + \frac{\dot{p}_{g}}{M_{w/g}}\right) + S_{w}\sum_{\beta} B^{\beta}\dot{\mu}^{\beta}$$
(3.48)

$$\dot{v}_{g} = N_{ij}\dot{\varepsilon}_{ij} + X_{ij}\dot{Y}_{D} + \left(\frac{\dot{p}_{w}}{M_{w/g}} + \frac{\dot{p}_{g}}{M_{g/g}}\right) + S_{w}\sum_{\beta}\Pi^{\beta}\dot{\mu}^{\beta}$$
(3.49)

$$\dot{m}^{\beta}_{bound} = S_{ij}{}^{\beta} \dot{\varepsilon}_{ij} + Q_{ij} \dot{Y}_D + B^{\beta} S_w \dot{p}_w + \Pi^{\beta} S_g \dot{p}_g + S_w \sum_{\beta} Z^{\beta} \dot{\mu}^{\beta}$$
(3.50)

$$\dot{Y}_{D} = V_{ij}\dot{\varepsilon}_{ij} + Y_{ij}\dot{D} + W_{ij}S_{w}\dot{p}_{w} + X_{ij}S_{g}\dot{p}_{g} + S_{w}\sum_{\beta}Q_{ij}{}^{\beta}\dot{\mu}^{\beta}$$
(3.51)

In Eqs. (3.47-3.51), the thermodynamic response coefficients are defined through:

$$L_{ijkl} = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon}\right), \qquad M_{ij} = \left(\frac{\partial^2 W}{\partial \varepsilon \partial p_w}\right) = \left(\frac{\partial^2 W}{\partial p_w \partial \varepsilon}\right), \qquad N_{ij} = \left(\frac{\partial^2 W}{\partial \varepsilon \partial p_g}\right) = \left(\frac{\partial^2 W}{\partial p_g \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial p_g}\right) = \left(\frac{\partial^2 W}{\partial p_g \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial p_g}\right) = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon \partial \varepsilon}\right), \qquad S_{ij}{}^\beta = \left(\frac{\partial^2 W}{\partial \varepsilon \partial \varepsilon}\right),$$

$$\left(\frac{\partial^2 W}{\partial \varepsilon \partial \mu^{\beta}}\right) = \left(\frac{\partial^2 W}{\partial m_{bound} \partial \varepsilon}\right), \quad \frac{1}{M_{w/w}} = \left(\frac{\partial^2 W}{\partial p_w \partial p_w}\right), \quad \frac{1}{M_{w/g}} = \left(\frac{\partial^2 W}{\partial p_w \partial p_g}\right) = \left(\frac{\partial^2 W}{\partial p_g \partial p_w}\right), \quad B^{\beta} = \frac{1}{M_{w/w}} = \frac$$

$$\left(\frac{\partial^2 W}{\partial p_w \partial \mu^\beta}\right) = \left(\frac{\partial^2 W}{\partial m_{bound} \partial p_w}\right), \quad \Pi^\beta = \left(\frac{\partial^2 W}{\partial p_g \partial \mu^\beta}\right) = \left(\frac{\partial^2 W}{\partial m_{bound} \partial p_g}\right), \quad \frac{1}{M_{g/g}} = \left(\frac{\partial^2 W}{\partial p_g \partial p_g}\right), \quad Z^\beta = \frac{\partial^2 W}{\partial p_g \partial \mu^\beta}$$

$$\begin{pmatrix} \frac{\partial^2 W}{\partial m_{bound} \partial \mu^{\beta}} \end{pmatrix}, \qquad V_{ij} = \begin{pmatrix} \frac{\partial^2 W}{\partial \varepsilon \partial Y_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 W}{\partial Y_D \partial \varepsilon} \end{pmatrix}, \qquad W_{ij} = \begin{pmatrix} \frac{\partial^2 W}{\partial p_w \partial Y_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 W}{\partial Y_D \partial p_w} \end{pmatrix}, \qquad X_{ij} = \begin{pmatrix} \frac{\partial^2 W}{\partial Y_D \partial v_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 W}{\partial Y_D \partial v_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 W}{\partial Y_D \partial v_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial^2 W}{\partial Y_D \partial v_D} \end{pmatrix}$$

$$\begin{pmatrix} \frac{\partial}{\partial p_g \partial Y_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial}{\partial Y_D \partial p_g} \end{pmatrix}, Q_{ij} = \begin{pmatrix} \frac{\partial}{\partial m_{bound} \partial Y_D} \end{pmatrix} = \begin{pmatrix} \frac{\partial}{\partial Y_D \partial m_{bound}} \end{pmatrix}, \text{ and } Y_{ij} = \begin{pmatrix} \frac{\partial}{\partial Y_D \partial Y_D} \end{pmatrix}$$
The set of constitutive equations (Eqs. (2.47), (2.51)) are closed, comparisonly, bit

The set of constitutive equations (Eqs. (3.47) - (3.51)) are already geometrically linear due to the earlier assumption of infinitesimal strain and Cauchy stress. These equations can be further physically linearized with the assumption that the thermodynamic response coefficients L_{ijkl} , M_{ij} , N_{ij} , S_{ij}^{β} , B^{β} , Π^{β} , $\frac{1}{M_{w/w}}$, $\frac{1}{M_{w/g}}$, $\frac{1}{M_{g/g}}$, and Z^{β} are material-dependent constants.

It is noted that when the pore fluid chemistry does not affect the stress and pore volume responses (i.e. $S_{ij}^{\ \beta} = 0$, $B^{\ \beta} = 0$, and $\Pi^{\ \beta} = 0$), the classical Biot theory of poroelasticity

emerges [110]. For isotropic materials, M_{ij} , N_{ij} , and $S_{ij}^{\ \beta}$ are diagonal tensors and can be replaced with scalars α_w , α_q , and ω^{β} respectively:

$$M_{ij} = \alpha_w \delta_{ij}, N_{ij} = \alpha_g \delta_{ij}, \text{ and } S_{ij}{}^\beta = \omega^\beta \delta_{ij}$$
(3.52)

Here, α_w and α_g are the Biot coefficients for water and gas respectively, ω^{β} is the swelling coefficient of each component, and δ_{ij} is the Kronecker delta. It is noted that for binary solutions $\omega^{\beta} = \omega^0 M^c / RT$ where ω^0 is the common swelling coefficient representing both solute and solvent, M^c is the molar mass of solute, R is the universal gas constant, and T is the temperature [182]. Also, since gas does not cause any swelling Π^{β} will remain zero. It is emphasized that $\sum_{i=w,g} \alpha_i = \alpha$ where α is the Biot coefficient of the saturated porous medium [225]. It is also assumed that α_i are proportional to the respective saturation of each individual phase ($\alpha_i = S_i \alpha$) where $\sum_i S_i = 1$ [225].

The thermodynamic response coefficient L_{ijkl} is then the fourth-order elastic stiffness tensor written using the strain equivalence theory proposed by Lemaitre [213]:

$$L_{ijkl} = (1-D)G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) + (1-D)\left(K - \frac{2G}{3}\right)\delta_{ij}\delta_{kl}$$
(3.53)

Where *G* is the rock's shear modulus, *K* its bulk modulus, and D is the damage variable. According to the equivalent strain concept proposed by Lemaitre [213], the virgin material's elastic constitutive equation can be used for the damaged material by multiplying the elasticity matrix with the damage variable. It is noted that the stiffness tensor formulation is chosen to be in terms of the shear modulus (*G*) as it was observed in Chapter-2 that under isotropic stresses no micro-structural alteration (i.e. damage) is expected. Using Eqs. (3.52-3.53), Eqs. (3.47-3.49) can be written as:

$$\dot{\sigma}_{ij} = (1-D)\left(K - \frac{2G}{3}\right)\dot{\varepsilon}_{kk}\delta_{ij} + (1-D)2G\dot{\varepsilon}_{ij} - \alpha_w\dot{p}_w\delta_{ij} - \alpha_g\dot{p}_g\delta_{ij} + S_w\sum_{\beta}\omega^{\beta}\dot{\mu}^{\beta}\delta_{ij}$$
(3.54)

$$\dot{v}_w = \alpha_w \dot{\varepsilon}_{kk} + \left(\frac{\dot{p}_w}{M_{w/w}} + \frac{\dot{p}_g}{M_{w/g}}\right) + S_w \sum_\beta B^\beta \dot{\mu}^\beta$$
(3.55)

$$\dot{\upsilon}_g = \alpha_w \dot{\varepsilon}_{kk} + \left(\frac{\dot{p}_w}{M_{w/g}} + \frac{\dot{p}_g}{M_{g/g}}\right) + S_w \sum_\beta B^\beta \dot{\mu}^\beta$$
(3.56)

Furthermore, as was investigated and concluded in Chapter-2, the effect of water/gas pore pressures is negligible in damage evolution i.e. $W_{ij} = X_{ij} = 0$ and invoking the strain equivalence concept $V_{ij} = 0$. Hence, we have:

$$\dot{Y}_D = Y_{ij}\dot{D} \tag{3.57}$$

3.4.4. Field equations

Prior to deriving the field equations, the chemical potential (μ^{β}) in the constitutive equations (Eqs. 3.47-3.51) are replaced by making further simplifications through the assumption of an ideal solution with a single solute where the solute chemical potential can be estimated as [182,226]:

$$\dot{\mu}^c \approx \frac{RT}{M^c} \ln C^c \tag{3.58}$$

Where *R* is the gas constant, *T* is the system temperature, M^c is the solute molar mass, and C^c is the mass fraction of the solute which is related to the water mass fraction ($C^w = 1 - C^c$). It is noted that the ideal solution assumption holds for dilute solutions. Furthermore, a linear approximation of Eq. (3.58) yields [182,226]:

$$\dot{\mu}^c \approx \frac{RT}{M^s} \frac{\dot{C}^c}{\bar{C}^c} \tag{3.59}$$

Where \bar{C}^c is the average solute mass fraction over the range of interest. Rearranging the Gibbs-Duhem equation, the chemical potential of water is then expanded [172,200,227]:

$$\dot{\mu}^{w} \approx \frac{1}{\bar{\rho}^{w}} (\dot{p}_{w} - \bar{\rho}^{c} \dot{\mu}^{c}) \tag{3.60}$$

where, $\bar{\rho}^w$ and $\bar{\rho}^c$ are the density of water and solute relative to the unit fluid volume respectively.

3.4.4.1. Momentum balance

Considering the mechanical equilibrium condition:

$$\frac{\partial \sigma_{ij}}{\partial x_i} = 0 \tag{3.61}$$

and incorporating Eqs. (3.59-3.60) into Eq. (3.54), yields the constitutive equation for stress field:

$$(1-D)\left(K-\frac{2G}{3}\right)\dot{\varepsilon}_{kk}\delta_{ij} + (1-D)2G\dot{\varepsilon}_{ij} - \alpha S_g\nabla\dot{p}_g\delta_{ij} - S_w(\alpha) -\frac{\omega^0 M^c}{RT\bar{\rho}^w}\nabla\dot{p}_w\delta_{ij} + \frac{S_w\omega^0}{\bar{C}^c}(1-\frac{\bar{\rho}^c}{\bar{\rho}^w})\nabla\dot{C}^c\delta_{ij} = 0$$
(3.62)

Eq. (3.62) can be written in terms of the displacements [182]:

$$(1-D)G\nabla^{2}\dot{u}_{i} + (1-D)\frac{G}{1-2\upsilon}\nabla(\nabla\cdot\dot{u}_{i}) - \alpha S_{g}\nabla\dot{p}_{g}\delta_{ij}$$

$$-S_{w}\left(\alpha - \frac{\omega^{0}M^{c}}{RT\bar{\rho}^{w}}\right)\nabla\dot{p}_{w}\delta_{ij} + \frac{S_{w}\omega^{0}}{\bar{C}^{c}}\left(1 - \frac{\bar{\rho}^{c}}{\bar{\rho}^{w}}\right)\nabla\dot{C}^{c}\delta_{ij} = 0$$
(3.63)

Where v is the rock's Poisson's ratio and the solid displacements (u_i) are related to the strain through:

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \tag{3.64}$$

3.4.4.2. Mass balance for water, gas, and solute without the sink/source term It is recalled that during the derivation of the stress constitutive equation, it was assumed that no interfacial exchange or mixing occurs between water-gas phases which makes the second term of Eq. 3.30 negligible. Now, Eq. (3.30) is modified to derive the phenomenological equations with the addition of the thermodynamic driving forces and corresponding fluxes using Onsager reciprocity [228]. It is noted that damage is not included in the formulation of transport phenomenological equations. It is reiterated that such phenomenological equations relate the thermodynamic driving forces to their consequent fluxes [172,182] – in this case, the water, gas, and solute fluxes. Hence, the phenomenological equations including gas transport can be written as:

$$\boldsymbol{u}^{w} = -\frac{L^{11}}{\bar{\rho}_{w}} \nabla p_{w} - \frac{L^{12}}{\bar{\rho}_{w}} \nabla p_{g} - L^{13} \nabla (\mu^{c} - \mu^{w})$$
(3.65)

$$\boldsymbol{u}^{g} = -\frac{L^{21}}{\bar{\rho}_{g}} \nabla p_{w} - \frac{L^{22}}{\bar{\rho}_{g}} \nabla p_{g} - L^{23} \nabla (\mu^{c} - \mu^{w})$$
(3.66)

$$J^{c} = -\frac{L^{31}}{\bar{\rho}_{w}}\nabla p_{w} - \frac{L^{32}}{\bar{\rho}_{w}}\nabla p_{g} - L^{33}\nabla(\mu^{c} - \mu^{w})$$
(3.67)

Here, the thermodynamic driving forces are ∇p_w , ∇p_g , and $\nabla (\mu^c - \mu^w)$. It is assumed that the hydraulic gradient of water causes only water flux and similarly pressure gradient of gas causes only gas flux. Therefore, it consequently follows that $L^{12} = L^{21} = 0$. It was already assumed that there is no solute present in the gas phase; hence $L^{23} = 0$. It is also rightly assumed that the effect of water and gas pressure on solute transport is minimal allowing $L^{31} = L^{32} = 0$. It is noted that Onsager's symmetry [228] is not inherently invoked here as is mostly considered in the literature, but rather is arrived at using valid assumptions. Whether the symmetry holds or not is subject to specifically designed experiments which will not be discussed here for now. It is noted that for dilute solutions which can be assumed to be ideal, the following approximation can be applied [182]:

$$\nabla(\mu^c - \mu^w) \approx \frac{RT}{\bar{C}^w \bar{C}^c M^s} \nabla C^c$$
(3.68)

Where \bar{C}^c and \bar{C}^w are the average mass fraction of solute and water respectively. Therefore, the transport equations for water, gas, and solute phases are derived as:

$$\boldsymbol{u}^{w} = -\frac{kk_{rw}}{\tau_{w}} (\nabla p_{w} + \Re \frac{RT}{M^{S} \bar{C}^{w} \bar{C}^{c}} \nabla C^{c})$$
(3.69)

$$\boldsymbol{u}^g = -\frac{kk_{rg}}{\tau_g} \nabla p_g \tag{3.70}$$

$$J^{c} = -(1 - \Re)D_{e}\nabla C^{c}$$
(3.71)

Where $\boldsymbol{u}^w, \boldsymbol{u}^g$, and \boldsymbol{J}^c are the water, gas, and solute flux vectors respectively. Also, D_e is the effective solute diffusivity coefficient, k is the absolute permeability of the porous media, k_{rw} and k_{rg} are the water and gas relative permeability respectively. In addition, \Re is the reflection coefficient or the membrane efficiency of the shale which varies from 0 to 1 and τ_w and τ_g are the dynamic viscosities of water and gas respectively.

The time evolution of variation of compressible/incompressible fluid contents (ζ) is expressed as [182]:

$$\dot{\zeta}^{i} = \frac{\dot{m}_{i}}{\bar{\rho}_{i}} \approx \dot{\nu}_{i} + \frac{S_{i}\phi\dot{p}_{i}}{K_{f,i}}$$
(3.72)

where $K_{f,i=w,g}$ is the fluid bulk modulus for water and gas respectively. For incompressible water, as is obvious, the second term on the right of Eq. 3.72 becomes negligible due to its large fluid bulk modulus. Now, invoking the continuity equation (mass balance for water, gas, and solute) yields:

$$(\rho_w \zeta^w) \cdot + \nabla \cdot (\rho_w \boldsymbol{u}^w) = 0 \tag{3.73}$$

$$\left(\rho_g \zeta^g\right)^{\cdot} + \nabla \cdot \left(\rho_g \boldsymbol{u}^g\right) = 0 \tag{3.74}$$

$$\rho_s S_w \dot{C}^c + S_w (\rho_c \boldsymbol{u}^w \nabla C^c + \nabla \cdot (\rho_c \boldsymbol{J}^c)) = 0$$
(3.75)

where, u^w , u^g are the fluxes of pore water and gas respectively. It is inherently realized from Eq. (3.75) that the solute transfer in the gas phase and the effect of capillary suction on solute transfer have been neglected. In addition, assuming water is the wetting phase, the capillary pressure, p_c is defined as:

$$p_c(S_w) = p_g - p_w \tag{3.76}$$

where,

$$S_w + S_q = 1$$
 (3.77)

It should be mentioned that the wettability alteration through chemical reaction by the exposed fluid can be readily included in the model if the equation for the chemical-thermal and pressure-dependent capillary suction is known which can replace Eq. 3.76. Substituting Eq. (3.55) into Eq. (3.73), assuming water phase to be incompressible $(\rho_w = \text{constant})$, and using $B^{\beta} = \frac{1}{\kappa} (\alpha - 1) \omega^{\beta}$ proposed by Heidug and Wong [172] (*K* here is the bulk modulus of porous medium), the time evolution of variations in water and gas contents are obtained as:

$$\dot{\zeta}^{w} = \alpha_{w}\dot{\varepsilon}_{kk} + \left(\left[\frac{1}{M_{w/w}} + \frac{S_{w}\phi}{K_{f,w}} + \frac{S_{w}\omega^{o}(\alpha - 1)M^{c}}{KRT\bar{\rho}^{w}} \right] \dot{p}_{w} + \frac{1}{M_{w/nw}} \dot{p}_{g} \right)$$

$$+ \frac{S_{w}\omega^{o}(\alpha - 1)}{K\bar{C}^{c}} (1 - \frac{\bar{\rho}^{s}}{\bar{\rho}^{w}})\dot{C}^{c}$$

$$\dot{\zeta}^{g} = \alpha_{g}\dot{\varepsilon}_{kk} + \left(\left[\frac{1}{M_{w/g}} + \frac{S_{w}\omega^{o}(\alpha - 1)M^{c}}{KRT\bar{\rho}^{w}} \right] \dot{p}_{w} + \left[\frac{S_{g}\phi}{K_{f,g}} + \frac{1}{M_{g/g}} \right] \dot{p}_{g} \right)$$

$$+ \frac{S_{w}\omega^{o}(\alpha - 1)}{K\bar{C}^{c}} (1 - \frac{\bar{\rho}^{s}}{\bar{\rho}^{w}})\dot{C}^{c}$$
(3.79)

In arriving at Eq. 3.79, an important implicit assumption is asserted that when water loss occurs during well shut-in due to capillary dominant forces, there is negligible gas hydraulic pressure gradient and hence the negligible change in gas density during the shut-in period. It is this assumption that makes the substitution of density by an equation-of-state unwarranted. It is obvious that when gas production is initiated, several complex flow regimes develop over the range of large pressure drops and the Darcy velocity regime (as given by Eq. 3.70) will be short-ranged or perhaps non-existent. Hence, all assumptions associated with Darcy flow are also now associated with the time evolution of gas content (Eq. 3.79). Now substituting the water and gas fluxes (Eqs. 3.69 and 3.70), and the time change of water and gas contents (Eqs. 3.78 and 3.79), into water and gas continuity equation (Eqs. 3.73-3.74), yields the water and gas pressure equations as:

$$\alpha_{w}\dot{\varepsilon}_{kk} + \left(\left[\frac{1}{M_{w/w}} + \frac{S_{w}\phi}{K_{f,w}} + \frac{S_{w}\omega^{o}(\alpha - 1)M^{c}}{KRT\bar{\rho}^{w}} \right] \dot{p}_{w} + \frac{1}{M_{w/g}}\dot{p}_{g} \right) + \frac{S_{w}\omega^{o}(\alpha - 1)}{K\bar{C}^{c}} \left(1 - \frac{\bar{\rho}^{c}}{\bar{\rho}^{w}} \right) \dot{C}^{c} = \frac{kk_{rw}}{\tau_{w}} \left(\nabla^{2}p_{w} + \Re \frac{RT}{M^{S}\bar{C}^{w}\bar{C}^{c}} \nabla^{2}C^{c} \right)$$
(3.80)

$$\begin{aligned} \alpha_{g}\dot{\varepsilon}_{kk} + \left(\left[\frac{1}{M_{w/g}} + \frac{S_{w}\omega^{o}(\alpha - 1)M^{c}}{KRT\bar{\rho}^{w}} \right] \dot{p}_{w} + \left[\frac{S_{g}\phi}{K_{f,g}} + \frac{1}{M_{g/g}} \right] \dot{p}_{g} \right) \\ + \frac{S_{w}\omega^{o}(\alpha - 1)}{K\bar{C}^{c}} \left(1 - \frac{\bar{\rho}^{c}}{\bar{\rho}^{w}} \right) \dot{C}^{c} = \frac{kk_{rg}}{\tau_{g}} \nabla^{2} p_{g} \end{aligned}$$
(3.81)

Finally the coupling coefficients, $M_{\alpha/\beta}$ can be defined as [120]:

$$\frac{1}{M_{g/g}} = \frac{1}{M_{g/w}} = \frac{1}{M_{w/w}} = \frac{\phi}{K_C}$$
(3.82)

Where, $K_c = -\frac{dS_w}{dp_c}$ is the inverse capillary pressure derivative defined using the fractal concepts [229]:

$$\frac{dS_w}{dP_c} = (D_f - 3)P_{cmin}{}^{3-D_f}P_c{}^{D_f - 4}$$
(3.83)

$$K_c = -\frac{1}{(D_f - 3)} P_{cmin}{}^{D_f - 3} P_c{}^{4 - D_f}$$
(3.84)

The solute transfer equation can be obtained by substituting Eq. (3.71) into Eq. (3.75). Keeping the convective term ($\rho_s u^w \nabla C^c$) in Eq. (3.75), we arrive at:

$$\rho_s S_w \dot{C}^c + S_w (\rho_c \boldsymbol{u}^w \nabla C^c + \nabla \cdot (-\rho_c (1 - \Re) D_e \nabla C^c)) = 0$$
(3.85)

Equations 3.63, 3.80, 3.81, and 3.85 form a set of constitutive equations that describe the dynamic change of thermodynamic state variables of displacement, gas, and water pressure as well as solute transfer in a shale water-gas system.

The set of general Eqns. 3.57, 3.63, 3.80, 1.81, and 3.85 consists of several material constants and two-phase coefficients that need to be established to be able to obtain a numerical solution. It is noted that quantitative damage characterization experiments have not been performed in this dissertation due to the complexity associated with experimental investigation of the time evolution of chemical damage of tight reactive rocks such as shales. Hence, Eq. 3.57 needs special consideration for the complete set of constitutive equations to be solved in the absence of such experiments.

3.4.4.3. Damage evolution

As discussed earlier, when micro-structural deterioration of material is discussed in the framework of continuum mechanics, the state variable called the damage variable (D), is utilized. In this dissertation, this variable is assumed isotropic across the REV and hence is a scalar. It is emphasized that micro-structural deterioration will cause only slight

micro-cracking which does not necessarily lead to permanent deformation. However, such deterioration is manifested in the reduction of mechanical properties of the material due to a reduction in grain-to-grain cohesion. In other words, the energy dissipated due to micro-structural deterioration is in fact used to reduce the material cohesion by chemical reaction influencing the mechanical properties although a minor initiation of the micro-cracks due to such chemical reaction is inevitable. The strain regime can remain elastic during such deterioration of the material which is true for most brittle materials [208–211]. Also, since there is no cyclic mechanical loading nor chemical drying-wetting cycles, this assumption of negligible permanent deformation remains valid.

The dissipated energy due to micro-structural deterioration can be represented as the loss in elastic strain energy density (w_e) of the REV. The elastic strain energy density is defined as [213]:

$$dw_e = \sigma_{ij} d\varepsilon_{ij} \tag{3.86}$$

The thermodynamic force causing the micro-structural alteration recalled from Eq. 3.57 is Y_D . Based on the Helmholtz free energy potential (*W*), it can be defined as [213]:

$$Y_{\rm D} = \frac{\partial W}{\partial D} \tag{3.87}$$

The thermodynamic force of damage can be related to the elastic strain energy density by [213]:

$$Y_D = \frac{w_e}{1 - D} \tag{3.88}$$

The above equation implies that the thermodynamic force associated with damage is proportional to the elastic strain energy density with a proportionality constant 1/(1 - D). The proportionality constant increases with an increase in damage (*D*). Thus, if the

strain energy density can be calculated, the thermodynamic force causing damage can also be subsequently estimated. For purely mechanical damage, Eq. 3.86 becomes:

$$w_e = \int (1-D) L_{ijkl} \varepsilon_{ij} d\varepsilon_{ij} = \frac{1}{2} (1-D) L_{ijkl} \varepsilon_{ij} \varepsilon_{ij}$$
(3.89)

Furthermore, the shear energy and hydrostatic energy can be split to give the following expression for Y_D [213,220]:

$$Y_D = \frac{\sigma_{eq}^2}{2(1-D)} \left[\frac{1}{3G} + \frac{1}{K} \left(\frac{\sigma_H}{\sigma_{eq}} \right)^2 \right]$$
(3.90)

where $\sigma_H = \frac{1}{3}tr(\sigma_{ij})$ is the hydrostatic pressure, and $\sigma_{eq} = \sqrt{\frac{2}{3}tr(\sigma_{ij} - \sigma_H\delta_{ij})}$ is the equivalent stress where $\sigma_{ij} - \sigma_H\delta_{ij}$ gives the deviatoric stress.

In addition to mechanical stresses that cause the micro-structural alteration (damage) of the material by micro-cracking, there can be additional mechanisms such as chemical interactions that can also cause deterioration of the material's micro-structure through cohesion reduction between bulk constituents. This warrants an additional damage variable due to chemical micro-structural deterioration. The derivation of the thermodynamic force and the corresponding chemical damage variable is not straightforward. A chemo-mechanical coupling damage parameter needs to be defined. It is assumed that the effect of chemical damage, as the mechanical damage, is to influence the material's mechanical properties through reduction of the elastic stiffness. For this, a new and independent chemical damage variable (D_{chem}) is defined distinguishing it from the mechanical damage variable (D_{mech}) [230–234]. The elastic constitutive relation, neglecting other terms, then can be written as:

$$\dot{\sigma}_{ij} = (1 - D_{mech})(1 - D_{chem})L_{ijkl}\dot{\varepsilon}_{ij} = (1 - D_{total})L_{ijkl}\dot{\varepsilon}_{ij}$$
(3.91)

where the total damage variable is defined as:
$$D_{total} = D = D_{mech} + D_{chem} - (D_{mech} * D_{chem})$$
(3.92)

Mechanical deterioration of the micro-structure is assumed to be negligible in this dissertation ($D_{mech} \approx 0$) as the shale reservoir does not undergo continuous loading; only an abrupt change in in-situ stresses occurs post-hydraulic fracturing. Chemical damage, however, is significantly active due to the combined action of water-solute-clay interactions. To formulate the evolution of D_{chem} , inspiration from conventional continuum damage mechanics is taken. Based on the stress constitutive equation (Eq. 3.47), stress (σ) can be defined in $\sigma - \mu$ space instead of $\sigma - \varepsilon$ space:

$$\sigma_{ij} = S_w \omega^c \mu^c \delta_{ij} \tag{3.93}$$

Substituting Eq. 3.93 into Eq. 3.89, the following expression for the dissipated energy is obtained:

$$dw_e = S_w \omega^0 \mu^c \delta_{ij} d\mu^c \tag{3.94}$$

Integrating Eq. 3.94 and invoking the definition of ω^c and the Gibbs-Duhem relationship (Eq. 3.60), the following expression for Y_D is obtained:

$$Y_D = \frac{S_w \omega^0 R T (C^c)^2}{2(1-D)(\bar{C}^c)^2}$$
(3.95)

Next, the entropy production (dissipation) due to micro-structural deterioration is equated to the dissipation by chemical interactions [235]:

$$Y_D \dot{D} = \dot{\mu}^c dC^c \tag{3.96}$$

Solving for *D*:

$$\dot{D} = \frac{2(1-D)\bar{C}^{c}\Delta C^{c}}{S_{w}\omega^{0}(C^{c})^{2}}$$
(3.97)

The slight micro-cracks initiation due to clay-fluid interactions is reflected in the absolute permeability on the continuum scale. Based on the observations made in Chapter-2; chemically-induced micro-fractures only appear considerably in presence of shearing (anisotropic) stresses. It is therefore assumed that the permeability alteration by these micro-fractures occurs only during shearing, thus Eq. 3.98 is considered only when shearing (anisotropic) stresses exist. Hence, with the evolution of D_{chem} the absolute permeability of the matrix (REV) is updated as follows [236–239]:

$$k = k_0 \left(\frac{\phi}{\phi_0}\right)^3 e^{\alpha_D * D_{chem}} \tag{3.98}$$

Where α_D is a constant, k_0 and ϕ_0 are the initial permeability and porosity respectively. It is assumed here that in the absence of chemical damage, there will be no change in the permeability of the system. The porosity (ϕ) after micro-structural alteration is given by [239,240]:

$$\left(\frac{\phi}{\phi_0}\right)^3 = \left(1 + \frac{\Delta\varepsilon_v - \Delta\varepsilon_{swell}}{\phi_0}\right)^3 \tag{3.99}$$

Where the Δ symbol represents the difference between the current and initial value of a parameter, ε_v is the volumetric strain, and ε_{swell} is the swelling strain. It is assumed that the swelling strain is recoverable. The swelling strain is derived from the stress constitutive equation by dividing the swelling stress component by the bulk modulus (*K*):

$$\varepsilon_{swell} = \frac{S_w \omega^0 \Delta C^s}{\bar{C}^c K} \tag{3.100}$$

The development of the two-phase, damage chemo-poroelastic constitutive theory has now been concluded. The following chapters in the dissertation will be based on different experimental protocols established in this dissertation to either obtain the coefficients as input or to evaluate the extent of each coupling process (through experiments). The values of the input parameters used in the numerical simulation of the constitutive equations have been discussed in Chapter-5.

3.5. Conclusions

A fully coupled set of constitutive equations based on non-equilibrium thermodynamics and continuum mechanics principles was developed to address the shale water loss problem. The equations of momentum, water, and gas transport as well as solute transport are coupled to satisfy the thermodynamics laws. Biot theory of poroelasticity for single fluid porous media was extended to porous media containing two immiscible fluids with fluid-shale interaction and consequent micro-structural alteration effects i.e. a two-phase, damage chemo-poroelastic constitutive model was proposed which is a significant advancement of previous works e.g. that of Heidug and Wong [172]. Observations from micro-scale investigations in Chapter-2 were used to guide the development and simplification of the constitutive model. The complexity of the model lies in obtaining the coefficients or material constants as input. This can be achieved through experiments or through already established saturation-dependent relationships. Experiments can also be used to evaluate the significance of each coupling process. What sets this model apart from previous works is that it incorporates the effects of chemical interaction-related swelling and consequent micro-structural alteration. Also, it does not combine the water and gas phases and treats them separately through two continuity equations. The development of the model was guided by certain assumptions which have been stated at different stages of the derivation. The subsequent chapters will be focused on strategies adopted to obtain input coefficients and to validate the assumptions used to simplify the model. The proposed constitutive model can be used to investigate the uptake of the hydraulic fracturing fluid into shale gas formations, design the hydraulic fracturing

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operation, borehole stability in unsaturated organic-rich shale formations and also the prediction of gas production and enhanced recovery of shale gas reservoirs.

Chapter 4. Experimental investigations and system assessments

4.1. Hydration-induced and stress-restrained coupled damage evolution of shale The contents of this chapter are from "A Multiscale Study on Shale Wettability: Spontaneous Imbibition Versus Contact Angle" in *Water Resources Research*, DOI: 10.1029/2019WR024893.

4.1.1. Introduction

The constitutive model developed in the previous chapter (Chapter-3) contains complex physical processes and coupling terms that need to be understood before the model can be solved and used for water uptake characterization of shales. In this chapter, a series of experiments along with theoretical analysis was performed to shed light on the physical processes involved in water uptake and use these understandings for further simplification of the constitutive model. This chapter includes investigating a) the water uptake by shale matrix due to hydration induced damage and the hydration stress limit within the context of wettability characterization (Chapter 4-1), b) the role of chemical osmosis in water uptake and the water diffusion into shale matrix (Chapter 4-2) and c) two-phase flow characterization of tight rocks (Chapter 4-3). All these physical processes are triggered as the hydraulic fracturing (HF) fluid contacts the shale matrix and stays exposed during the shut-in period.

The theories proposed to explain shale matrix hydration and its effect on HF fluid loss are macroscopic perspectives and remain untested at pore-scales. This is mainly because shales are strongly heterogeneous with complex pore networks and poorly understood connectivity. These include water adsorption in clay minerals, osmosis, and capillary suction [241–243]. It has already been mentioned in Chapter-1 that entrapment in micro-fractures is not the focus of this dissertation. Rather, the focus is to assess the extent of

water uptake by shale matrix. Shales have both organic and non-organic porosities that show contrasting behavior to their supposed wettability [99]. Hence, fluid behavior in shales is not well understood due to a lack of practical approaches – both theoretical and experimental [244].

Well shut-in is a typical operation carried out after HF. It is during this shut-in that water loss occurs in shales. Shut-in is performed to allow the fracture to close on the proppant pack as a consequence of stresses on the fracture. During shut-in, chemical breakers also get ample time to break down and reduce the viscosity of the HF fluid. The amount of shut-in can thus have impacts on early and late production rates from the wells which is still an open area of research. It was reported by some researchers that for water-wet formations longer shut-in times led to an increase in cumulative gas production from some fields [245,246]. On the other hand, some studies suggested that long shut-in times did not influence the cumulative production but only the early production rate [73,247].

Irrespective of the duration of a shut-in, water loss occurs in shales post HF. The imbibition of HF fluid by shale matrix and consequent damage is known to be a cause. Such damage is a result of the fluid-matrix interactions such as hydration due to the presence of clay minerals and their associated effects such as the creation of micro-fractures. Some clay minerals can expand up to 20 times their original volume e.g. smectite and mixed-layer illite [248]. The negatively charged clay minerals attract cations and its associated (hydrated) water between the inter-layer platelets leading to swelling [9]. Such swelling can be classified as either crystalline or osmotic. While crystalline hydration causes only a slight expansion by the addition of few molecules of water on clay surfaces, osmotic hydration is much more significant [155,249]. In general, higher valence cations are more strongly adsorbed than low valance cations. Therefore, clay

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minerals that have low valence in-situ cations exhibit higher swelling due to higher exchangeability with high valance cations [21].

Hence, when clay mineral content is significant, it should cause higher amounts of water uptake in shale matrix post-HF. While clay swelling can block the pore system and reduce permeability [250], some studies suggested that the swelling stress could create micro-fractures (along the bedding plane) and improve permeability and hydrocarbon production [251]. It is noted that the damage due to hydration has been known to cause wellbore stability issues [252,253].

Since hydration-induced damage is structural, computed tomography (CT) techniques have been used to characterize its extent [254]. Siddiqui et al. [89] stated that an important parameter - the in-situ reservoir stress - was missing in most laboratory shale hydration experiments. This, in turn, could be the cause for inconsistencies in shale water uptake when its wettability is characterised by different techniques i.e. inconsistencies between contact angle (CA) and spontaneous imbibition (SI) based wettability judgement of shales due to stored water in created micro-fractures. They critiqued that under large in-situ stresses, such significant hydration-induced damage was not possible unless the stresses acting on the matrix element were anisotropic (shearing) in nature.

Attempts have been made to study shale hydration and/or permeability evolution under in-situ stresses [157,255,256]. These studies investigated shale fracture hydration and permeability changes assisted with CT scanning under different confining conditions, but shale wettability was not deciphered. Also, their experimental conditions did not represent truly spontaneous imbibition i.e. forced imbibition was conducted where water was pumped at certain pressures through the inlet side of the core at different confining conditions in laboratory experiments. This creates an additional viscous effect and thus cannot be accurately used to reconcile the discrepancies. In addition, in all these studies

the imaging resolution was not sufficient to capture the micro-scale fracture initiation that is an essential characteristic of the shale hydration phenomenon. The low-resolution images disallow detection and characterization of the micro-fractures e.g. their apertures. Therefore, in this chapter shale hydration under confinement was investigated using an improvised technique aided with high-resolution micro-CT scanning capable of easily detecting pre-existing and newly evolved both macro- and micro-fractures. In addition, the CA measurements were performed to compare with water uptake (SI) measurements. Digital image correlation (DIC) on the high-resolution images was additionally performed to quantify the Green-Lagrangian strains. This was then used to provide new insights into the relation between in-situ stresses and hydration-induced micro-fracture initiation through substantiation with numerical calculations from Poisson-Boltzmann theory. It is noted that the purpose here was not specifically to quantitatively characterize the hydration-induced damage using CT as has been done, but rather to assess the extent of the induced damage under isotropic in-situ stresses and its effect on water uptake in shale. Hence, a combination of experimental and numerical analyses was used to address the issue.

4.1.2. Experimental methodology

4.1.2.1. Materials and fluids

The salts used to prepare the ionic solutions (NaCl, KCl, CaCl₂, and MgCl₂) were procured in powder form from Chem-Supply Pty Ltd Australia (purity = 99.7 wt%). All salt solutions were prepared in deionized (DI) water (18.2 M Ω ·cm resistivity at 25°C). Soltrol-130, an iso-paraffinic solvent (specific gravity γ = 0.76), which was used as model oil, was procured from Chevron Phillips Chemical Company. Soltrol-130 is made up of C₁₂-C₁₄ iso-alkanes with a dynamic viscosity (μ) of 1.14 cP. Additionally, the crude oil (molecular weight = 143.68 g/mol, $\gamma_0 = 0.768$; oil-water interfacial tension $\sigma_{ow} = 11.6$ mN/m) used in this study was donated by an offshore oil and gas company.

4.1.2.2. Organic rich shale sample

The organic-rich shale sample was extracted from Irwin River Coal Measures (IRCM) at a depth of 3012 m from the Perth Basin, Western Australia as previously discussed in Chapter-2 in detail. The organic carbon content was 2.85 wt. % as measured by LECO CN analysis and the mean vitrinite reflectance (R_o) was 0.52 % with a standard deviation of 0.05 %. The major mineral phases of the sample were obtained through XRD analysis. These were quartz (27.1 wt. %), muscovite (14.3 wt. %), kaolinite (9.6 wt. %), chlorite (9.6 wt. %), illite (28.2 wt. %), albite (9.3 wt. %), and pyrite (1.9 wt. %). Pore size distribution (PSD), measured by mercury intrusion and nitrogen adsorption, as well as other properties for this sample, have been reported previously [151]. To measure the concentration of major in-situ cations of the shale, the ion-displacement method was used [22] where a known volume (7 mL) of 1.0 M aqueous NH₄Cl solution was added to a known amount of shale rock powder (2 g; grain size $< 25 \mu$ m) which was oven dried for 24 hours. The mixture was thoroughly agitated for 24 hours using an automatic rotary mixer. The supernatant was collected after settling of powder particles, filtered, and then analysed using inductively coupled plasma optical emission spectrometry (ICP-OES). The average values of several supernatant analyses are presented below (Figure 4.1). It was found that the shale contained mostly Na^+ and K^+ cations followed by Ca^{2+} and Mg^{2+} . The decreasing order of concentration is $Na^+>K^+>Ca^{2+}>Mg^{2+}$.



Figure 4.1 Concentration of in-situ cations in the organic-rich shale tested

4.1.2.3. Contact angle measurements

The contact angle-measuring set-up (Figure 4.2) is made up of a high-definition Basler acA1600-20gm GigE camera with a Sony ICX274 CCD sensor capable of delivering 20 frames per second at two megapixel resolution. The camera is connected to a computer through its designated Pylon software to capture and store the images. ImageJ software (DropSnake plugin) was then used to perform the drop shape analysis and measure the contact angles. Constant average drop size of ~33 μ L was used for consistency i.e. such droplet sizes ensure the size of the heterogeneities on the surface is comparatively much smaller than the droplet. The contact angles were measured once the drops had reached a stable state. The effect of droplet size on contact angle values has been studied previously [257,258] but is not our focus of investigation as the values here are used to make relative or comparative conclusions regarding wettability i.e. using a constant droplet size for all measurements eliminates inconsistencies in such comparisons.

To ensure repeatability of measurements, two or more droplets were tested for each ionic solution, and the average values measured were reported. The heterogeneity of real surfaces such as those of rocks always produces a scatter of measurements and there is no standard consensus regarding the average of how many measurements are considered appropriate. It is however rational to have several measurements resulting in an average value that can be then used for comparisons, such has been followed in this study. The standard deviation of different measurements was within $\sim 5^{\circ}$. All shale substrates used in the contact angle measurements were polished step-wise up to 1200 grit sandpaper. The polishing time was kept constant for all substrates for consistency. The substrates were rinsed with isopropanol followed by 24 hours of vacuuming and oven drying at 105°C. Isopropanol was used as it displaces water, dissolves oil, and dries quickly. It also washes away any residue and does not alter the surface wettability after rinsing due to its nonreactivity with most minerals. Also, the oven temperature (105°C) was set such that it only dries the bulk or surface water (if any) and does not affect the clay-bound water. The substrates were then allowed to reach room temperature (~25°C) in a desiccator before the contact angle measurements. It is noted that the use of plasma cleaner is limited as it can remove the organic matter on the surface along with contaminations.



Figure 4.2 Schematic of contact angle measurement setup (Source: own work)

The surface roughness obtained after polishing was measured with the Bruker Contour 3D GT-K optical profiler utilizing the green/white light interferometry technique (Figure 4.3). The average surface roughness (S_a) measured was around 0.77 µm for several substrates. Thus, a considerably flat surface was created, which enables high repeatability of the contact angle measurements [259]. It is noted that the scale bar (Figure 4.3) from - 18 to +23 µm includes the few outlier points which make the lowest pit height and the highest peak height vary by a significant margin. However, the average roughness of 0.77 µm reflects all the surface profile contributing points. It is challenging to have ultrasmooth surfaces for natural materials such as rocks; however, the effect of varying roughness on contact angle measurements was minimized by polishing all substrates down to a similar level. It is noted that some equations such as Wenzel or Cassie-Baxter can be used for correction of surface roughness on the contact angle, however, recent studies raised a significant question on the applicability of the proposed equations for geomaterials [260]. It is noted that in such measurements, the average surface roughness

 (S_a) of the scanned area (A) [261,262] is characterized by the average of the absolute value of the height measured [263]:



Figure 4.3 Surface profile of shale substrate after 1200-grit sandpaper polishing

4.1.2.4. Imbibition experiments

Shale hydration was performed through spontaneous imbibition (SI) experiments. Several small cores (6.5 mm diameter x 5 mm length) were drilled from a larger rock sample. The cores were then oven-dried, cooled in a desiccator to room temperature, and later suspended in an analytical weighing balance (Sartorius Entris323-1S; 0.0001 g accuracy), while being completely immersed in the liquid (Figure 4.4). For consistent imbibition comparison among different samples, quantitative metrics are needed. However, it is known that standard metrics such as the Amott wettability index [264] or the USBM wettability index [265] cannot be applied to shale rocks due to their tight pore network [89]. Hence, to quantitatively characterize imbibition in this study, the normalized weight increase of the samples is used i.e. increments in sample weights (g) with respect to their original weights (g) as shown in Eq. 2. This is equivalent to the percentage (%) increase

in weight of the samples (equivalently the percentage of fluid imbibed) which is plotted against time in the subsequent sections.

% increase in weight =
$$\frac{W_t(g) - W_{\text{original}}(g)}{W_{\text{original}}(g)} \times 100$$
(4.2)

where W_t is the weight of the sample after a certain imbibition time t and $W_{original}$ is the original sample weight. Any increase in sample weight was recorded until equilibrium was reached. Equilibrium here refers to the state in time where no more increase in sample weight is observed with the caveat that the true end of osmotic processes is unknown and weight might still be increasing, albeit extremely slowly. The imbibition tests were performed for 0.1 M and 0.5 M ionic solutions (NaCl, KCl, CaCl₂, and MgCl₂). It must be noted that all-faces-open (AFO) boundary conditions were used during the tests as the liquid was free to enter the core from all exposed faces.



Figure 4.4 Imbibition experimental setup

4.1.2.5. X-ray micro-computed tomography (μ-CT) imaging

Micro-CT imaging non-destructively maps the variation of relative radio-density in a sample so that the internal structure of the sample can be visualized [266]. Hence, to capture any change in internal sample structure due to fluid exposure, the samples were imaged before and after spontaneous imbibition, both, in the unconfined and confined state, using a high resolution, large field, helical μ -CT scanner. The μ -CT scanner

specifications are reported in Sheppard et al. [267]. Scanning was performed at 120 kV voltage and ~100 μ A current resulting in a resolution of 12.5 μ m voxel size. Recent advances in μ -CT image processing have been utilized to investigate the petrophysical and rock mechanical properties [166,268–270]. To perform a voxel to voxel comparison between the images obtained before and after the experiments, the images were registered using a 3D image registration technique [267,271,272]. Registration is a process wherein different image data sets are transformed into one coordinate system (c.f. [273]). After image registration, the converging active contours (CAC) method was used for image segmentation [274]. This method uses an advanced approach based on the watershed algorithm and active contour methods. Segmentation of an image simply means partitioning it into multiple segments to make it more meaningful and easier to visualize. Avizo 9.7.0 software was used for 3D visualization of the tomographic images.

For the experiment, two cylindrical cores (S1 and S2) of diameter 25.4 mm and length 30 mm were drilled out of the organic-rich shale. Both cores were first dry scanned after which S1 was exposed to de-ionized (DI) water at ambient conditions under an unconfined state such that one end of the core was exposed to water. Periodically the increase in weight of S1 was recorded as the water imbibed into the shale until equilibrium was achieved. Then, one end of S2 was similarly exposed to water under confinement of ~3.45 MPa (500 psi) by placing it in a special aluminium core holder which was X-ray transparent. Since the mounting of S2 inside the core holder did not allow for periodical recording of the continuous incremental weight, thus initial dry and final wet weight was used to estimate the amount of water imbibed. The duration of exposure in this test was the time taken by S1 to reach equilibrium. Both S1 and S2 were scanned again in the wet state. After the wet scan, S2 was oven-dried at 105°C to restore the original weight by evaporating the imbibed water. Then, one end of S2 was just immersed in crude oil and

the increase in weight was recorded until equilibrium was reached. It is noted that after oil imbibition a re-scan of S2 was not performed as no effect of oil on the micro-structure was expected. Also, only DI water was used to study the effect of confinement as it causes the most significant alteration of shale micro-structure due to its high reactivity with clays; Environmental Scanning Electron Microscopy (ESEM) was later used to additionally examine the micro-structural changes induced by each ionic solution.

It was highlighted earlier that previous investigations of shale hydration under confinement were performed under dynamic imbibition conditions where some injection pressure was used to hydrate the core [158,255,275]. However, in this study, to represent truly spontaneous imbibition conditions, the core holder cap was left slightly untightened leaving a small space between the cap and the sample surface, Figure 4.5. To prevent the confining liquid (DI water) from leaking through this space, silicon glue was applied. Then, through the inlet, DI water was introduced in the space between the cap and sample including the tubing. Subsequently, the inlet was sealed after water overflow, signifying complete filling of the tubing and the core holder space. The core holder was held upside-down to nullify the gravity effects. The confining pressure was applied and maintained around the core by connecting the Teledyne ISCO pump to the confining pressure port.



Figure 4.5 (a) Design and (b) setup of spontaneous imbibition test using confinement pressure

4.1.2.6. Environmental SEM (ESEM) imaging

Environmental Scanning Electron Microscopy was additionally used to investigate the occurrence of micro-fractures in the samples exposed to the various solution at very high resolution [276]. ESEM has an essential advantage over the traditional SEM, as it allows direct observation of wet samples without any preliminary treatment, though substrates could also be coated with reflective materials for better imaging. Several 4 x 4 x 4 mm cubic sub-sample substrates were cut out of the organic-rich core and polished stepwise up to 1200 grit sandpaper to obtain a smooth surface. The substrates were rinsed with isopropanol followed by 24 hrs vacuuming at 105°C after which they were transferred to a desiccator to reach room temperature and subsequently moved to the FEI Quanta 200 ESEM chamber at the target temperature of 25°C. The whole surface of the substrates

was scanned to ensure no pre-existing micro-fractures existed. The samples were then submerged in different aqueous ionic solutions (NaCl, KCl, CaCl₂, and MgCl₂) at different concentrations (0.1 M and 0.5 M) for 24 hrs. After fluid exposure, the samples were again examined with ESEM to investigate the formed micro-fractures.

4.1.2.7. Digital image correlation (DIC)

To investigate the creation of micro-fractures under different stress scenarios, 2D DIC was applied to the μ -CT z-direction slices, to calculate the generated strain in the sample due to hydration. This technique was introduced in the 1980s to replace expensive and in many cases limited physical strain-measuring devices [277,278]. Its ability to estimate strains with reasonable accuracy has been well documented with experimental validation using strains measured by devices such as strain-gauges [279–281]. In particular, DIC proved to be efficient in detecting micro-cracks in geo-materials [282,283]. Particularly, it was shown that for in-plane and small-strain measurements (such as in this study), DIC is accurate [277,284]. The steps that were followed during the 2D DIC analysis of μ -CT slices are outlined below:

i) The intensity of dry and wet μ -CT slices was first equilibrated using a developed Matlab code, i.e. their greyscale histograms are adjusted (and matched) to have a uniform greyscale across images.

ii) The equilibrated images are then converted to 8-bit format and pixel-to-pixel registration is performed [285] for exact geometrical alignment of both images.

iii) The equilibrated 8-bit registered dry-wet images were loaded into Matlab code (Ncorr) [286] for DIC analysis where the dry image serves as the reference image and the wet image as the current image. The dry image (reference image) is divided into several smaller circular subsets. Deformation of these subsets is then tracked on the wet image

based on the transformation of the coordinates of the points within the subsets. In Ncorr a linear first order transformation is used:

$$\tilde{\mathbf{x}}_{cur_{i}} = \mathbf{x}_{ref_{i}} + \mathbf{u}_{rc} + \frac{\partial \mathbf{u}}{\partial \mathbf{x}_{rc}} (\mathbf{x}_{ref_{i}} - \mathbf{x}_{ref_{c}}) + \frac{\partial \mathbf{u}}{\partial \mathbf{y}_{rc}} (\mathbf{y}_{ref_{i}} - \mathbf{y}_{ref_{c}})$$
(4.3)

$$\tilde{y}_{cur_i} = y_{ref_i} + v_{rc} + \frac{\partial v}{\partial x_{rc}} (x_{ref_i} - x_{ref_c}) + \frac{\partial v}{\partial y_{rc}} (y_{ref_i} - y_{ref_c})$$
(4.4)

Where x_{ref_i} and y_{ref_i} are coordinates of an initial reference subset point on the dry image, x_{ref_c} and y_{ref_c} are coordinates of the centre of the reference subset, \tilde{x}_{cur_i} and \tilde{y}_{cur_i} are coordinates of the subset in the wet image, u and v are displacements in the x and y directions, respectively. Subscripts i and j indicate the relative location of points on dry and wet images with respect to the centre of the respective subsets. Also, subscript rc implies that transformation is being tracked from the reference (dry) to the current (wet) image. Green-Lagrangian strains are then calculated (Eqs. 4.5 - 4.6) for each pixel based on patch pixel displacement in a selected region of interest using the displacement gradients. Displacement gradients used in the strain calculations are obtained using the strain window algorithm. More in-depth details of DIC calculations using Ncorr can be found in Blaber et al. [286].

$$\varepsilon_{\rm xx} = \frac{1}{2} \left(2 \frac{\partial u}{\partial x} + \left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial v}{\partial x} \right)^2 \right) \tag{4.5}$$

$$\varepsilon_{xy} = \frac{1}{2} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \frac{\partial u \partial u}{\partial x \partial y} + \frac{\partial v \partial v}{\partial x \partial y} \right)$$
(4.6)

$$\varepsilon_{yy} = \frac{1}{2} \left(2 \frac{\partial v}{\partial y} + \left(\frac{\partial u}{\partial y} \right)^2 + \left(\frac{\partial v}{\partial y} \right)^2 \right)$$
(4.7)

4.1.3. Results and discussion

4.1.3.1. Contact angle measurements

Soltrol-130 and crude oil almost completely spread (~0° contact angle) on the shale surface, whereas DI water exhibited partial spreading (Figure 4.6). Furthermore, the

contact angle increased with ionic concentrations for both, monovalent (NaCl, KCl) and divalent (CaCl₂, MgCl₂) ionic solutions (Figure 4.7, Figure 4.8, and Table 4-1). The average contact angle values indicate that the shale had a higher affinity for more diluted solutions. Also, the rock seemed to have a slightly stronger affinity towards monovalent solutions. This behaviour was also apparent at higher concentrations except for CaCl₂ where the rock seemingly had a stronger affinity for CaCl₂ than NaCl. The weakest affinity was observed for MgCl₂ at both low and high concentrations.





Figure 4.6 Liquid drops on shale surface for (a) Soltrol-130, (b) crude oil and (b) DI

water in air



Figure 4.7 Brine drops on shale surface for (a) 0.1M NaCl, (b) 0.1M KCl, (c) 0.1M CaCl₂ and (d) 0.1M MgCl₂ brines in air at ambient conditions



Figure 4.8 Brine drops on rock surface for (a) 0.5M NaCl, (b) 0.5M KCl, (c) 0.5M



	Contact Angle, degrees			
Concentration, M	NaCl	KCl	CaCl ₂	MgCl ₂
0.1	32.7	31.1	35.9	41.3
0.5	39.4	35.9	37.6	47.4

 Table 4-1. Contact angles for different aqueous ionic solutions in air at ambient conditions

4.1.3.2. Imbibition experiments

Spontaneous imbibition of liquids into dry samples was measured and the samples' percent weight increase (Eq. 4.2) was plotted versus elapsed time (Figure 4.9). All tests were run for approximately 170 hours although equilibrium was reached much earlier, between 20-50 hours depending on the composition of the imbibed liquid. After the SI experiments, the samples were kept immersed in the respective ionic solutions and weighted again after three months; no further weight increase was found, signifying that the equilibrium was reached.

Clearly, divalent ionic solutions (CaCl₂, MgCl₂) were imbibed more rapidly than the corresponding monovalent ionic solutions (NaCl, KCl) at both, low and high salt concentrations. Moreover, except for KCl, all ionic solutions exhibited lower imbibition at a higher salt concentration (0.1 M versus 0.5 M). Soltrol-130, on the other hand, imbibed the least.



Figure 4.9 Weight increase of shale sample vs. time for (**a**) 0.1 M solutions and (**b**) 0.5 M solutions with Soltrol-130 shown on both plots (measured at ambient conditions)

4.1.3.3. Discrepancies between wettability estimated by contact angles and spontaneous imbibition

Contradicting results for the shale wettability were observed from contact angle (CA) and spontaneous imbibition (SI) measurements, which has also been reported previously by other researchers [75,287]. For instance, Soltrol-130 completely spread on the shale surface implying a very high affinity of the rock for oil. It is thus expected that the oil is imbibed most by the rock. However, on the contrary, Soltrol-130 imbibed least compared to any ionic solution at any concentration. Also, among the ionic solutions, MgCl₂ exhibited the highest contact angle at both 0.1 M and 0.5 M ionic concentrations, implying that the shale had a lower affinity for it, whereas, again contrarily, it was most imbibed at both ionic concentrations tested. This contradiction between CA- and SI-based wettability is an indication of the different processes occurring in each experiment; and these need

to be scaled correctly so that they can be consistently compared, and water uptake can be properly characterised.

CA is a localised measurement that is significantly influenced by multiple factors such as surface roughness [288–290], surface cleanliness [291–293], and mineral heterogeneity [294,295]. Such measurements are also typically conducted on a two-dimensional (2D) flat surface; pseudo-flat for a real geo-material as nano-level surface imperfections cannot be removed. It is thus noted that in-situ pore-scale contact angles during SI can be significantly different from those observed on flat surfaces. It was in fact proven through advanced image analysis techniques that pore-scale contact angles have many wide distributions [295]. It is realized that any surface CA measurement technique would find it challenging to produce an average CA representative of the pore-scale CA distribution owing to the same factors mentioned above (roughness, cleanliness, heterogeneities). These factors give rise to what is called contact angle hysteresis (CAH) that is usually characterized (on the surface) by advancing and receding CAs. However, it is still debatable to conclude, for unconventional rocks which have a very complex pore structure, whether a single average surface CA or even CAH can be representative of insitu pore-scale contact angles. Hence, as is being increasingly realized [89,296], SI seems more likely to be representative of fluid behaviour in a rock as it considers the pore-scale mineral heterogeneity, pore morphology, and any clay mineral effects. In lieu of this, more advanced techniques such as SI combined with imaged in-situ pore-scale CAs are gaining prominence [295,297] which gives newer pore-scale insights. For instance, for a water-wet carbonate rock the average surface CA was compellingly found to be equivalent to the average CA of the pore-scale CA distribution but the similar observation was not observed for mixed-wet or oil-wet carbonates [297].

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Fixating henceforth the discussion on SI, the assumption that capillary forces are the only driving forces in SI can lead to misinterpretation as it is well known that the existence of clay minerals in the rock induces additional chemo-mechanical forces which interfere [22,146]. We thus postulate that a) entropic forces and b) chemically driven micro-structural alterations can significantly influence fluid imbibition which is elaborated further below.

4.1.3.3.1. Osmotic forces

Entropic effects (caused by ion concentration gradients), are well known to occur in shales [76,145,298,299]. It is recalled here that we measured the ionic concentrations of the major cations in the shale sample by ICP-OES; and decreasing in-situ cation concentrations (Na⁺>K⁺>Ca²⁺>Mg²⁺) were observed i.e. monovalent cations had a much higher concentration. Therefore, the observed lower uptake of Na⁺ and K⁺ solutions when compared to Ca^{2+} and Mg^{2+} solutions, is apparently related to the native (relatively) high concentration of Na⁺ and K⁺ ions in the shale. This is supported by the reduced water imbibition at higher cation concentrations (Figure 4.9). Interestingly, at 0.5 M ionic concentration, the increasing trend of ionic solution uptake (Na⁺<K⁺<Ca²⁺<Mg²⁺) follows exactly the inverse trend of major in-situ cation concentration in the shale (Na⁺>K⁺>Ca²⁺>Mg²⁺). A similar inverse correlation was observed at 0.1 M concentration $(K^+ < Na^+ < Ca^{2+} < Mg^{2+})$ except that K^+ uptake was lower than that of Na⁺. The nonmonotonous behaviour of K⁺ has been observed previously [299–301]. The reason for this exceptional behaviour is that K⁺ has swelling inhibiting characteristics due to its versatile hydration and leachability properties. Mechanistically, the K⁺ ion has the smallest hydration radius and inhibits swelling by forming only one to two hydration layers while other cations, for example, Na⁺, can hydrate up to three or even four layers

[29,302]. Therefore, these observations suggest the presence of entropic forces in the shale sample to different extents.

4.1.3.3.2. Chemically driven micro-structural alterations

Micro-structural alterations were investigated by μ -CT and ESEM imaging. Such imaging allows for direct visualization of the micro-structural alteration that occurred due to chemical reactions of the imbibed ionic solutions with the clay minerals. Before delving into details, a summary of these multi-scale techniques is presented below in Table 4-2.

Imaging method	Objective	Specific comments	Voxel or Pixel size	Resolution
		Samples can be	12.5 µm	0.08 pixels/µm
μ-CT		imaged under		
	To detect	confinement		
	hydration induced			
	micro-structural			
	alteration at their	Samples can be		
FSFM	respective scales	imaged only at	0.05 µm	20 pixels/µm
LSLIVI		unconfined		
		conditions		

Table 4-2 Summary of multi-scale techniques used in this study

4.1.3.3.2.1.µ-CT imaging

 μ -CT was used to image cylindrical cores before and after spontaneous imbibition of water and oil (see Section 4.1.2.5). The equilibrated increase in sample weight was 1.27 % for unconfined S1 (black curve in Figure 4.10) and 0.7 % for confined S2 after 800 hours (i.e. 33 days) of water imbibition (green triangle in Figure 4.10). Interestingly, the amount of imbibed oil was just 0.19 % which is much lower than the amount of water imbibed at both unconfined and confined conditions (red curve in Figure 4.10).



Figure 4.10 Increase in sample weight vs. time for DI water and oil during imbibition

The grey-scale tomographs and segmented images showing the dry and wet unconfined and confined samples are visualized in Figure 4.11 and Figure 4.12. Note that the bright spots in the images are constituents with high X-ray absorption (e.g. pyrite).

Clearly, unconfined S1 generated several new hydration-induced micro-fractures, while hydration during (confined) S2 imbibition did not generate any new micro-fractures. In fact, a pre-existing micro-fracture was almost completely closed (at least at the scale of the resolution limit) under 3.45 MPa confinement. Such micro-fracture closure leads to a

dramatic decrease in permeability, consistent with significantly lower water imbibition in S2 (Figure 10). Much lower imbibition of oil in unconfined conditions is therefore linked to its non-reactivity with clays and inherent inability to generate new micro-fractures or matrix adsorption.

The evolved micro-fractures in S1 were parallel to the weak bedding planes. Hydration of clay minerals along these weak planes generates stresses which are sufficiently strong to fracture the rock when it is not countered by any external forces. However, under 3.45 MPa confinement, existing micro-fractures closed, and no new fractures appeared. This also implies that swelling stresses are less than 3.45 MPa in magnitude.

Furthermore, for S1, the segmented dry fracture porosity (i.e. the fracture porosity visible on the μ -CT images) was ~1.5 %, which increased approximately two times to 2.8 % after DI water imbibition. At equilibrium, the total amount of water imbibed was 0.497 cm³, which, when divided by the bulk volume $(\frac{\pi}{4}(2.54cm)^2(3cm) = 15.2cm^3)$, results in a mass-balance porosity of 3.3% which is very close to the segmented (fracture) porosity (2.8%) of the wet scanned S1.



Figure 4.11 3D visualization of grey scale tomograph of dry and wet samples at unconfined and confined conditions



Figure 4.12 3D visualization of segmented images to identify the micro-structural changes due to water uptake at (a)-(f) unconfined conditions and (g)-(l) confined conditions (Note: First column is the segmented image, second column is a transparency filter showing micro-fractures inside, and third column is extracted micro-fractures)

In addition, it is noted that both the evolved and pre-existing micro-fractures have rough textures. Such roughness was shown to play an additional role in dictating the wettability of the compositionally homogenous rocks such as carbonates (made up of > 95% calcite) [297]. The trapping of water in tiny roughness associated interstices caused lower wetting-phase pore-scale contact angles [297]. In such cases with high mineral homogeneity, it is easier to implicate specific parameters affecting the wettability. In shales, however, this becomes challenging due to large compositional heterogeneity caused by the presence of various minerals such as clays, organic matter, quartz, calcite, etc. The above analysis shows that while the micro-structural alteration under no external stress can lead to micro-fracture generation and permeability enhancement thus more water uptake, such behaviour is very limited under confining pressure. This is consistent with what was observed in Chapter-2 where the isotropic stress prevented the sample swelling thus micro-structural alteration i.e. shearing stress, on the other hand, caused damage to the sample.

4.1.3.3.2.2.ESEM imaging

Dry ESEM images show the presence of clay minerals (Figure 4.13 (a)). In addition, initial ESEM images of the dry shales showed no micro-fractures on the scanned surfaces (representative image is shown for one of the substrates in Figure 4.13 (b)). However, after 24 hours of exposure to the various ionic solutions, several micro-fractures of varying apertures were observed (Figure 4.14 and Figure 4.15). Water uptake created micro-fractures due to induced hydration when no hydrostatic confinement was applied on the sample even though the shale sample was rich in illite which is not as swelling as smectitic clay minerals. No micro-fractures were observed on the sample surface exposed to the 0.5 M KCl solution (as seen on the lower magnification image, Figure 4.15 (b)).

The average fracture apertures (w_f) for rest of the cases are also shown on the figures, it ranged from 0.2 μ m – 3.6 μ m.



Figure 4.13 (a) High magnification ESEM image showing presence of clay minerals, (b) Low magnification representative dry image showing no pre-existing fractures present



Figure 4.14 Micro-fractures developed in organic rich shale after 24 hours exposure time to (a) 0.1 M NaCl, (b) 0.1 M KCl, (c) 0.1 M CaCl₂, and (d) 0.1M MgCl₂ brines



Figure 4.15 Micro-fractures developed in organic-rich shale after 24 hours exposure time to 0.5 M (**a**) NaCl, (**b**) KCl (shown at a lower resolution of 300 μm to signify absence of micro-fractures over the whole surface), (**c**) CaCl₂, and (**d**) MgCl₂ brines

ESEM and μ -CT images show that under unconfined conditions, water-wetness is overestimated by SI due to the creation of the micro-fractures; and confined conditions are required for a more reliable wettability estimate. However, lower imbibition of oil under unconfined conditions when compared with DI water even at confined conditions (Figure 4.10) asserts the water-wetness of the shale when the water-matrix and water-microfracture interactions are considered.

The observed localized micro-structural alteration is consistent with previously reported micro-macro scale permeability variation in shales caused by such ionic solutions. For instance, an increase in shale permeability was reported when exposed to relatively high CaCl₂ concentrations (1.0 M) [22,303,304]. Similarly, higher electrical conductivity, higher volumetric strain, and lower osmotic pressure were observed in clay-rich specimens at higher CaCl₂ concentrations [305]. Kwon et al. [303] hypothesised that such behaviour is related to the cation selectivity of clay surfaces, while Rao and Mathew [304] and Roshan et al. [22] discussed that this behaviour is linked to different diffuse double layer (DDL) thicknesses, where different ionic solutions influence the transport properties differently, e.g. by capillary or osmotic flow mechanisms. In fact, it is intuitive that a micro-scale coupling process between the pore structure and DDL thickness exists which in turn leads to the macro-scale permeability variation when the shale is exposed to different ionic solutions especially in rocks that are not rich in swelling smectitic clay minerals like montmorillonite. The creation of micro-fractures in this study, as observed through µ-CT and ESEM for a shale rich in illite with negligible smectite, is explained further through theoretical interpretations.

4.1.3.3.2.3. Magnitude of hydration induced strains

In order to assess whether micro-fractures were formed under tension and to investigate the likelihood of micro-fracture development under confined stress, 2-D digital image correlation (DIC) was performed on high-resolution (12.5 µm/pixel) dry-wet orthogonal slices in the z-direction (Figure 4.16) from µ-CT imaging. In addition, if any microfractures were not segmented during the segmentation of the 3D μ -CT images, they would be identified as high strain (ε) regions. The strain field (Figure 4.17) determined by DIC shows high positive strain (red colour) around newly generated micro-fractures, especially in the xy- and y-direction whereas the pre-existing micro-fracture is surrounded by negative strain. This implies that the width of the pre-existing microfracture was reduced (compression) due to the creation of new micro-fractures on either side of it, which opened up as a result of tensile failure (hence positive strain). In fact, it was found that the average width of the pre-existing micro-fracture was reduced by 20 μm (as measured via ImageJ software), however significant new micro-fractures also appeared. Such coupled dynamics of new fracture-openings and existing fracture-closures were also similarly observed in shale pyrolysis studies where temperature-induced fracture evolution caused partial or significant closure of existing fractures [306,307]. This indicates that studying the local strain is important to accurately characterize the permeability alteration due to fracture dynamics. Also, no significant high strain was observed elsewhere implying that the 3D segmentation of the μ -CT images in detecting evolved micro-fractures was accurate.



Figure 4.16 Orthogonal (z-direction) greyscale (792nd) slice of the registered (a) dry S1,

and (\mathbf{b}) wet S1 after 33 days of water imbibition.










Figure 4.17 Strain-fields (ε) in the (a) x-, (b) xy-, and (c) y- directions

Further to the strain calculations, in order to quantify the induced stresses caused by these micro-structural changes, the repulsive forces created between two negatively charged surfaces were estimated via the linearized Poisson-Boltzmann equation [159]. In this calculation, it was assumed that the surface charge is not significantly high. Note that this assumption was made in relation to the highly charged artificial materials typically considered (in material science), while the clay surfaces considered here have only a relatively low negative surface charge. It was also assumed that the Stern layer is absent, and the interaction distance is well-beyond the attractive Van der Waals force boundary. With the above assumptions, one can develop the following expression for the double layer disjoining pressure (Π_{EDL} ; Eq. 4.8) [308]:

$$\Pi_{\rm EDL} = 64 k T n^{\infty} \tanh^2 \left(\frac{z e \psi_0}{4 k T}\right) \exp(-\kappa d)$$
(4.8)

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_p k_B T}{2n^{\infty} e^2 z^2}}$$
(4.9)

where κ is the Debye length (given by Eq. 4.9), *d* is the distance between surfaces, *T* is temperature, ψ_0 is the surface potential, n^{∞} is the ionic concentration in the bulk solution, *z* is ion charge, ε_p is the permittivity of pore fluid in presence of charged surfaces, *e* is the elementary electric charge and k_B is Boltzmann's constant. Eq. 4.8 was subsequently solved for two constant surface charges with monovalent and divalent solutions having different ionic concentrations (0.1 M and 0.5 M). The values of the different parameters used in the calculation are tabulated below (Table 4-1). It is clear (Figure 4.18) that the highest repulsive pressure generated hardly passes 1.4 MPa (200 psi) for $\psi_0 = 25$ meV at surface separation < 3 nm. Also, as the ion valency and concentration increase, the DDL thickness decreases.

Parameter	Value	Unit	
е	1.60x10 ⁻¹⁹	Coulomb (C)	
Т	303	Kelvin (K)	
n^{∞}	100 and 500	mol/m ³	
Ζ	+1 and +2	Unitless	
ϵ_p	6.95x10 ⁻¹⁰	Farads/m	
k _B	1.38x10 ⁻²³	Joule/K	
ψ_{0}	5 and 25	meV	
	l	l	

Table 4-3 Values of different parameters used in Eqs. 4.8 and 4.9





Figure 4.18 Repulsive disjoining pressure (psi) for monovalent and divalent ionic solutions between two negatively charged surfaces as a function of distance between the two surfaces of potential (a) $\psi_0 = 5$ meV and (b) $\psi_0 = 25$ meV

Based on the above theoretical investigation, an explanation for the creation of microfractures in the illite-rich shale is now made. Mercury and nitrogen-adsorption porosimetry [151] showed that a significant number of nano-pores were present in the shale used in this study i.e. ~39% of the pores lay in the range of 2.7 to 7 nm. Thus, in such tight nano-pores, the overlapping of the developed electric or diffuse double layer (DDL) causes extra repulsive stresses to act on the pore walls which forces the rock apart at unconfined conditions (externally un-countered). This is further confirmed by high magnification wet ESEM images (representative image is shown for 0.5 M NaCl solution (Figure 4.19) where clay minerals that caused micro-fracture creation are visible.



Figure 4.19 Representative ESEM image showing clay minerals within created micro-

fracture

On a laboratory scale, despite the argument that spontaneous imbibition tests are better indicators of fluid behaviour in rock (as several factors such as compositional heterogeneity, pore structure morphology, clay content, etc. are incorporated), reasonable conclusions can only be drawn if the correct stress conditions are taken into account. Under confined conditions where swelling and/or consequent micro-fracture initiation is inhibited, wettability judgment can be quite different from that for unconfined conditions. It is also noted that the stress regime discussed in this study is of hydrostatic nature. The effect of shear stresses on the formation of micro-fractures was discussed and shown in Chapter-2 [146].

4.1.4. Conclusions

One of the hypotheses of significant water uptake (HF fluid uptake) in shale matrix is linked to its fluid forces controlled by entropic (osmosis) and capillary forces [241,309] as well as consequent micro-structural alteration [158]. Capillary forces in particular are controlled by shale wettability that is also important for gas reserve estimates, production efficiency, environmental impacts, etc. [89,310]. However, detailed wettability quantification controlling water uptake in shale and the various mechanisms responsible are still only poorly understood. In particular, contact angle (CA) and spontaneous imbibition (SI) measurements have resulted in contradictory results [79,90,91,95,99,101,122,157,311,312]. Thus, in this Chapter, the CA and SI tests for various liquids (aqueous and oleic) were performed to determine the shale wettability having the main objective to a) reconcile the previously reported contradictions in the literature and b) investigate the micro-structural evolution and associated swelling stress generation. To do so, the shale samples subjected to the SI tests were also characterized in the dry and wet state by ESEM and μ -CT imaging.

It has been argued that SI is more representative of shale wettability because CA measurements are localised and sensitive to multiple factors such as surface roughness while the SI can take into account the heterogeneity, pore structure morphology, and clay minerals effect. However, new conclusions from our study show that the affinity of the shale for a specific liquid (i.e. wettability) obtained from SI is much more strongly dependent on the chemistries of the liquid and the in-situ constituents of the rock than contact angles. While CA for 0.1 and 0.5 M concentrations only varies by a few degrees amongst different ionic solutions, the SI measurements vary by one order of magnitude in some cases. Additionally, the measured in-situ cation concentration showed that monovalent cations (Na⁺, K⁺) were present in the samples in significantly higher amounts than divalent cations at both, low and high, concentrations. This implies that wettability judgement of clay-rich rocks (like shales) needs to be made with caution and with full knowledge of the rock's various mineral constituents and their individual behaviour with the respective fluid's chemical composition.

Further, to prevent bias in wettability judgement, we showed that it is essential to eliminate micro-fracturing during the SI tests (i.e. the tests should be conducted under confined conditions). The evolved micro-fractures enhance the water-based fluid uptake and thus biased wettability judgement is made. It is noted that such micro-fracture initiation is caused by chemo-mechanical processes (clay swelling due to hydration and entropic ion movement).

More importantly, theoretical investigations using stress calculations via the Poisson-Boltzmann equation revealed the cause of micro-fracture creation in non-smectitic shales such as the one used in this study. We showed that the repulsive stresses due to electric double layer overlapping in tight nano-micro-pores lead to such creation of microfractures even in rocks containing only slightly swelling clay minerals such as illite.

Such theoretical calculations also showed that when the hydration stresses are not strong enough to overcome the confinement pressure, no micro-fracture evolution is expected whether in smectitic shales or non-smectitic shales. Thus, unprecedented rigour in wettability judgement based on CA and unconfined SI led to over-estimated waterwetness due to the creation of micro-fractures giving rise to discrepancies. Water uptake measurements under reservoir stress conditions are therefore required. For instance, in this study, higher water uptake in confined conditions compared with oil uptake at unconfined conditions accurately implies (not over-estimates) the water-wetting nature of this specific shale rock.

Importantly, the results of this study show that the swelling stresses cannot cause microstructural alteration under isotropic stress conditions and the magnitude of swelling stress generated for the tested organic-rich shale was relatively low to induce changes to the sample. This identifies the low magnitude of the swelling process in the constitutive theory and will later assist in further simplifying our constitutive model for the numerical solution.

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4.2. Chemical osmosis and diffusion process in organic-rich shales Most of the contents of this chapter are from "Configurational diffusion transport of water and oil in dual continuum shales" in *Scientific Reports*, DOI: 10.1038/s41598-021-81004-1.

4.2.1. Introduction

Shales are tight rocks with complex properties [313–315]. Understanding water and oil flow in shale matrix is critical to understand the role of shale matrix in causing fluid loss during hydraulic fracturing which is a major environmental and technical concern [67,82]. There has been a wide discrepancy in water uptake observed in many shales around the world as discussed in Chapters-1 and 4.1. In presence of air (inviscid medium), oil spreads more than water on a shale's surface, whereas its capillary uptake by the shale pores is significantly lower than that of water. This has led to an incomplete understanding of water and oil diffusion mechanisms in shales igniting research interest in the fundamental-level causes of such an intriguing phenomenon. Implicating water reactivity with clays and consequent micro-fracture initiation as the sole reason for higher water uptake by shale matrix was confuted in a recent study [129]. Therein, it was revealed that even when micro-fracture initiation was avoided with confinement, water uptake by shale matrix was still much higher than oil uptake.

The water and oil spreading is usually assessed by contact angle (CA) measurements and the uptake capacities by spontaneous imbibition (SI) tests [89] i.e. when capillarity is considered as the sole driving force of imbibition, the process is referred to as spontaneous imbibition [316]. It is usually not known whether the water or oil droplets during CA measurements on shale are in a Wenzel state, Cassie-Baxter state, or a meta-stable Cassie-Baxter state [317–319]. What is clear is that the complete spreading of oil (zero CA) does imply its attainment of the lowest energy state with no energy barriers remaining to be overcome [320]. On the same sample in an inviscid medium, slight water repellence (acute CA) implies there are active energy barriers associated with the water droplet. This is an important implication since during capillary flow, the porous surface area is not polished, and hence offers energy barriers for the water and oil to overcome. It is, however, interesting to note that the effect of such energy barriers on the change in CAs (and hence its influence during capillary flow) may not be significant [320,321]. Therefore, the stark difference in water and oil uptake capacities of shale pores requires an explanation beyond the concept of wetting states and energy barriers. In this chapter, therefore, first, the role of chemical osmosis as an additional driving force of water in shale matrix is investigated. It is then postulated and later confirmed that the existence of configurational diffusion in the shale pore system is another controlling mechanism of flow.

4.2.1.1. Osmosis in shales

Osmosis across a membrane refers to the transport of water (or solvent) from a region of higher water activity to lower water activity [85,322]. A higher water activity corresponds to lower solute concentration whereas a lower water activity corresponds to higher solute concentration i.e. the flow of water during osmosis is from diluted to concentrated solutions [323]. When thermal and electrical equilibrium prevails, the flow of pure solvent due to a chemical gradient across a membrane is referred to as chemical osmosis (or chemo-osmosis). The flow of solvent will cease only after pressure across both sides of the membrane is balanced.

Clay-containing soils and rocks (e.g. shales) have been known to act as semipermeable membranes that cause chemo-osmotic flow by inhibiting the passage of solutes [324]. The extent to which a semipermeable membrane inhibits the entry of ions into the pore space is called its membrane efficiency [325]. It is also known as chemo-osmotic efficiency (ω) or reflection coefficient (σ) [326,327], but to not confuse with symbols used in earlier chapters, it will be denoted by \Re in this dissertation. An ideal membrane is theoretically defined as one that completely blocks the flow of solutes i.e. its membrane efficiency is unity ($\Re = 1$). Contrarily, a membrane that allows complete passage of solutes has a membrane efficiency of zero ($\Re = 0$). Shales are classified as 'non-ideal' membranes where \Re usually lies between zero and one [249,323,328].

For 'non-ideal' or 'leaky' membranes like shales, transport of solutes can occur in both directions [329,330]. Also, hydrated ions transport the water with them causing a countercurrent flow of water and solutes [331]. When shale matrix is in contact with saltbased hydraulic fracturing (HF) fluid, depending on the salinity difference between the in-situ pore fluid and HF fluid, water can travel into or out of the shale due to chemical osmosis. Additionally, water can be transported along with hydrated ions. Moreover, the presence of clay minerals results in cation exchange reactions which further complicates the process. Hence, the prediction of membrane efficiency is not an easy task [323]. Membrane efficiency can further depend on several factors including clay mineral type, cation exchange capacity (CEC), porosity, permeability, stress, salinity gradient, and composition of the HF fluid [323,326,327,332,333]. Estimation of membrane efficiency is essentially needed as an input for flow constitutive equations during numerical simulations. The membrane efficiency is usually estimated in the laboratory using the pore pressure transmission test (PPTT) [334-336]. A special triaxial cell was designed for PPTT measurements in this chapter. The setup and details are discussed in Section 4.2.2.2.

4.2.1.2. Configurational diffusion

Imbibition is a ubiquitous phenomenon pertaining to the physics of fluids in porous media e.g. during multi-phase flow in rocks. While SI is generally implied to mean the uptake of fluids, in the jargon of molecular dynamics, the physics of this uptake process (as an exclusive effect of capillarity) is classified as diffusion in a mathematical sense. Depending on the type of porous media or that of diffusing fluids, diffusion can be unique or a combination of ordinary diffusion, Knudsen diffusion, surface diffusion, shapechangeable diffusion, and configurational diffusion [337–340].

Amongst these diffusion regimes, configurational diffusion is the least understood with no well-defined theory or diffusivity equations. The other regimes, on the other hand, are well described in the literature with accurate diffusivity estimation theories available. Generally, only a fluid molecule with a size smaller than the pore opening can diffuse through that pore. Configurational diffusion, also referred to as hindered or restricted diffusion is when molecular sizes of diffusing fluids are appreciably larger than the pore opening resulting in a denial of entry into such pores [341,342]. Configurational diffusion has been widely observed in varying kinds of porous media [341,343–345]. The existence of configurational diffusion was realized and extensively studied by chemical scientists for analysing the flow of fluids through zeolite catalysts [341]. Pioneering and ensuing subsurface porous media scientists, however, continued developing analytical models to predict SI in porous media seemingly without considering the concept of configurational diffusion as an important controlling mechanism [346–351]. Consequently, unexplained experimental deviations from their developed analytical models still exist especially for complex fluids [352] and heterogeneous porous media such as shales [353]. Experimental investigation of configurational diffusion in geomaterials, however, offers significant challenges. Amongst the available experimental techniques, digital methods seem to be more robust for such investigations.

It has already been known that gravimetric fluid uptake studies fail to distinguish between the dominant uptake mechanisms for water and oil respectively for many cases [129,353,354]. The slopes of weight increment curves have been often used to interpret the overall uptake of fluids. Nevertheless, due to the tight coupling between different mechanisms in play, it cannot be ascertained how accurate these interpretations are. Such uncertainties pertaining to fluid flow in rocks are inherently due to the inability to visualize what occurs in-situ at a point-in-time and space. In this regard, imaging techniques have gained profound prominence [295,297,306,355–358]. However, such imaging is marred with limitations despite the progress made in the enhancement of image quality and improvement of imaging resolutions [272,285,359,360]. For instance, to distinguish between phases, tracers are usually required whereas such tracers can themselves induce unwanted effects [361]. Such limitations have been overcome using neutron imaging because of the strong attenuation of neutrons by hydrogen atoms [361]. Hydrogen-rich fluids such as water and oil can hence be easily tracked and distinguished from other phases without using tracers.

In neutron imaging, neutrons are transmitted when they pass through an object. The intensity of transmitted neutrons forms the basis for neutron imaging [361], in which both 2D and 3D images can be produced. For instance, DiStefano et al. [362] studied the height of spontaneous water rise in Eagle Ford shale fractures using 2D neutron radiographs. Similarly, Roshankhah et al. [363] used both 2D radiographs and 3D tomograms to investigate the generation and propagation of hydraulic fractures in Marcellus shale. Recently, the potential of dual X-ray and neutron tomography techniques was demonstrated on a Middle Eastern shale to distinguish between different phases such as

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fractures, kerogens, and other minerals [364]. Similarly, neutron radiography was also used for conventional rocks like sandstones [365]. The important advantage of neutron imaging is that at even lower image resolution, the response is yet sensitive to hydrogen atom clusters present in the voxel and therefore the hydrogen atoms can be accurately tracked.

As part of this chapter, the utilisation of the dual potential of X-ray and neutron tomography techniques to digitally investigate configurational diffusion in shales is explored to explain the difference in water and oil uptakes i.e. X-ray imaging was used to map the internal micro-fractures and neutron imaging was employed to track the hydrogen atoms both in the fractures and the matrix. It is noted that that the imaging of shale pores is not the intention of the imaging study. Hence, two organic-rich shale samples have been subjected to unconfined water and oil uptake with initial 3D X-ray, and timely neutron imaging has been used to provide insights into their respective uptake dynamics. Pore size characterization techniques including Small Angle X-ray Scattering (SAXS) and Focused Ion Beam - Scanning Electron Microscopy (FIB-SEM) have been used to support the conclusions. Also, theoretical corroboration of the configurational diffusion of water and oil in shales has been developed to support the experimental observations.

4.2.2. Experimental methodology

4.2.2.1. Shale and fluid samples

For PPTT experiments, the same shale (IRCM organic-rich shale from the Perth Basin) was used as in Chapter 4.1. For the diffusion experiments, organic-rich shale (ORS) samples from the Middle Velkerri Formation (MVF), Beetaloo sub-basin located in the state of Northern Territory, Australia, were used. Details of the ORS's petrophysical

properties of MVF were published previously [148]. LECO CN analysis of MVF sample showed that it contained 3.15 wt. % total organic carbon (TOC) content. X-ray diffraction (XRD) analysis found major clay minerals present to be illite-muscovite (15.7 wt. %) and illite-smectite (7.4 wt. %). Through mercury intrusion, it was found that matrix porosity was as low as 0.84%. Also, significant layering and micro-fractures along weak planes were found to exist in the MVF samples [148]. For PPTT experiments, the fluids used were 0.1M, 0.5M, and 1.0M KCl ionic solutions prepared in de-ionized (DI) water (18.2 M Ω ·cm resistivity at 25°C). The KCl salt was procured in powder form from Chem-Supply Pty Ltd Australia (purity = 99.7 wt%).

The fluids used in this study for contact angle and fluid uptake tests were DI water (DIW) and an isoparaffinic solvent (Soltrol-130) procured from Chevron Phillips Chemical Company. Soltrol-130 is made up of C_{12} - C_{14} iso-alkane and was used as the oil-phase. It had a dynamic viscosity of 1.14 cP and a specific gravity of 0.76. Henceforth, DIW and Soltrol-130 are simply referred to as water and oil respectively.

4.2.2.2. **Pore pressure transmission test (PPTT)**

In PPTT, a cylindrical sample is usually used. Small cylindrical cores (25 mm diameter, and 5mm length) were drilled out of the bigger IRCM shale sample and subsequently cleaned and oven-dried at 100°C. The schematic of the PPTT test is shown in Figure 1. Such a setup has become a standard and has been used previously with modest changes [323,324,329,334,336,366–373]. The shale samples were initially saturated with 1.0M KCl solution using the vacuum-desiccator method. The shale sample was then wrapped in a rubber jacket and sandwiched between the top and bottom steel caps. The top cap had two ports for circulation of fluid upstream while the bottom cap had one port that was closed and was used to measure the downstream pressure. A confining pressure of ~1500 psi (10.3 MPa) was applied around the sample. Initially, 1.0M KCl solution was circulated

upstream (P_u) at a pressure of around ~1000 psi (6.9 MPa). The downstream pressure (P_d) gradually increased and stabilized at a value slightly lower than the upstream pressure. This hydraulic pressure difference ($P_u - P_d \neq 0$) implied that chemo-osmotic forces exist between 1.0M KCl and different salinity pore fluid due to the dissolution of the precipitated in-situ salts in the pores. A hydraulic perturbation of ~50 psi (0.34 MPa) is applied upstream and after pressure stabilization, chemical perturbation is applied. For this, in separate tests, 0.1M and 0.5M KCl solutions are circulated at the same pressure, which slowly replaced the upstream 1.0M KCl solution through the back-pressure regulator (BPR) connected to the second port of the top cap. When a lower water activity fluid is introduced upstream, water flowed out from the shale sample leading to a drop in P_d for a short while after which P_d started increasing again to stabilize at a new value. This initial pressure drop after chemical perturbation gives the measure of the membrane efficiency of shale using:

$$\Delta P = \Re \frac{RT}{V_{w}} \ln \left(\frac{a_{1.0MKCl}}{a_{wf}} \right)$$
(4.10)

where ΔP is $P_u - P_d$, \Re is the membrane efficiency, R is the gas constant, T is the system temperature, V_w is the partial molar volume of water, $a_{1.0MKCl}$ is the water activity of the shale pore fluid (assumed 1.0M KCl), and a_{wf} is the water activity of the upstream fluid in contact with the shale. The water activities were calculated using the Norrish-Ross procedure (c.f. [374,375]). This procedure estimates the contribution of each solute using binary models such as Norrish's equation, then multiplies each contribution to get the overall water activity of the solution [374]. It is noted that such mathematical calculation procedures are as effective as experimental determination of water activities as they have both empirical and theoretical basis. Also, the implicit assumptions associated with such models do not significantly impact the water activity accuracy in shale rocks e.g. the assumption of negligible interactions among solutes or negligible interaction of solutes with macromolecules.



Figure 4.20 Schematic of the PPTT experimental setup (Source: own work)

4.2.2.3. Configurational diffusion

4.2.2.3.1. Contact angle (CA) and spontaneous imbibition (SI)

As explained previously, the CA measuring setup consisted of a high definition Basler acA1600 20gm GigE camera with a Sony ICX274 charge-coupled device (CCD) sensor. Such a combination provides a two-megapixel resolution and delivers 20 frames per second. Digital images were captured using the GigE connection to a computer and a designated Pylon software. CAs were measured using the ImageJ software (DropSnake plugin) [376]. A constant drop volume of ~6 μ L was used for consistency and to ensure repeatability three drops were made at different locations of the shale surface. Average CA was reported for the three drops including the average of left and right CAs.

For SI, two small cores (12.5 mm diameter x 26 mm length) were drilled parallel to bedding planes from a larger ORS sample (henceforth referred to as ORS1 and ORS2).

The cores were then oven-dried at 105°C for 24 hours, then cooled in a desiccator to room temperature, and dry weighted. ORS1 was then exposed to water and ORS2 to oil from one of their faces (Figure 4.21). The cores were removed from the water/oil bath, their surfaces wiped with a damp towel, and weighted using a weighing balance (Sartorius Entris323-1S; 0.0001 g accuracy). This process was repeated until no more apparent change was observed in sample weights. To quantitatively characterize imbibition, percent increments in sample weights (g) with respect to their original weights (g) was used as shown in Eq. 4.11 [129]:

% increase in weight =
$$\frac{W_t(g) - W_{\text{original}}(g)}{W_{\text{original}}(g)} \times 100$$
(4.11)

where W_t is the weight of the sample after a certain imbibition time t and $W_{original}$ is the original sample weight.



Figure 4.21 Schematic of water/oil imbibition setup

4.2.2.3.2. X-ray computed tomography

The samples were imaged using a high-resolution X-ray micro-computed tomography (μ -CT) scanner in dry condition. The scanner uses helical scanning technology to produce images with high fidelity and signal to noise ratio. The scanner obtains a series of projections (radiographs) from the sample along a helical trajectory at different viewing angles. The projections specify the cumulative attenuation of the X-ray beam through the sample, more details about the scanner and its specifications can be found elsewhere

[267]. A reconstruction algorithm based on Katsevich [271] is then used to reconstruct a 3D image (tomogram) from the projections. The reconstructed 3D tomogram is generally displayed generally in a 16-bit greyscale image. Each data point in the 3D image represents the effective X-ray attenuation coefficient of the sample at that point. The μ -CT image resolution/voxel size was 6.2 μ m for both samples (Figure 4.22 (a)). To enhance the greyscale μ -CT image quality, anisotropic diffusion (AD) and unsharp mask (UM) [377] filters were used. AD filter merges regions of similar grey-scale values and intra-region smoothing is promoted over edge smoothing. AD filter often causes some degree of blurring, which is reduced by UM filter. It has been shown that the application of AD and UM is highly effective for fractured rocks [378,379]. It is noted that the μ -CT imaging was conducted to map the internal structure of the micro-fractures in shale samples. This combined with neutron imaging will later assist us to investigate the water/oil distribution in micro-fractures.

4.2.2.3.3. Neutron tomography

Neutrons have unique properties compared to other sub-atomic particles, i.e. electrons or protons. They are uncharged, can penetrate deeply into matter, and interact with the nucleus of an atom rather than with the diffuse electron cloud. Neutrons are also attenuated significantly by hydrogen compared with most other elements [380]. Therefore, the hydrogen-rich matter, e.g. water or oil in the fractures and pores of ORS1 and ORS2 can be easily distinguished from abiotic non-hydrogenous porous media and its contents [361,364]. ORS1 and ORS2 were neutron scanned in 3D at dry conditions initially after X-ray scanning, and then thrice during SI tests (after taking out from water/oil baths respectively) after 1 day, 4 days, and 13 days.

In this study, neutron imaging was conducted on the DINGO beamline [381] at OPAL research reactor in the Australian Nuclear Science and Technology Organization

(ANSTO), Sydney. The instrument was set with the Photometrics 5 Megapixel (5056 x 2968) IRIS CMOS camera. In order to yield an image at a pixel size of 13.6 μ m, a 100 mm lens was coupled with a 0.02 mm thick Gd₂O₂S:Tb scintillation screen, thus resulting in a field of view of about 70x41 mm². The tomographic scan consisted of 1800 angular projections, covering a range of 180°, and of 3 accumulations with an exposure time of 15 seconds acquired at each step angle. This was done to improve the image quality since the sum of short time radiographs produces a higher signal-to-noise ratio (SNR) when added together than the equivalent longer exposure. The total acquisition time for one sample was around 24 hours. The projections were first treated by applying an outlier removal filter with a 5-pixel radius and threshold of 50. Then the accumulations were summed up for each step angle. Flat field normalization with dose correction and dark current subtraction was applied. The data were processed using the Octopus code for tomographic reconstruction [382], and the obtained slices were recomposed and evaluated using the Avizo 9.7.0 software (Figure 4.22 (b)). The tomographic reconstructions were further de-noised by applying the AD filter.

4.2.2.3.4. Image registration and segmentation techniques

To perform a voxel-by-voxel comparison of the images obtained using neutron tomography and μ -CT techniques and to highlight the 3D distribution of water or oil in the shale samples, all the images obtained from each sample were registered. For registration, a 3D image registration technique developed by Latham et al. [285] was employed. The technique solves a transformation problem with 7 degrees of freedom using a multi-resolution optimisation search strategy and provides a pair of images with identical dimensions. Since the neutron tomography images were obtained at a resolution of 13.6 μ m, the voxel size of micro-CT images was also altered from 6.2 μ m to 13.6 μ m to obtain images with an identical voxel size allowing for a voxel-by-voxel comparison

specifically in the fractures. The subsequent digital rock analyses were thus performed at a resolution of 13.6 μ m; however, where high-resolution information was required high-resolution μ -CT images were used.

The registered images were then used for image segmentation, i.e. the process of classifying the greyscale images into two or more phases that are homogeneous with respect to some characteristic [267]. Converging active contours (CAC) was used for image segmentation of images. The method uses the gradient and local intensity information simultaneously, details of CAC method are explained by Sheppard et al. [267]. The 3D images were segmented into four phases: (i) solid including organic and inorganic minerals, (ii) empty fractures (including fracture spaces filled with air), (iii) fluid-saturated fractures (filled with either water or oil), and (iv) fluid-saturated matrix (water or oil that moved from the fractures into the matrix (Figure 4.22 (c)).



Figure 4.22 3D representations of ORS: (a) the greyscale neutron tomography image (black = fractures/micro-fractures, grey = solid matrix, (b) the grey-scale μ -CT image (black = fractures/micro-fractures, grey and white = organic and inorganic minerals),

and (c) segmented image (grey = solid phase, red: empty fractures, blue = fluidsaturated fracture spaces and yellow = diffused liquid).

4.2.2.3.5. Small angle X-ray scattering (SAXS)

SAXS analysis was performed to ascertain the sub-nano level pores in the ORS. A tightly collimated beam of X-rays with known intensity and of fixed wavelength (λ) is scattered on contact with a highly transmitting sample [383]. Such scattering occurs due to the scattering contrast between different constituents residing in the sample. The intensity of the scattered radiation is then measured against the scattering angle (Θ), which is then converted to scattering vector (Q = $4\pi/\lambda \sin(\Theta/2)$) with units of Å⁻¹ [383,384]. More indepth details of SAXS technique can be found elsewhere [383,385].

SAXS data for each sample was collected for 25 minutes on an Anton Paar SAXSPoint 2.0 system using a copper (Cu) microfocus X-ray source and Dectris Eiger R 1M detector. The data was circularly averaged, adjusted for transmission and sample thickness, placed on an absolute scale using water as a secondary standard (where I(0) = 0.01633 cm⁻¹ at 25°C), and had the background subtracted. The data was analysed using the PRINSAS software [386]. The scattering length density (SLD) was calculated to be 2.25×10^{11} cm⁻² using the measured mineral composition from XRD and literature densities. For SLD calculations, the code developed by Paul Kienzle at the National Institute of Standard and Technology (NIST) was utilized (cf. [387]). The details of calculations including the equations used can be found in Hinde [388]. The SAXS data for ORS is shown in Figure 4.23.



Figure 4.23 SAXS data for ORS

4.2.2.3.6. Focused Ion Beam – Scanning Electron Microscopy (FIB-SEM)

The FIB-SEM images of the Beetaloo shale were obtained using the Carl Zeiss AURIGA CrossBeam equipment. A low-energy argon ion beam (Hitachi IM4000 ion milling machine) was used to mill a 0.5 mm² surface area of the sample. The sample was platinum-coated before being mounted on the equipment. Different spots on the sample were then imaged to check for nano and sub-nano pores.

4.2.3. Results and Discussion

4.2.3.1. Shale membrane efficiency from PPTT

The raw pressure data for hydraulic and chemical loadings is plotted in Figure 4.24. The osmotic pressures observed are plotted in Figure 4.25 which also includes the plot of Eq. 4.10 for different values of membrane efficiencies (\Re). The red and black points represent the two PPTT tests with upstream fluids of 0.1 M and 0.5 M KCl respectively. As seen (Figure 4.24), the pressure drop after chemical perturbation was very low. It was around 5.5 psi (0.04 MPa) with chemical perturbation using 0.5 M KCl and around -9 psi (-0.06

MPa) using 0.1 M KCl. It is pointed out here that the sharp fluctuations in pressure data after chemical loading is due to a fault with the secondary pump used. The resultant membrane efficiencies were between 0.01 - 0.04 (Figure 4.25). This implied that the inhibition of solutes was negligible, and they could easily pass through the shale pore system. Usually, low porosity shales under compaction exhibit high membrane efficiencies when high concentration fluids are used [389]. However, despite the shale being compacted during the test, and despite there being a significant chemical gradient imposed between the external and pore fluids, a negligible pressure drop implied that there was very little osmotic suction for this specific shale.

The chemo-osmotic pressure drop vanished with time as ion diffusion between the external and pore fluid occurred. The pressure drop dissipated quickly externally (as measured by the transducers) but further within the sample, the dissipation could take much longer [389]. Furthermore, it is noted that when external and pore fluid water activities are equal, no chemo-osmotic effects such as shale swelling are expected. However, when the sample is unconfined, significant swelling of the shale sample has been observed in previous studies even when external and pore fluid water activities were matched [389–391]. This swelling can be inhibited when modest confinement is applied to the samples as was also observed in the PPTT tests done on the IRCM shale in this study [129,389,392,393]. Hence, when subsurface shale reservoirs are under sufficient in-situ vertical and horizontal stresses, chemo-osmotic swelling should not be expected to play a major role in causing hydraulic fracturing fluid loss at least for the organic-rich shales with a similar composition to the shale samples tested herein.



Figure 4.24 Raw pressure data profiles for PPTT



Figure 4.25 Chemo-osmotic pressure drop due to chemical loading in PPTT

experiments

4.2.3.2. Configurational diffusion discussion

4.2.3.2.1. Contact angle (CA) and spontaneous imbibition (SI)

As exemplified in Figure 4.26, in CA tests while oil completely spread ($\sim 0^{\circ}$ CA) on the ORS surface (in presence of air), water exhibited a larger contact angle. The average water CA was 55.2° with a standard deviation of $\sim 4.1^{\circ}$.



Figure 4.26 Illustrative examples of (a) water droplet CA and (b) complete spreading of oil droplet

In the conventional definition of capillarity, this implies that during SI tests of each phase in the presence of air, water should imbibe much less than oil. However, in SI tests, the contrary was observed where oil imbibed less than water (Figure 4.27). This anomalous observation has been widely reported [89], yet there is no clarity on why it so happens. It is noted that pure capillary behaviour will scale linearly with t^{0.5} based on the Washburn theory [346]. A half (½) slope line is drawn in Figure 4.27 to infer the proportionality of water/oil uptake with t^{0.5}. As seen in Figure 4.27, only the first few hours of uptake are characterized by capillarity, and deviation from ½ slope line begins only after a few hours of the start of fluid uptake. The varying deviations of water and oil signify that different mechanisms are in play in their respective uptakes. Deviations from ½ slope as such occur when boundary conditions begin to influence the fluid movement [394]. Hence, here, such deviation implies the void space in the first continuum (pre-existing fractures) is filled and further uptake is governed by the properties of the second continuum (the matrix including fractures with nano-scale aperture). Water is influenced by further entropic effects (such as osmosis due to clay minerals) although such effect was shown to be rather insignificant from PPTT tests conducted in this chapter. Nevertheless, as discussed earlier, gravimetric curves are unable to provide insights into specific flow dynamics of fluids within the bulk's porous media. Hence, to "see" what transpires inside the porous media, X-ray and neutron imaging, as well as SAXS, was performed, analysis of which is discussed subsequently.



Figure 4.27 Water and oil uptake (normalized to initial sample weight) in ORS1 and

ORS2

4.2.3.2.2. Flows in the first and second continuum

To assess the oil and water imbibition into the fractures of the shale samples (the first continuum), the 3D neutron images were registered to the 3D X-ray images for both samples ORS1 and ORS2 exposed to oil and water respectively. As discussed, neutron imaging determines only the hydrogen (water or oil) distribution while the fracture spaces are extracted from X-ray images. It is emphasized that water and oil identified in both continuums are molecular clusters as the resolution cannot track single molecular flow. The fraction of the pre-existing fractures filled by oil and water were quantitatively identified from registered and segmented 3D X-ray and neutron images of ORS1 and

ORS2 (Figure 4.28). As seen in Figure 4.28, oil was imbibed in these pre-existing fractures more than water. This is consistent with the results obtained from contact angle measurement showing strong oil wetness (complete spreading) of the sample in the presence of air.



Figure 4.28 The segmented internal structure of ORS1 (top) exposed to water and ORS2 (bottom) exposed to oil showing empty fracture space (red) and the fraction of fracture space filled with water/oil (blue) at 1 day, 4 days, and 13 days

However, the gravimetric curves (Figure 4.27) showed that cumulative water uptake was always higher than oil despite having relatively minor hydration-induced fractures in ORS1. Hence, it is intrigued if the water is not in the fractures, then where is it? This inquisitiveness is satiated by realizing that there is significant water diffusion into the shale matrix (second continuum) through the fracture planes (Figure 4.29 (top)). Neutron imaging at 1 day showed significant water already diffused into the matrix from the fracture. This is asserted by the water gravimetric curve (Figure 4.27) where deviation from ½ slope was already evident before 1 day of water exposure. A similar deviation was also observed for oil, and as seen diffusion of oil also occurred from the fracture to the matrix although at a much lower rate (Figure 4.29 (bottom)).

Further, from the segmented 3D X-ray and neutron images, a quantitative analysis was performed. As shown in Table 4-4, fracture porosity (ratio of empty fracture volume to sample bulk volume) as estimated from X-ray images are 1.925% for ORS1 and 0.365% for ORS2. The fraction of fractures filled with water (ORS1) is 4.07%, 8.74%, and 27.1% after 1 day, 4 days, and 13 days of exposure respectively. On the other hand, the fraction of fractures filled with oil (ORS2) is 30.4%, 44.1%, and 49.2% after 1 day, 4 days, and 13 days of exposure respectively. It is evident that oil was imbibed much higher by the fractures in ORS2 than was water in ORS1. It is noted that relative measurements are of interest to compare between oil and water and actual quantitative value is not of interest i.e., measured within the obtained resolution.

However, when diffusion (flow into the second continuum) is quantitatively analysed, it was seen that the void fraction of invaded matrix filled with fluid was 1.2%, 1.7%, and 3.7% after 1 day, 4 days, and 13 days of exposure respectively (Table 4-4). Contrastingly, oil diffusion into the matrix was just 0.29%, 0.57%, and 0.88% after 1 day, 4 days, and 13 days of exposure. This is also evident from 3D neutron images where significant water

diffusion occurred into the matrix (yellow regions) from the fracture (red regions) compared to negligible diffusion of oil (Figure 4.28).

	ORS1			ORS2		
	1 day	4 days	13 days	1 day	4 days	13 days
Fracture porosity	1.925	1.925	1.925	0.365	0.365	0.365
Fluid saturation in fracture	4.07	8.74	27.17	30.39	44.16	49.19
Fluid saturation in matrix (diffused from fracture)	1.21	1.68	3.73	0.29	0.57	0.88

Table 4-4 Quantitative analysis from 3D segmented images



Figure 4.29 Segmented internal structure of ORS1 (top) and ORS2 (bottom) showing empty plus water/oil filled fracture space (red) and water/oil diffusion into matrix (yellow) at 1 day, 4 days, and 13 days

4.2.3.3. Pore structure and configurational diffusion

As discussed earlier, the fracture system showed oil wetness consistent with CA measurements however water diffused to the shale matrix more than oil as seen from Figure 4.29. This is contrary to the CA measurement where the shale samples have lower

hydrophilicity (in air) (55.2° CA for water versus 0° for oil) i.e. the overall system wettability was strongly oil-wet and slightly water-wet. It is known that two sets of distinct pore systems exist in the shale matrix: organic and inorganic. The organic pore system is generally oil-wet [395,396]. It has been shown that this organic matter must exceed 5% of the total sample weight in order to have strong oil-wet pore connectivity [396]. TOC of 3.15 wt. % in the ORS used in this study hence implies that oil-wet pathways in the ORS pore network are poorly connected for oil uptake. The contribution of oil-wet organic matter porosity to the overall fluid uptake in ORS is thus lower than that of inorganic constitutes which have comparatively connected pathways. The inorganic pore system (which includes clays) can have varying wettability and it remains unknown to what extent it dictates the overall observed wettability behaviour of organic-rich shales [89]. These factors, combined, affect the water/oil uptake by shale. To put things in perspective, there are several mechanisms in play:

i) potential oil uptake, due to capillarity, into oil-wet organic matter that has a low volumetric contribution to the matrix (in this case ~3.15 wt. %) and limited connectivity
ii) potential oil uptake, due to capillarity, into inorganic constitutes that can be oil-wet and have strong connectivity

iii) potential water uptake into inorganic pores due to combined capillarity and osmotic forces.

Additional osmotic forces have proven to be responsible for water uptake into inorganic clay constitutes of the shale matrix [22,129]. The electrostatic charges of clay surfaces forming the pore wall (or between the clay interlayers) play a significant role in aqueous fluid flow transport. This phenomenon is directly linked to pore sizes i.e. pore size dictates the effective flow path in the nano-pores. These essentially charged nanopores lead to

diffusio-osmosis (a combination of electro- and chemo-osmotic flow of water) that enhances the aqueous solution diffusion process. These phenomena have been well studied in chemical science [322,397] where water movement in charged nano-channels has been investigated. Subsurface flow-related studies in this regard also showed that water uptake into shale is influenced by chemical gradient along with capillary forces [398].

The oil uptake into organic pores due to capillary forces cannot lead to significant oil uptake as the amount and connectivity of organic matters are often limited [396]. It is however not yet clear why the oil is not imbibed into oil-wet inorganic matter, but water is. This cannot be simply due to osmotic forces being stronger than capillarity as many shale samples rich in non-swelling clays, which are expected to develop minimal osmosis, still imbibe more water than oil [129]. Further, it is known that reverse osmotic flow of water out of the shale occurs when the ionic concentration of shale is lower than exposed fluid. However, water uptake into shale (with non-swelling clays) at very high ionic concentration was still significantly higher than oil [129].

It was observed in Barnett shale using small-angle and ultra-small angle neutron scattering (SANS and USANS) that there was restricted methane in pores with radii <30 nm whereas water diffused unrestricted into the smallest of pores. In larger pores, there was no observed competition for pore accessibility. Also, in another study on Barnett and other shales, it was shown that smaller pores (<1 nm) were resolved using carbon dioxide (CO₂) than with nitrogen (N₂) implying that the pore accessibility of different molecules is unique [399]. Other such studies have also shown that shales can have significant nanoporosity [400]. Therefore, configurational diffusion is shown to construe the anomalous water/oil infiltration process into the shale matrix unexplainable by capillary or osmotic concepts.

In order to investigate this further, the pore size distribution of the ORS from 0.3 to 32 nm was measured using SAXS (Figure 4.30). The presence of such pores will support the configurational diffusion concept as a cause of restricted flow and storage of oil molecules in them. The results show a significant fraction of pores in the sub-nanometre region. These pores are accessible to water (which is about 2.7 Å in size) but become inaccessible to oil molecules with molecular lengths on the nanometre scale for the C_{12} - C_{14} isoparaffins used here. The presence of such pore sizes corroborates the configurational diffusion hypothesis. The lower oil uptake is hence simply due to a physical barrier for effective diffusion of its molecules into the shale matrix compared to water molecules. Configurational diffusion has been well observed and documented in the flow of hydrocarbons through zeolite catalysts in chemical science [10,341]. Hence, configurational diffusion of molecules can be significant in such pores. The FIB-SEM images (Figure 4.31) also show significant nano-pores present in the shale sample and supporting such behaviour.



Figure 4.30 Sub-micron pore size distribution from SAXS for ORS



Figure 4.31 FIB-SEM images of shale sample

Therefore, such observations support our hypotheses that while the mineral and organic constitutes might be strongly oil-wet (in the air), they do not have the right pore size to accumulate the oil molecules and allow its physical passage. Water, on the other hand, can readily move through nano-scale pores and diffuse faster into the matrix than oil. This will be more pronounced when moving from relatively larger mesopores to micropores [401]. We further employ the non-equilibrium thermodynamics to derive the constitutive equations for such behaviour to investigate whether the theory can also support the observed behaviour.

4.2.3.4. Theoretical exposition and its link to constitutive behavior

A porous medium infiltrated with a fluid can be theoretically characterized in two ways: as a heterogeneous medium with distinct mixtures of solid and fluid, or as a single continuum with effective solid and fluid properties [172]. The single continuum viewpoint was previously adopted in Biot's theory of poro-elasticity [110]. It was further proved efficient developing in many advanced constitutive equations [115,116,182,198,402]. Hence, the single continuum concept is adopted here. For this, principles of non-equilibrium thermodynamics were employed. The internal energy of a macroscopic region in the porous medium, at isothermal conditions, will change only with the ingress and egress of fluid mass and with the dissipation occurring therein due to fluid movement in respect to the solid skeleton. To arrive at fluid transport equations, it is assumed that such dissipation is only due to friction between solid/fluid phases during flow (no chemical reaction occurs) where macroscopic expression for entropy production is given by:

$$0 \le T\gamma = -\mathbf{I}^{j} \cdot \nabla \mu^{j} \tag{4.12}$$

where γ is entropy production rate, *T* is temperature, I^{j} is fluid mass flux for the general case where j = w, o, c for water, oil, and any dissolved component (e.g. in water) respectively. The mass flux is given by:

$$\boldsymbol{I}^{j} = \rho^{j} (\boldsymbol{v}^{j} - \boldsymbol{v}^{s}) \tag{4.13}$$

Where ρ^{j} is the fluid density, v^{j} is velocity, and v^{s} is the velocity of the solid phase. It is more convenient to replace the mass fluxes (which are relative to solid velocity) with diffusion fluxes (J^{j}) that is relative to the fluid's barycentric velocity (v^{g}):

$$J^{j} = \rho^{j} (\boldsymbol{v}^{j} - \boldsymbol{v}^{g}) \tag{4.14}$$

where $\boldsymbol{v}^{\boldsymbol{g}} = \sum_{j} (\rho^{j} / \rho^{t}) \boldsymbol{v}^{j}$ and $\rho^{t} = \sum_{j} \rho^{j}$. It is thus obvious that the two types of fluxes are related through:

$$J^{j} = I^{j} - \rho^{j} (\boldsymbol{v}^{g} - \boldsymbol{v}^{s}) \tag{4.15}$$

Here, Darcy velocity is introduced using:

$$\boldsymbol{u} = \boldsymbol{\phi}(\boldsymbol{v}^g - \boldsymbol{v}^s) \tag{4.16}$$

where ϕ is the porosity of the medium. Also, recalling the Gibbs-Duhem equation for a fluid [172]:

$$\sum_{j=w,o,c} \bar{\rho}^{j} \nabla \mu^{j} = \nabla p_{pore} \tag{4.17}$$

where $\bar{\rho}^{j} = \rho^{j}/\phi$ and the summation can be dropped in the case of one fluid system (with no dissolved species). Using Eqs. (4.16) and (4.17), Eq. (4.12) can be further simplified to:

$$0 \le T\gamma = -\boldsymbol{u} \cdot \nabla p_{pore} - \sum_{f=w,o,c} \boldsymbol{J}^{j} \cdot \nabla \mu^{j}$$
(4.18)

For the specific case, when no dissolved components are present in the fluids (e.g. DIW and Soltrol-130), Eq. 4.18 becomes:

$$0 \le T\gamma = -\boldsymbol{u} \cdot \nabla p_{pore} - \boldsymbol{J}^j \cdot \nabla \mu^j \tag{4.19}$$

where now j = w, o for water (DIW) or oil (Soltrol-130) respectively and ∇p_{pore} is the fluid pressure in the porous medium. In the case of spontaneous imbibition (SI), it is simply the capillary pressure (∇P_c). From the dissipation, two forces are identified: capillary pressure ($-\nabla P_c$) and chemical potential ($-\nabla \mu^j$). Using the framework of irreversible processes, a linear relation between fluxes and forces exists such that:

$$\boldsymbol{u} = L_{11} \nabla P_c + L_{12} \nabla \mu^j \tag{4.20}$$

$$\boldsymbol{J}^{\boldsymbol{j}} = L_{21} \nabla P_c + L_{22} \nabla \mu^{\boldsymbol{j}} \tag{4.21}$$

where L_{mn} are phenomenological coefficients where m, n = 1,2. Since it was already stated that water (DIW) and oil (Soltrol-130) do not contain any dissolved species, the above equations represent the fluid flux each due to capillarity and diffusion respectively. The above phenomenological equations are further simplified by assuming that, in the case of fluids with no dissolved species, capillary and diffusive flow due to change in chemical potential is negligible due to constant chemical potential of the fluid i.e. $\nabla \mu^{j} =$
0. It is noted that Onsager symmetry is not invoked here [228]. Onsager's microscopic time reversibility has been disputed in specific cases [403] although it may be valid for particular situations [85]. In this case, when the same capillary force can cause different fluxes (either capillary or diffusive) depending on the pore size, it is clear that Onsager's transport matrix symmetry does not hold.

Next, the phenomenological coefficients (L_{11}, L_{21}) can be estimated by first realising that capillary flow, such as during SI, can be described as laminar due to its quasi-static nature and hence can be characterized by Poiseuille's law:

$$\boldsymbol{u}^{j} = \frac{A_{p}r^{2}}{8\mu_{j}}.\,\boldsymbol{\nabla}P_{c} \tag{4.22}$$

where A_p is the total cross-sectional pore area assuming parallel cylindrical pores, r is the pore radius, μ_j is the fluid viscosity, ∇P_c is the capillary pressure gradient across the porous body. Second, under the same capillary pressure gradient, when the fluid molecules encounter pores with openings comparable to their sizes, the flow is then transformed into a diffusion process. The diffusion flow rate of fluid molecules is given by [404,405]:

$$J^{j} = \frac{D_{j}\bar{V}_{j}A_{p}}{RT}.\nabla P_{c}$$

$$\tag{4.23}$$

where D_j is the diffusivity of the fluid, \bar{V}_j its molar volume, R is the universal gas constant, and T is temperature. The phenomenological coefficients (L_{11}, L_{21}) are then the coefficients of ∇P_c in Eqs. (4.22) and (4.23) respectively. The contribution of the capillary and diffusive flow of water towards the total flow can be estimated by taking the relative ratio. Since fluid properties for water are known easily than for oil, we have for water (j = w):

$$\frac{u^{w}}{u^{w} + J^{w}} = \frac{1}{1 + \frac{8\eta_{w} D_{H_{2}O} \bar{V}_{H_{2}O}}{r^{2} R T}}$$
(4.24)

Using the respective values of diffusivity, viscosity, molar volume, and *RT* at 25°C: $D_{H_2O} = 2.295 \times 10^{-9} m^2/s$, $\eta_w = 8.9 \times 10^{-4} Pa.s$, $\bar{V}_{H_2O} = 0.000018 m^3/mol$, and *RT* = 2477.6 *J/mol*, the ratio of capillary and diffusive flows to the total flow versus pore radius can be generated by solving Eq. 4.24 (Figure 4.32). Figure 4.32 indicates that the laminar Poiseuille's flow (or Darcy's flow) dominates beyond the 2 nm pore size value while below 2 nm, diffusive flow initiates its significance and becomes dominant at small pore sizes (<0.5 nm).



Figure 4.32 Fraction of total flow due to capillarity and diffusion

At such small pore sizes where the size of molecules is comparable, configurational diffusion is significant where the easy passage and storage of such molecules in these pores is hindered. When molecular sizes are much larger than the pore size that they are approaching, strong repulsion leads to a complete impasse. In fact, in studies related to biological membranes, it was observed that diffusion of molecules is hindered at pore sizes even 20 times larger than the molecular sizes [405,406]. This occurs due to a

combination of steric and viscous drag effects. The diffusion coefficient of fluid in a porous medium thus cannot be a single value, rather varying based on the pore size distribution. Below a critical pore size, configurational diffusion is significant and must be incorporated in fluid flow models. A simplified restriction factor for effective diffusion was developed by Pappenheimer et al. [407]:

$$\frac{D_c}{D_e} = \frac{(1 - \lambda_r)^2}{1 + 2.4\lambda_r}$$
(4.25)

where D_c is the configuration diffusion coefficient, D_e is unrestricted diffusion coefficient in larger pores and $\lambda_r = d_m/d_p$ is the ratio of fluid molecular diameter (d_m) to pore diameter (d_p) . Figure 4.33 (based on Eq. (4.25)), clearly shows the reduction of effective diffusion (D_c/D_e) with pore radius. As seen for different molecules, hydrocarbons always have lower diffusivity than water due to their larger molecular sizes. The molecular sizes of different molecules were taken from Breck [408]. Configurational diffusion is thus more pronounced for heavier and larger molecules such as oil (C₁₂-C₁₄) than for water. This theoretical exposition corroborates our experimental results and satiates the intriguing question of why oil always imbibes much less than water into shale matrix despite spreading more than water on shale surface.



Figure 4.33 Restricted diffusion versus pore size for molecules of different sizes

It is noted that the theory of configurational diffusion is based on simplified assumptions such as considering molecules to be spherical and pores cylindrical. It is, therefore, able to predict only part of the impasse of molecules [407,409]. This implies that the configurational diffusion coefficient can be much lower than theoretically predicted values. Also, such a simplified theory is unstable at extremely low pore sizes (<1 nm). The need for experiments hence is not eliminated. For instance, in a realistic shale matrix pore network, larger pores may be preceded by narrower pore throats where configurational diffusion could be significant. Hence, a substantial number of larger pores also remain inaccessible to such molecules drastically lowering their cumulative uptake. Thus, an accurate theory of configurational diffusion is incomplete and thus warranting further research.

An illustration of the heterogeneous water diffusion is shown here using a 2D neutron radiograph at 13 days (1 pixel = $13.6 \,\mu$ m). As seen in Figure 4.34 (a), the brightest region is inside the fracture where the concentration of water molecules is very high. The lesser brighter regions in the matrix correspond to water diffused into the matrix. A yellow line

is drawn across the fracture whose pixel profile is shown in Figure 4.34 (b). As can be seen, there is non-uniform diffusion on both sides of the fracture. On the left side, ~100 pixels are detected with water molecules whereas, on the right side, ~300 pixels are detected with water molecules. As discussed earlier, attributing a diffusion coefficient for such diffusion is pointless as there is significant spatial and pore size-dependent variation.



Figure 4.34 Illustration of water diffusion using (a) neutron radiograph for ORS1 at 13

days and (b) pixel profile of yellow line drawn across the fracture

4.2.4. Conclusions

The pore pressure transmission tests (PPTT) conducted on the IRCM shale sample revealed that the membrane efficiency ($\sigma \equiv \omega \equiv \Re$) of the shale matrix was between 0.01 - 0.04. Hence, the shale is not expected to exhibit any significant chemo-osmotic swelling effects. The value will be used as an input in solving the constitutive equations developed in Chapter-3.

A combination of X-ray and neutron imaging supported with SAXS and FIB-SEM techniques was further used in this chapter to reveal that higher water uptake by organicrich shale matrix against the capillary prediction is due to pore inaccessibility by the larger oil molecules i.e. configurational diffusion of molecules. The theoretical constitutive models were further developed using the non-equilibrium concept to support the experimental observations. Significantly smaller water molecules can diffuse through much smaller pore-throats and reside in pores inaccessible by oil. This study highlights that retardation of fluid diffusion due to a subtle phenomenon – the inaccessibility of pores smaller than the size of the fluid molecules – can cause a significant anomaly in theoretically predicted fluid volumes. This further implies improving the theory of fluid uptake in porous media.

It is hence perceived that i) higher the organic matter content, faster the hydrocarbon diffusion occurs and ii) if oil-wet pores of inorganic matrix constitutes are within nano-scale, the role of the capillarity is relatively limited especially due to oil molecular size causing low oil uptake whereas water can still diffuse into these nano-scale pore throats assisted by osmotic forces. Therefore, the fewer the micropores exist in the inorganic constitutes of the shale matrix, the higher the rate of oil diffusion will be.

4.3. Two-phase flow characterization in clay-rich rocks: a fractal-based

approach

The contents of this chapter are from "**Caveats of using fractal analysis for clay rich pore systems**" in *Journal of Petroleum Science and Engineering*, DOI: 10.1016/j.petrol.2020.107622.

4.3.1. Introduction

In two-phase flow, the presence of more than one phase disturbs the flow behavior of the other phase and vice versa. For e.g., if saturation of the wetting fluid increases, the cross-sectional area available for wetting phase flow also increases while it decreases for the non-wetting phase. Such microscopic effects are represented at the macro-scale using the relative permeability concepts. Relative permeability is strongly coupled to capillary pressure. Owing to this coupling, several studies have proposed estimation methods of relative permeability from capillary pressure data [410–412]. Such correlations were developed to avoid the use of lengthy experiments to measure relative permeability. Capillary pressure, on the other hand, is more abundantly measured using mercury intrusion techniques (MICP), even for unconventional shale rocks. Hence, relative permeability can be extrapolated from MICP data with the knowledge of fluid wettability and the use of correlations e.g. Brooks and Corey [412]. Fractal formulations of relative permeability are recent advancements (or adaptations) of such correlations.

Two-phase flow in clay-rich rocks such as shales is of particular importance to understand the hydraulic fracturing fluid uptake into shale matrix. Due to issues around conducting forced imbibition in clay-rich rocks, and the transient nature of pore structure due to exposure of clay minerals to external fluids, the experiments to characterize the two-phase flow in such rocks is rather limited. This has led to using fractal-based theories of twophase flow for clay-rich and tight rocks. This is particularly important as an input for constitutive equations including the model developed in this dissertation (Chapter-3) where relative permeability and capillary pressures are of interest and needed.

4.3.1.1. A brief review of fractal concepts

Increasing global energy demand has pushed exploration and production of hydrocarbons from unconventional shale rocks which were otherwise difficult and economically strenuous to produce due to having very low permeability. Hydrocarbon recovery is partly dependent on the interaction of the fracturing fluid with the reservoir matrix in the hydraulically generated conduits. Such kinds of fluid flow in low permeability shales are controlled significantly by its pore microstructure which, therefore, must be accurately characterized. However, low permeability rocks are usually associated with complex geology, lithology, and heterogeneity which make it difficult to characterize its pore structure [146,413–415]. Moreover, their pore structure usually has a wide pore-size distribution (PSD) consisting of mostly micro-nano pores/pore-throats presenting a challenge for characterization by conventional techniques [151,416–418]. Such a complex pore structure also makes fluid flow prediction significantly challenging.

To overcome such challenges, fractal-based transport analysis has garnered attention as the application of fractal techniques allows the derivation of expressions for petrophysical, flow, and hydraulic properties [419–429]. The term 'fractal' was coined by the mathematician Benoit Mandelbrot for irregular surfaces or shapes that have the same level of irregularity at all scales. The same level of irregularity at all scales results in a power-law relation. The term 'fractal' has then been borrowed and used by many researchers subsequently to interpret a certain thing or measurement having power-law characteristics. Recently, fractal-based techniques have been widely used to characterize rock pore-throat morphology, heterogeneity, connectivity, tortuosity, flowing ability (relative permeability) etc. Katz and Thompson (1985) showed experimentally that porosity and pore volume of sandstones are fractals (self-similar) over a wide range of scales (1nm – 100µm) and follow scaling power-law. Several studies since then have investigated fractal characteristics of various porous media [421,431–443]. Despite the rock's complex nature, it was argued in previous studies that the pore structure exhibited good fractal characteristics. The sui generis characteristic of fractals is that irrespective of the unit, they obey the following scaling power-law [436]:

$$M(L) \sim L^{D_f} \tag{4.26}$$

where, *M* can be the length, area, pore volume or PSD and D_f is the fractal dimension which can be constant over a range of length (or magnification) scales, *L*. It is also noted that porous media are statistical fractals and are not exactly self-similar unlike the mathematical fractals Koch curve, Sierpinski carpet, etc. [444]. In other words, for mathematical fractals (exactly self-similar) all points on a log-log plot of Eq. 4.26 lie exactly on a straight line while for statistical fractals (real rocks) they lie approximately very closely around the straight line [445]. It is assumed in most porous media fractal studies that the condition for the porous media to be a fractal is that its PSD should follow the following fractal scaling law [425,436]:

$$n(L \ge r) = \left(\frac{r_{max}}{r}\right)^{D_f} \tag{4.27}$$

where *n* is the number of pores, *L* is the length scale, r_{max} is the maximum pore size, *r* is any pore size smaller than r_{max} and D_f is the fractal dimension of PSD. D_f often varies between 0 to 2 in two dimensions and between 0 to 3 in three dimensions. The total number of pores, *N* is then given by:

$$N = \left(\frac{r_{max}}{r_{min}}\right)^{D_f} \tag{4.28}$$

It is also always considered in porous media fractal studies that for the porous media to be a fractal, it must also satisfy the condition $\left(\frac{r_{min}}{r_{max}}\right)^{D_f} \approx 0$ or $r_{min} \ll r_{max}$ [431]. An approximate criterion of $r_{min} < 0.1 r_{max}$ is generally considered acceptable [431,436].

While the above general fractal formulation seems to be statistically consistent, the matter of contention, however, is that there is no definite proof of the same. There is no proof that Eq. 4.28 can be applied to all types of pore systems at every range of pore sizes. Hence, based on such formulations many analytical petrophysical relationships have been developed assuming further simplifications can be inappropriate especially those based on mercury intrusion capillary pressure (MICP).

When PSD is used to estimate the fractal dimension (D_f) , MICP curves are more convenient than other techniques such as scanning electron microscopy (SEM), thin section image analysis, gas adsorption, and nuclear magnetic resonance (NMR) analysis [446–458]. Estimation of fractal dimension from MICP can be based on either wetting phase saturation (S_w) [426,458] or mercury saturation (S_{Hg}) [414,457]. The choice of the method is arbitrary and there does not seem to be any evidence that a particular method exists for a rock type or if it influences the analysis.

Another point of contention is that MICP-based fractal methods assume a constant unchanging pore network leading to a single value of the fractal dimensions (D_f) at all length-time scales. Using the MICP-based D_f for a transient pore network (e.g. in clayrich rocks) causes errors and uncertainties in all fractal analyses including fractal estimation of relative permeabilities, fractal estimation of fluid flow, etc. of clay-rich rocks. Such errors and uncertainties are specifically intensified during immiscible twophase flow in clay-rich porous media where incompatible fluids encounter the in-situ clay minerals e.g. imbibition of hydraulic fracturing fluid from fracture conduits into the reservoir matrix. It is noted that the prediction of such a two-phase transport phenomenon is important to estimate the hydrocarbon recovery. The MICP-based D_f estimation approach can cause grave reservoir management issues such as improper reservoir performance prediction, production optimization, forecasting, etc. These issues are usually manifested in two-phase numerical simulation in which the fractal-estimated petrophysical properties are used as input [459–462]. As mentioned, input data are fractally-estimated because experimental estimation of these properties is challenging for low permeability clay-rich rocks.

MICP-based D_f value could be valid for rocks having low or negligible clay content and following fractal law. This is because the minimum presence of clays does not hinder fluid flow. However, when rocks contain a significant amount of swelling clay minerals like smectite or mixed-layer illite/smectite, the validity of the above assumption is questionable. This is because on contact with external fluids (e.g. fracturing fluid) these clay minerals swell and significantly alter the pore network. The alteration of the pore network is in the form of pore-throat blocking, reduction in pore sizes, clay flocculation (especially for kaolinitic clays), etc. Such a change in pore structure causes the fractal dimension to deviate from the original value (representing the original pore structure). The current fractal models which assume an unchanging pore network, however, do not accommodate a transient (or dynamic) pore network.

Therefore, before proposing a theoretical improvement of such fractal models in this study, a systematic investigation was performed to narrate a cautionary tale regarding the

caveats on using the fractal petrophysical formulations in predicting fluid flow when uncorrected for clay swelling effects. Since fluid flow experiments in low permeability clay-rich rocks is a daunting challenge, this was achieved with oil-water flow simulation of clay-rich low permeability sandstone rocks. In order to do this, MICP-converted oilwater capillary pressures and fractal-based oil-water relative permeabilities were used as input and the results were compared with experimentally observed oil recoveries. The three reactive (clay-rich) low permeable sandstone samples were taken from an actual well at different depths. Special and routine core analyses were performed to estimate mineralogy, clay content, porosity, permeability, wettability, capillary pressure curves, etc. to minimize errors in simulation-experiments comparison judgements. Next, based on a sound theoretical framework, a novel approach of MICP-based fractal model was derived using the concept of porosity reduction by clay swelling. The model was then compared with experimentally estimated capillary pressure.

4.3.2. Fluids and samples characterization

A synthetic fluid (which was used in spontaneous imbibition experiments) was prepared with the following salt components (Table 4-5) to be used as exposing fluid [463]:

Table 4-5 Fluid properties and composit	tion

Conductivity	pН	Density	TDS	HCO ₃ -	Cl	SO ₄ ²⁻	Na ⁺	Ca ²⁺	Mg ²⁺	Fe ²⁺
(µS/m)		(g/cc)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
22.55	7.95	1.015	24500	616	11100	245	6120	148	26	17

The field crude oil (specific gravity $\gamma_0 = 0.798$) used in spontaneous imbibition experiments had a molecular weight (MW) of 143.68 g/mol. Its composition is shown in Table 4-6. Oil-water (brine) interfacial tension (IFT) was measured as 11.6 mN/m using the pendant-drop [464]. A drop of oil was injected out of a needle placed in the brine and its images were taken. The images were then analysed using ImageJ software according to Eq. 4.29 and measured dimensions in Figure 4.35 (D was measured as 2.479 mm, d as 1.509 mm and 1/H (representing the value S) from the literature [464] as 1.2):

$$\sigma_{ow} = \frac{\Delta \rho g D^2}{H} \tag{4.29}$$



Figure 4.35 Oil drop in brine for measurement of interfacial tension using pendant drop

method

Table 4-6 Composition of crude oil

Component	Mol. Wt.	Fraction
	(g/mol)	mole %
C1	16.04	0.00
C2	30.07	0.04
C3	44.10	0.16
i-C4	58.12	0.10
n-C4	58.12	0.37
i-C5	72.15	0.39
n-C5	72.15	0.61
C6	84.00	4.09

C7	96.00	6.48
C8	107.00	16.68
C9	121.00	12.99
C10	134.00	16.38
C11	147.00	12.13
C12	161.00	8.63
C13	175.00	6.88
C14	190.00	3.99
C15	206.00	2.73
C16	222.00	1.60
C17	237.00	1.15
C18+	1424.72	4.60
Mole %		100.00
Mol. Wt.		143.68

Due to the ultra-low permeability and porosity, fluid flow experiment in shale rocks are cumbersome. Hence, to be able to perform flow experiments as well as to mimic the clay content of shales, three low permeability sandstone rocks samples containing a significant amount of clays (named henceforth as S1, S2, and S3) cored at three different depths (1480, 1483, and 1548 m respectively) from a shaly reservoir in Japan were used in this study. Routine and special core analyses performed on the samples are described below.

4.3.2.1. X-ray diffraction (XRD) and scanning electron microscopy (SEM)

XRD of the three low permeability sandstone samples revealed that all samples contain a significant amount of clays with mixer layer illite/smectite (I/S) as the most dominant clay mineral. XRD data are summarized in Table 4-7.

	Sample	S 1	S2	S 3
	Depth, m	1480.08	1483.78	1547.65
D11	Quartz	38.5	42	31.7
Bulk mineralogy,	Plagioclase	20.2	10	7.1
xx+ 0/	Pyrite	2.6	2.5	2.5
WL. 70	Analcime	0	0	20.5
	Pyroxenes	1.8	2.1	0.5
	Total clay	36.9	43.4	37.7
	Illite+Mica	0.9	0.3	0.6

Table 4-7 XRD data of all samples

Clay breakdown,	Kaolinite	0.1	0.1	0
	Chlorite	0.1	0.1	0.3
wt. %	Mixed Layer I/S	35.8	42.9	36.8

SEM images were also acquired using the FEI Quanta 200 environmental SEM. The images clearly showed the complex nature of samples' pore micro-structure where significant clay coating the pores and pore-throats is visible. Representative images for all three samples are shown below (Figure 4.36).





Figure 4.36 Representative SEM images showing clay minerals coating the structure for samples (a) S1, (b) S2, and (c) S3

4.3.2.2. Cation exchange capacity (CEC)

Ion displacement method [465] was used to estimate the CEC of the individual major exchangeable cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) of the low permeability sandstone samples. In order to measure the major exchangeable cations, the samples were first 195

fragmented and then milled to a powder. They were then oven-dried at 105°C for 24 hours. The samples weighing around 2g were exposed to 7ml of 1M NH₄Cl solution. It was then placed on a rotating Ferris wheel for 24 hours to have the complete mixing. Suspended solutions were then centrifuged at 3000 rpm for 30 minutes. After the particle settlements, the supernatants were collected and filtered through 0.2µm filter paper. The concentration of major exchangeable cations was then measured using inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Table 4-8). The alkalinity was also measured by gran titration on an aliquot of the supernatant to correct for any contribution of Ca²⁺ in the solution originating from the dissolution of calcium carbonate minerals. It is noted that for each mole of alkalinity in the supernatant ¹/₂ mole of Ca²⁺ should derive from the dissolution of carbonate minerals and not the exchanger assuming no other source of alkalinity [465].

Sample	Alkalinity	CEC	CEC	Clay content
			(corrected)	
#	meq/L	meq/L	meq/100g	wt. %
S1	0.01	46.57	16.85	36.9
S2	0.35	80.28	28.20	43.4
S3	1.92	82.53	26.88	37.7

Table 4-8 Measured CEC for all samples (corrected for alkalinity)

4.3.2.3. **Porosity and permeability**

Sample porosity and permeability were measured using CoreLab CMS-300 Automated Permeameter which can make measurements at a range of confining pressures up to 9800 psig (67.6 MPa). Porosity was measured by helium gas using Boyle's law and permeability was measured by transient pressure decay technique (using air) [466,467]. Permeability measurements were performed at confining pressures of ~800 psi (5.5 MPa). Porosity and permeability values are presented in Table 4-9.

Sample	Depth (m)	Rock	Lithology	K (mD) (Klinkernberg corrected)	Porosity (%)
S1	1480.08	silt	silty claystone	0.511	26.9
S2	1483.78	silt	silty claystone	0.448	23
S3	1547.65	sand	argillaceous sandstone/siltstone	0.085	22.9

Table 4-9 Sample porosities and permeabilities

4.3.2.4. Wettability

The wettability of rock samples was estimated through oil-water contact angle measurements as they are more representative of in-situ conditions than measurements performed in the air [89]. Sample substrates were initially polished step-wise up to 1200 grit sandpaper and air-cleaned. Although the effect of variable surface roughness on contact angle measurement is well-known, it was not considered in this study [468], however, the polishing time was also kept the same for all samples to maintain similar roughness among them and avoid inconsistencies. The substrates were then placed in a contact angle measuring setup (Figure 4.37(a)) i.e. it was exposed to the prepared synthetic fluid. The oil droplet was then dispersed on the sample from below and a high-resolution Basler acA1600-20gm GigE camera with a Sony ICX274 CCD sensor capable of delivering 20 frames per second at 2MP resolution was used to capture the drop images [129]. Drop analysis was then performed using the DropSnake plugin in ImageJ software

to calculate the contact angles. The average contact angles of several drops on each sample are listed in Table 4-10 and representative images are shown in Figure 4.37(b).



Figure 4.37 (a) Contact angle measurement setup and (b) Oil-water contact angles for samples (i) S1, (ii) S2, and (iii) S3

Table 4-10 Measured averaged oil-water contact angles for the samples

Sample	Oil-water contact angle (°)
S1	116.3
S2	127.5
S3	118.8

4.3.2.5. Mercury intrusion capillary pressure (MICP) measurement

Cleaned and oven-dried sample plugs were weighed, and each placed in the bulb of a selected penetrometer so that the pore volumes of the samples were approximately 70-80% of the volume of the penetrometer stem. The sample and penetrometer were weighed together. The penetrometer containing the sample was loaded into the Micromeritics

Autopore IV 9500 porosimeter. The penetrometer was evacuated to a pressure of less than 50 μ m of mercury (Hg) and then filled with mercury at a pressure of 0.5 psia. The bulk volume of the sample was determined at this point. Mercury was injected into the core plug at increasing incremental pressures from 1 to approximately 55000 psia to represent non-wetting phase saturation (S_{Hg}) build-up. At each pressure point, mercury intrusion was monitored while the pressure was held constant. Equilibrium was set at 60 seconds per point. The pressure and the total volume for that point were recorded. The threshold pressure, where mercury injection into the pore structure begins, is identified as the pressure where the rate of mercury injection increases rapidly. Cumulative apparent injection up to this threshold pressure was subtracted as surface porosity from the measured data before subsequent calculations were made. MICP data is presented in Figure 4.38.



Figure 4.38 Semi-log plot of capillary pressure (P_c) vs. S_{Hg} for samples (a) S1, (b) S2, and (c) S3

4.3.3. Fractal-estimated oil recovery in clay-rich rocks

In order to highlight the errors and uncertainties of conventional fractal-based estimation of two-phase flow in clay-rich rocks, the difference between experimental and simulated oil recoveries from spontaneous imbibition of fracturing fluid into three oil-saturated clay-rich low permeability sandstone samples were calculated. For the convenience of the reader, the details of the simulation and its related experimental work are presented in Appendix-A. In order to perform this analysis, the MICP-based capillary pressures and fractal-estimated oil-water relative permeability curves (obtained using the MICP-based D_f) were used as input in two-phase flow simulation of clay-rich low permeability sandstone rocks and their comparison is presented herein.

4.3.3.1. Spontaneous imbibition experiment and comparison with simulation

Since all three low permeability sandstone samples are strongly water-wet (based on oilwater contact angles), high capillarity brine spontaneously imbibes into the samples as soon as they are immersed in it (the spontaneous imbibition experiments are presented in Appendix-A). Although the weight was recorded for 100 hours, it was observed that the oil recovery plateau was reached much earlier for all samples i.e. black curves in Figure 4.39. Using smaller sample sizes (10x10x5 mm) allows for faster attainment of equilibrium. It was seen that oil recovery was highest for S3 followed by S2 and S1. Equilibrium experimental oil recovery was around 19% for S3, 17.6% for S2, and 10% for S1. The oil recovery is presented in terms of initial oil in place (IOIP) in the oilsaturated sample.

Simulation of the above-performed spontaneous imbibition experiments was conducted with MICP-based oil-water capillary pressures and fractal-based relative permeability data as input (see Appendix-B). The simulation was performed for around 100 hours, the same duration for which the imbibition experiments were performed. The oil recovery vs. time is plotted in Figure 4.39 (red curves) for all samples. It is seen that, during numerical simulation, the oil recovery plateau was reached much earlier than in experiments.

When compared with experimental oil recovery, it can be seen that (Figure 4.39), for all samples, simulated oil recovery is higher than experimental oil recovery. The largest margin of difference was observed for S1 followed by S2 and S3. Even with appropriate input data and boundary conditions, the mismatch between experimental and simulated oil recoveries highlights the uncertainties, discrepancies, and errors of using the MICPbased oil-water capillary pressures and MICP-based D_f for the relative permeability inputs in the simulation of two-phase flow in clay-rich rocks. With increasing water saturation, more clay encounters the water leading to swelling which reduces the porethroat radius and leads to an increase in capillary pressures at the same saturation values. Since further discussion and fractal model development is based on the fact that the pore network is altered due to clay swelling, few illustrations using environmental SEM are presented in Appendix-B. Furthermore, the relative permeability is also lowered due to blockage of pores as a result of clay swelling. These effects are not accounted for in the capillary pressure and relative permeability input data sets in the sense that the procedure to obtain such inputs is devoid of correction due to clay swelling effects. To clarify, oilwater capillary pressure input is obtained by converting measured MICP curves to oilwater capillary pressure curves using Eq. A.1. Also, since measuring relative permeability is a daunting challenge for clay rich low permeability rocks, it is estimated using fractal relations (e.g. Eqs. A.5-A.6) for which D_f is obtained using, again, uncorrected capillary pressure data (Eq. A.3). Hence, such procedures devoid of clay effects' correction in estimating petrophysical properties of clay-rich rocks, among other factors, lead to significant errors and uncertainties in numerical simulation.



Figure 4.39 Comparison of experimental and simulated spontaneous imbibition oil recovery vs. time for samples (a) S1, (b) S2, and (S3)

4.3.4. A new approach for MICP-based fractal technique for clay rich pore

systems

To model physical processes in a porous medium, the pore network geometry needs to be specified [469]. From a capillary pressure perspective, in principle, any pore opening geometry (cavity cross-section) is applicable if the equation is known for equilibrium between the external pressure applied over the spanned area of the opening and for the resistive force produced by interfacial tension around the perimeter of the opening (the solid, liquid, vapour interface). In other words, a proportionality constant for the relation $P_c \propto (1/r)$ needs to be established. Typically, this capillary pressure is assumed to be a function of saturation since in a typical MICP test intruded volume at any applied pressure is measured. However, recent research has shown that at actual pore-scale, capillary

pressure is a function of the interfacial area in addition to saturation [470,471]. Characterizing such an effect, though allows for overcoming the assumption of cylindrical capillaries, requires advanced imaging techniques. The effect of the interfacial area is more pronounced when there are disconnected phases in the pore system. However, for a piston-like displacement (laminar flow) the traditional capillary pressure-saturation relationship should suffice. Also, despite the issue around image resolution, it is not known how image-based curvature-calculated capillary pressures can be converted to pore size distribution. For this reason, the Young-Laplace equation ($P_c = 2\sigma \cos \theta / r$) has remained the operating equation of most MICP measurement machines till today.

Therefore, in this study, for the development of the improved model, the porous media is considered to be a bundle of circular capillaries (Figure 4.40) which allows us to use the Young-Laplace equation (also known as the Washburn equation) for the relation between pressure and radius [346]. Moreover, for rocks with high porosities, the capillary bundle model was found to be a reasonable approximation [472–476]. Since the sandstone samples used in this study have porosities, it is chosen to proceed with the capillary bundle model although this assumption has certain caveats which will be discussed later. During counter-current spontaneous imbibition, water is free to enter from both open ends of the capillary tubes (Figure 4.40 (a)).



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Figure 4.40 Schematic of the (a) capillary bundle model and (b) its cross-section From the usual arguments of fractal theory, it is known that the number of pores, N with radii greater than r are given by [431]:

$$N(>=r) = \left(\frac{r_{max}}{r}\right)^{D_f} \tag{4.30}$$

Where r_{max} is the maximum pore radius. Differentiating Eq. 4.30 with respect to r gives:

$$-dN = D_f r_{max}^{D_f} r^{-D_f - 1} dr = f(r) dr$$
(4.31)

Where $f(r) = aD_f r^{-D_f-1}$ and $a = r_{max}^{D_f}$ is a constant. The pore volume (V_p) for N number of pores is then given by [477]:

$$V_p = \int_{r_{min}}^{r_{max}} \beta r^3(dN) \tag{4.32}$$

Where β represents pore structure geometry and is a constant. For instance, $\beta = 1$ for a cube or $\beta = 4\pi/3$ for a sphere [477]. Substituting Eq. 4.31 in 4.32 results in:

$$V_p = \int_{r_{min}}^{r_{max}} \beta f(r) r^3 dr = -\frac{D_f a \beta}{3 - D_f} (r_{max}^{3 - D_f} - r_{min}^{3 - D_f})$$
(4.33)

Similarly, the volume of water imbibed in all capillary tubes with radii < r is given by:

$$V_w = -\int_{r_{min}}^r \beta f(r) r^3 dr = -\frac{D_f a \beta}{3 - D_f} (r^{3 - D_f} - r_{min}^{3 - D_f})$$
(4.34)

Hence, at any time the water saturation (S_w) is given by:

$$S_{w} = \frac{V_{w}}{V_{p}} = \frac{r^{3-D_{f}} - r_{min}^{3-D_{f}}}{r_{max}^{3-D_{f}} - r_{min}^{3-D_{f}}}$$
(4.35)

Assuming $r_{min}^{3-D_f} \sim 0$ [477], which is a valid assumption considering $r_{min} \ll r_{max}$, Eq. (4.35) can be simplified to:

$$S_w = \frac{r^{3-D_f}}{r_{max}^{3-D_f}}$$
(4.36)

As discussed earlier, in clay-rich rocks, the swelling of clay minerals when in contact with external fluid with different chemical composition results in the reduction of pore radius (Figure 4.41) leading to a corresponding increase in capillary pressure based on [346,478]:

$$P_c' = \frac{2\sigma_{ow}\cos\theta_{wo}}{r'} \tag{4.37}$$

Where P_c' is the increased capillary pressure at the reduced radius r'.



Figure 4.41 Schematic of clay swelling causing the reduced radius

Assuming the swelling process is instantaneous, the increase in capillary pressure at the same water saturation value causes a rightward shift in the original $\log (S_w) - \log (P_c)$ curve. The reduction of the radius (i.e. the extent of swelling) is not constant and may vary in tubes of different capillary sizes depending on factors such as the amount and type of clay content in these tubes. The point is to be able to predict this rightward shift in the original $\log (S_w) - \log (P_c)$ data so as to accommodate the clay swelling effects. Hence, it is first realized that the reduced radius (r') can be determined as a function of the original radius (r) through their ratio (α) defined as:

$$\frac{r}{r'} = \frac{P_c'}{P_c} = \alpha_f \tag{4.38}$$

It is important to note here that the choice of capillary bundle model is arbitrary and is not necessary to arrive at the above definition of α_f . Assuming any other proportionality constant between P_c and r leads to the same definition. Similar statement can be made for arriving at the $P_c - S_w$ relationship (Eq. 4.38). A capillary bundle depiction nonetheless aids in portraying the clay-swelling phenomenon. Since the reduction of radius is only activated on contact with water, substituting r in Eq. (4.36) with respective P_c and replacing with $P_c = \alpha_f P_c'$ results in:

$$S_w = \left(\frac{P_{cmin}}{\alpha_f P_c}\right)^{3-D_f} \tag{4.39}$$

Taking logarithm of both sides of Eq. (4.39) gives:

$$\log S_w = (3 - D_f) \log P_{cmin} - (3 - D_f) \log \alpha_f P_c$$
(4.40)

Eq 4.40 is linear, but it differs from the original Eq. A.3 with the incorporation of α to account for the increase in the original MICP-based oil-water capillary pressure. In order to predict the shift in the value of $log S_w - log P_c$, the value of α_f must be also physically derived. For this, the concept of porosity reduction due to clay swelling is used [14,479,480]:

$$\Delta \phi = (\phi_i - \phi_{min})(1 - e^{k_\phi S}) \tag{4.41}$$

Where $\Delta \phi$ is the change in porosity due to swelling, ϕ_i is the initial porosity, ϕ_{min} is the porosity when the swelling has been completed, *S* is the cumulative water absorption by the clays, and k_{ϕ} is the rock matrix swelling rate constant. Since the filling of capillary tubes of a particular radius and consequent swelling is assumed to be instantaneous, $S_w = 1$ in these capillaries, it can be validly assumed that S = 1. The change in porosity can be related to the change in pore volume (ΔV_p) through:

$$\Delta V_p = V_B \Delta \phi \tag{4.42}$$

Where V_B is the volume of the bulk system that contains the pore system which is a constant. Hence, the substitution of Eq. 4.41 in Eqn. 4.42 and using $V_{pi} = \phi_i V_B$, $V_{pmin} = \phi_{min} V_B$ gives:

$$\Delta V_p = (V_{pi} - V_{pmin})(1 - e^{k_{\phi}})$$
(4.43)

Knowing that for a capillary tube $V_p = \pi r^2 h$, Eq. 4.43 can be written in terms of change in radius squared as:

$$(r_i^2 - r^2) = (r_i^2 - r_{min}^2) (1 - e^{k\phi})$$
(4.44)

It is also understood from Figure 4.41 that only part of the capillary swells which contains clay. This means that the reduction of the capillary radius is proportional to the amount of clay content in that capillary. It is for simplicity assumed that each pore (i.e. capillary) has the same amount of clay as measured by XRD analysis. Hence, α can be determined as:

$$\alpha = \frac{r}{\sqrt{C_{\%}^{2}(r_{i}^{2} - r_{min}^{2})(1 - e^{k\phi})}}$$
(4.45)

Where $C_{\%}$ is the percentage of the radius that contained clay minerals i.e. the percentage of the radius that will swell along the length of the capillary and it has been assumed to be equivalent to the amount of clay content determined from XRD.

Another important parameter, r_{min} in Eq. 4.45, requires further attention. The expansive clay minerals (e.g. smectite or mixed-layer illite/smectite) swell significantly and can even completely close the pore-throats [14]. However, it is emphasized that the negatively charged clay minerals exhibit electrical diffuse double layer (DDL) expansion through adsorption of cations [22]. In a capillary-type pore, the swelling from opposite sides (Figure 4.41) can only come as close as the thickness of the DDL. When the DDL from opposite surfaces overlap, there is an extra repulsive force [481] that prevents the complete closure of the pores. Therefore, the minimum radius of any pore is equivalent to the thickness of the DDL given by the Debye length (κ^{-1}) [482]:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon RT}{2(N_a q_e)^2} \frac{1}{I}}$$
(4.46)

Where $\varepsilon = 6.95 \times 10^{-10} F/m$, R = 8.314 J/K/mol, T = 298K, $N_a = 6.022 \times 10^{23}/mol$, $q_e = 1.6 \times 10^{-19} C$, and *I* is the ionic strength in *mol/L*. Simplifying Eq. 4.46 gives the DDL thickness in μ m units which is essentially equivalent to r_{min} :

$$r_{min} = \kappa^{-1} = 3.09 \times 10^{-4} \sqrt{\frac{1}{I}}$$
(4.47)

and I is defined as [482]:

$$I = \sum_{i=1}^{n} C_i z_i^2$$
(4.48)

Where C_i is the concentration of each ion (in mol/L) and z_i is the valance of each ion. The ionic strength for the synthetic fluid in this study was calculated to be 0.286 mol/L (based on Table 4-5) and the Debye length was thus calculated to be $5.78 \times 10^{-4} \,\mu\text{m}$ or 0.578 nm. Hence, the final form of Eq. 4.40 is given by:

 $\log S_w = (3 - D_f) \log P_{cmin} - (3$

$$-D_{f} \log\left(\frac{r_{i}}{\sqrt{C_{\%}^{2}(r_{i}^{2}-r_{min}^{2})(1-e^{k_{\phi}})}}P_{c}\right)$$
(4.49)

Where $C_{\%} = 0.36$, 0.43 and 0.37 for samples S1, S2, and S3 respectively (as obtained from XRD – Table 4-7), $\kappa^{-1} = 0.58 \text{ nm}$, and r_i is the initial radius as obtained from MICP (i.e. before swelling). The value of k_{ϕ} used was 2.5 for S1, and 5 for S2 and S3. These values have physical meaning and the details of how these values for different samples were estimated are explained in Appendix-C. The theoretical-based development of the above equation (Eq. 4.49) can be used instead of the original Eq. A.3. as it is a first-step improvement for the altered pore-network behaviour under influence of reactive clay minerals. In other words, it corrects the capillary pressures for the clay content. Though fractal technique is based on statistics, all parameters in the equations have physical basis and their estimation does not require any history-matching or complex experimental techniques.

Now, to demonstrate the performance of Eqn. 4.49 in predicting the shift in MICP-based oil-water capillary pressures due to clay swelling, actual oil-water capillary pressures were measured using the centrifuge experimental method for samples S1, S2, and S3 respectively. When centrifuge data were plotted on $\log(S_w) - \log(P_c)$ plot (blue circles in Figure 4.42 (a)-(c), it is seen that the experimental data does not fall on the original MICP-based straight line (green circles in Figure 4.42) that it should supposedly and theoretically follow. Centrifuge capillary pressures have been used extensively for different rock types and often were not found to significantly differ from MICP capillary pressures [483–485]. However, as observed here, the experimental capillary pressures in the range of pore-throat radii in which they were measured were higher than those estimated from MICP (even though clay bound water correction was applied i.e. Eq. A.1). These higher capillary pressures should therefore be due to reduced pore-throat radii. The straight-line region of the experimental data is much steeper and clearly has a different value of D_f . Since centrifuge data do not span the whole pressure range as MICP, D_f for centrifuge data was calculated based on the limited number of points in the straight-line region. Table-6 below shows D_f values based on MICP and centrifuge data. It is evident that D_f value changed due to change in pore structure – highest change in D_f was for S1, followed by S3, and S2.

Sample		MICP-based	Centrifuge	% Change
S1	D_f	2.805	2.662	5
S2		2.911	2.934	0.7
S3		2.928	2.882	1.5

Table 4-11 D_f values from MICP and centrifuge data

Furthermore, when Eq. 4.49 is used (black line in Figure 4.42), it is seen that most of the experimental data is matched to a good extent implying that the input parameters in Eqn. 4.49 are based on sound physics. In other words, without any regression or parametric history-matching being performed, the correction factor α was able to accurately predict the actual capillary pressure data with enough accuracy. The R² values for the straight-line regions are shown on the plot (Figure 4.42). Despite the theoretical-based correction, a lacking in high correlation coefficient between Eq. 4.49 and actual capillary pressure data is due to the underlying caveats implicitly introduced with the use of simplified assumptions behind such fractal-based formulations. Hence, further improvements are critically needed, and current fractal-based formulations come with implicit caveats that are discussed in the next section.



Figure 4.42 Comparison plots of MICP-based, experimentally measured, and corrected MICP-based (Eqn. 1.24) oil-water capillary pressure curves, for samples (a) S1, (b) S2,

and (c) S3

4.3.5. Discussion

4.3.5.1. Experimental oil recoveries

Spontaneous imbibition of wetting-phase into a porous medium is assumed to be controlled solely by the capillary pressure phenomenon. The swelling of pores and pore-throats as the water imbibes these pores reduces the pore-throat radii causing an increase in capillary pressures as shown earlier (Figure 4.42). Thus, the oil ahead of the waterfront must overcome this increased capillary back-pressure which reduces the amount of oil recovered. In addition, during spontaneous imbibition, the wetting phase generally tends to enter the micro-pores first, displacing oil therein, thus oil also has a high tendency to get trapped due to the ink-bottle effect [486]. Therefore, low oil recoveries especially for strongly water-wet rocks are usually expected. At the end of spontaneous imbibition experiments, the water saturation in the samples as calculated were 0.1, 0.175, and 0.183 respectively in S1, S2, and S3. This corresponds to the maximum oil that can be recovered until the capillary forces are no longer active. The remaining oil must be extracted through the application of viscous forces such as water-flooding etc.

4.3.5.2. Comparison of experimental and simulated oil recoveries

Capillary pressure curves and relative permeability data exhibit significant sensitivity in two-phase fluid flow simulation in which they are used as input. Their input into a simulation model, when they have been reliably estimated, along with other rock and fluid properties should therefore accurately predict the fluid flow. However, the differences between simulated and experimental oil recoveries in this study highlight the role of clay

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content on oil-water two-phase flow. Clay-rich samples were chosen for this study to highlight how clay minerals affect fluid flow analysis due to swelling, flocculation, and pore or pore-throat blocking. All these phenomena lead to pore structural alteration and therefore fluid flow in such pores is affected significantly. More importantly, the trend of spontaneous experimental oil recoveries from the samples (S3>S2>S1) follows closely the trend of the CEC of samples (Table 4-8) which signifies the critical role clay minerals play in two-phase fluid flow.

4.3.5.3. **Reasons for mismatch and implicit caveats of fractal formulations**

Specifically, change in pore structure tends to change the fractal nature of the pore system i.e. a shift in the fractal dimension (D_f) . Thus, the estimated MICP-based value of D_f ceases to represent the actual (quasi-) dynamic pore structure giving rise to differences in simulated and experimental oil recoveries. The mismatch highlights the caveats behind such fractal models that are otherwise not discussed. It is reiterated that such discrepancies arise due to the fractal theory models' basis on a static unchanging pore structure. Also, such reactive effects of clays will occur on contact with external fluids previously unknown to the reservoir such as hydraulic fracturing fluids.

Thus, it was observed that the more transient S1 (higher deviation from MICP-based data), has the least amount of experimental oil recovery compared to S2 or S3. The pore size distribution (PSD) of the samples (Figure 4.43) shows that S1 and S3 have a similar number of micro and macro-pores but their permeabilities and oil recoveries were quite different. This implicates the complex role of transient pore networks in the two-phase fluid flow where simple petrophysical interpretations cannot be used to explain the observed flow behaviour. In fact, this was one of the main reasons why fractal approaches were being used to explain or even predict such behaviour. However, it was shown that

even the fractal approaches need significant improvements to accurately predict fluid flow in clay-rich rocks accurately.



Figure 4.43 S_{Hg} vs. pore throat radius for all samples

Moreover, the comparison of calculated and experimental capillary pressures (Figure 4.42) highlighted that the current MICP-based fractal formulation (e.g. Eq. A.3), even with clay swelling correction, is not stand-alone and universal. This consequentially implies that a single set of MICP-based capillary pressure data used in numerical simulation leads to errors and discrepancies. As was evidenced, clay swelling leads to an increase in capillary pressures and changes in fractal dimensions which would require updating of the capillary pressure data as input in reservoir simulation. The clay-swelling correction of MICP-based data using Eq. 4.49 will give nearly the same slope (and thus D_f) as the correction is in terms of only a scaling factor ' α_f ' on the theoretical MICP data. Therefore, relative permeability data (Eq. A.4-6) could not be improved for performing re-simulation of the experiments. Nonetheless, it is recognised that clay swelling will also

alter the relative permeability and not just the capillary pressure. Moreover, most fractal formulations including the model used in this study are based on the capillary bundle model that does not necessarily represent the actual pore network. The implicit assumption of this model that pore-throat radii equal pore-body radii is too fetched to be realistic on clay-rich rocks where clay minerals are more represented by sheet-like structures. Even for conventional rocks, the ratio of pore-throat radii to pore-body radii can significantly vary. Hence further research is warranted for more and better techniques to improve existing static-pore network fractal models for their applicability to clay-rich pore systems.

4.3.6. Conclusion

Two-phase flow investigation in clay-rich tight rocks offers significant challenges both experimentally and theoretically. Fractal-based models, therefore, have gained popularity in tight rocks to study the capillary pressures and relative permeability estimations. The MICP-based fractal approaches to estimate petrophysical properties in clay-rich low permeability porous media are however not universal at all length and time scales. The implicit caveats of holding these fractal formulations can be summarized as follows:

1.) The current fractal techniques represent the fluid dynamics only in static non-reactive porous media i.e. porous media whose pore network remains constant during fluid flow.

2.) The current MICP-based fractal formulations are inherently based on the capillary bundle model. Any pore system where it's pore-throat/pore-body ratio deviates significantly cannot be accurately analysed using such fractal formulations.

3.) The assumption of relating the number of pores to pore-throat radii from MICP based on the power-law scaling of the capillary pressure data seems to lack physical proof.

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This leads to severe errors and discrepancies in predicting two-phase fluid flow in such clay-rich rocks. As a direct consequence, hydraulic fracturing efficiency, productivity optimization, formation damage estimation, and control, acid stimulation processes, etc. in low permeability clay-rich rocks are all affected by a high uncertainty in their fractalbased simulations or predictions i.e. especially when the pore network begins to be influenced by clays, clay swelling causes a reduction in pore-radii and respective increase in capillary pressures. As a first critical step, such effects must be incorporated in the fractal models if they are to be used for such rocks. To accommodate these effects of clay minerals, an improvement in the current in-practice conventional MICP-based fractal model was proposed using physical principles. The new model corrects the theoretical MICP-based $\log(S_w) - \log(P_c)$ for increased capillary pressures during two-phase flow. Moderate correlation coefficients between model-corrected and experimental capillary pressures further highlight the complexities involved during fluid flow in clayrich rocks and how fractal theory needs to be used with caution while interpreting such flow. The comprehensive petrophysical investigations and model development presented in this study is the first step towards the improvement of predicting the two-phase flow behaviour in clay-rich rocks. The proposed model can be also used to obtain proper input for the developed constitutive equation especially for the two-phase flow of the derived equations.

Chapter 5. Numerical simulation of the developed constitutive equations and sensitivity analysis

5.1. Introduction

Partial differential equations (PDEs) (such as those derived in Chapter-3) can be solved using numerical techniques such as finite difference methods (FDM), boundary element (BEM) or finite element methods (FEM). This is done with the help of appropriate initial and boundary conditions along with proper discretization of the equations. In this dissertation, the COMSOL Multiphysics FEM platform was used to solve the coupled two-phase, damage chemo-poroelastic non-linear PDEs describing the shale water loss problem.

COMSOL Multiphysics is a commercial software well-known for modelling science and engineering coupled problems based on PDEs [487]. It has the ability to utilize various numerical solvers that use FEM along with adaptive meshing and error control techniques to solve different types of problems such as non-linear and linear, time-dependent and stationary, eigen-frequency, and modal analysis [487].

COMSOL Multiphysics has been used previously in several studies to solve both coupled and decoupled flow and geomechanics problems (PDEs) pertaining to different materials and geometries. There have been several numerical investigations using COMSOL which could not be validated due to their complexity in replicating laboratory experiments or the absence of analytical solutions. Some of such studies relevant to this dissertation are briefly mentioned here. Zheng et al. [488] studied the field-scale shale gas production decline rate in a horizontal well under geo-mechanical effects using COMSOL by incorporating a permeability-stress relationship into the model. Rokhforouz and Amiri [489] performed a simulation of coupled phase-field and Navier-Stokes equations in COMSOL to study pore-scale counter-current spontaneous imbibition in a twodimensional (2D) fractured porous medium. Tatomir et al. [490] solved coupled twophase flow and tracer transport in COMSOL for potential monitoring of CO₂ after geosequestration. Though analytical or experimental validation for their laboratory and fieldscale simulations could not be provided, they concluded that COMSOL is a robust platform to simulate two-phase flow and interfacial tracer transport. Bjørnarå et al. [491] tested several two-phase flow PDE formulations in COMSOL and found good agreement between them. They concluded that the traditional Buckley-Leverett [492] analytical results are not directly comparable to those from COMSOL simulation as it is a 1D equation and only solves for decoupled wetting phase saturation. Nonetheless, from their investigation too, COMSOL could be concluded as robust to be able to solve different kinds of two-phase flow in COMSOL to study gas migration and fracture propagation in bentonite barrier materials. They concluded that the hydro-mechanical behavior of bentonite satisfactorily matches experimental observations though exact comparison could not be provided due to the complexity of the problem.

However, more studies have extensively scrutinized and validated COMSOL to solve coupled multi-physics problems. Samea and Selvadurai [494] used COMSOL to solve coupled Fredholm integral equations obtained from the reduction of the mixed boundary value problem using Laplace and Henkel integral transforms. The equations were formulated to solve the problem of a circular disc in contact with a poroelastic medium. The numerical results from COMSOL were calibrated with theoretical (analytical) solutions endorsing the robustness of COMSOL to solve such coupled PDE problems. Zhou et al. [495] used COMSOL to study crack propagation using the phase-field modeling feature. After checking for the effects of various parameters such as length scale, mesh size, time step size, and critical energy release rate, they concluded that the

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results were accurate showing the feasibility of COMSOL for such analysis. Chahardowli et al. [496] solved, using COMSOL, a numerical model describing the wettability alteration mechanism during an imbibition process. Their oil recovery curves from COMSOL matched very well with experimental data signifying the accuracy of COMSOL in simulating such flow processes. Similarly, Taheri et al. [497] used COMSOL to solve for methane gas flow in a 2D coal matrix and validated their results with an analytical solution reasonably well.

Freeman et al. [498] performed a fully coupled thermo-hydro-mechanical (THM) modelling in COMSOL to study single and multi-phase flow coupled with geomechanics. Their results were verified using other numerical and analytical solutions from the literature. Nasir et al. [499] performed a coupled THM-geochemical simulation to study the nuclear repository potential of sedimentary rocks. They used the coupled COMSOL-PHREEQC platform for simulation and validated their results with experiments and previous modelling work. Zhang et al. [500] developed a semi-analytical solution to account for the effect of gravity on two-phase immiscible flows in layered reservoirs. The results of their semi-analytical solution compared well with 2D waterflooding simulations in COMSOL asserting that COMSOL can be used to solve complex fluid flow problems.

It is evident from the literature that COMSOL can be successfully used to solve coupled/decoupled flow and geomechanics problems with proper validation and verification [501–508]. It is also evident that problems defined by non-linear and complex PDEs are challenging to be analytically or experimentally validated. However, the decoupled validations portray the accuracy and robustness of COMSOL to simulate such problems. Hence, COMSOL Multiphysics is used in this dissertation to solve the coupled PDEs derived in Chapter-3 that describe the shale water loss problem. Each decoupled physical part of the system is verified using simplified existing analytical solutions or 219

published numerical data (Appendix-D). The implementation of those equations in COMSOL is discussed subsequently.

5.2. COMSOL Implementation

5.2.1. Model conceptualization

The shale rock is a porous medium characterized by pores and a solid skeleton where the pores are initially filled with gas (with irreducible water). After hydraulic fracturing, there are main hydraulic fractures and several hydraulically induced micro-fractures where the water resides. During the well shut-in period, water imbibes from the main fractures and the induced micro-fractures into the gas saturated matrix. Since the induced microfractures are hydraulically poorly connected to the main fracture [509,510], the imbibition modes from the main fracture and induced micro-fractures are different. From the induced micro-fractures, spontaneous imbibition is the main mechanism of water uptake by the shale matrix [511]. The extent of this spontaneous imbibition in causing water loss in shales has been the focus of this dissertation as stated in Chapter-1. It is also the focus of the simulation in this chapter. As the water imbibes, two-phase flow occurs in the shale matrix and micro-cracks develop in the rock due to weakening caused by water-shale interactions. These micro-cracks are a timely result of the chemically driven microstructural alteration of the matrix and should not be confused with the above-discussed hydraulically induced micro-fractures generated during hydraulic fracturing. The timedependent micro-structural deterioration of the matrix and two-phase flow is represented in a continuum way by assigning the simulation representative elementary volume (REV) values of porosity, relative permeability, capillary pressure, fluid saturations, and chemical damage variable. The external and in-situ water phase can contain ions which is represented by assigning solute concentrations to the respective water phases. The shale matrix is under the action of in-situ stresses due to its burial depth and hence

representative mechanical loads are applied to the REV. Considering the normal faulting stress regime, as the common case for shale reservoirs, the overburden stress and minimum horizontal in situ stress are assumed the highest and lowest stresses acting on the REV, respectively. Although the intermediate stress is relatively important on the mechanical response of the rocks, the minimum and maximum stress effect are shown to be dominating [512,513]. It is assumed that hydraulically induced micro-fractures have long lengths compared to their widths leading to the valid assumption of the plane strain problem. With these arguments, a 2D REV model can simulate the conditions of the shale matrix during well shut-in. The 2D domain geometry (REV) is thus shown in Figure 5.1.



Figure 5.1 Schematic of the 2D geometry, mesh, and boundary conditions used for simulating spontaneous imbibition from induced micro-fractures into shale matrix

5.2.2. Initial conditions

The initial water phase pressure in the REV is zero (0) MPa as it exists initially at irreducible water saturation (0.17). The initial gas-phase pressure is set as 34.5 MPa (5000

psi) based on the reservoir pressure of typical shale gas reservoirs with a saturation of 0.83. The gas reservoir pressure can vary with the burial depth and can sometimes be exceptionally high due to stratigraphic conditions. The initial and later water saturations are calculated using the auxiliary equations presented in Chapter-3 where the capillary pressure is known (from fractal theory). The initial gas saturation is obtained by subtracting water saturation from unity. The initial solute concentration of the REV is set as 0.5 mol/m^3 which obviously is dependent on the composition of in-situ pore water.

5.2.3. Boundary conditions

The flow boundary conditions for the 2D domain are set as a zero-flux top, bottom, and right boundaries, and constant pressure left boundary (Figure 5.1). The constant pressure on the left boundary is the water inlet pressure and the gas outlet pressure. The water pressure in the induced micro-fractures after well shut-in is usually below the reservoir pressure [514] representing spontaneous imbibition conditions. In this study, it is set as 20.7 MPa (3000 psi). Spontaneous imbibition is a slow process and progresses during the period of shut-in e.g. more than a week [514].

The imbibed water causes the gas to flow out of the induced micro-fracture-matrix face, i.e. a counter-current imbibition is modelled [83]. The solute boundary condition on the left boundary is set as 0.1 mol/m^3 such that the salinity of the in-situ water is higher than that of the fracturing fluid.

The mechanical boundary conditions are set as a roller for the bottom and right boundaries whereas the left and top boundaries can deform freely (Figure 5.1). In actuality, the value of such stresses depends on the burial depth of the gas reservoir and the stratigraphic location.

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5.2.4. Field equations and COMSOL modules

As observed from the performed experiments in Chapter-4, chemical osmosis was negligible in the organic-rich shale used in this study, hence the reflection coefficient is insignificant ($\Re \approx 0$). Also, it was observed that water adsorption does not induce significant swelling volumetric strains, hence swelling coefficient can be also assumed to be very small ($\omega^0 \approx 1 MPa$). Moreover, as observed from micro-scale investigations in Chapter-2, the surface deformation induced by fluid exposure was localized and considerably trivial compared to the sample volume. Hence, based on these observations we simplify the derived constitutive mode before solving them, where $\alpha_w \dot{\varepsilon}_{kk}$ and $\alpha_g \dot{\varepsilon}_{kk}$ can be neglected in Eqs. 3.80 and 3.81, respectively. Also, it can be assumed $\bar{\rho}^w >> \bar{\rho}^c$ and water as incompressible. Hence, based on these simplifications, the final field equations to be solved are:

$$(1-D)G\nabla^{2}\dot{u}_{i} + (1-D)\frac{G}{1-2v}\nabla(\nabla\cdot\dot{u}_{i}) - \delta_{ij}\alpha(S_{g}\nabla\dot{p}_{g} + S_{w}\nabla\dot{p}_{w}) + \frac{S_{w}\omega^{o}(\alpha-1)}{K\bar{C}^{c}}\dot{C}^{c} = 0$$
(5.1)

$$\left(\left|\frac{1}{M_{w/w}}\right|\dot{p}_w + \frac{1}{M_{w/g}}\dot{p}_g\right) = \frac{kk_{rw}}{\tau_w}(\nabla^2 p_w)$$
(5.2)

$$\left(\left[\frac{1}{M_{w/g}}\right]\dot{p}_w + \left[\frac{S_g\phi}{K_{f,g}} + \frac{1}{M_{g/g}}\right]\dot{p}_g\right) = \frac{kk_{rg}}{\tau_g}\nabla^2 p_g$$
(5.3)

$$\rho_s S_w \dot{C}^c + S_w (\rho_c \boldsymbol{u}^w \nabla C^c + \nabla \cdot (-\rho_c D_e \nabla C^c)) = 0$$
(5.4)

The two-phase formulation is supplemented by auxiliary equations to enable a closedform solution [513]. These are recalled from Chapter-3 (Section 3.4.4.2) as: $p_c(S_w) = p_g - p_w$ and $S_w + S_g = 1$. where

$$S_w = \left(\frac{P_{cmin}}{P_c}\right)^{3-D_f} \tag{5.5}$$

Furthermore, relative permeability is a key parameter characterizing the relative seepage of the two phases. This is obtained analytically through fractal technique as discussed in Chapter-4.3 and Appendix-A:

$$K_{rw} = S'^{\frac{11 - D_f}{3 - D_f}}$$
(5.6)

$$K_{rnw} = (1 - S')^2 (1 - S'^{\frac{5 - D_f}{3 - D_f}})$$
(5.7)

where

$$S' = \frac{S_w - S_{wi}}{1 - S_{wi}}$$
(5.8)

These field equations are solved using the FEM-based platform COMSOL through utilization of different modules and physics interfaces. The different modules and interfaces utilized in this dissertation have been briefly described below i.e. the COMSOL Users Guide can be referred to for detailed information [487]. Also, the constitutive theory field equations solved by each module and interface are presented without describing the details of the variables involved, which can be found in Chapter-3 (see Appendix-E for basic workflow of COMSOL Multiphysics simulations).

5.2.4.1. Structural mechanics (SM) module

The Solid Mechanics physics interface under the SM module is based on general continuum mechanics principles and is the aptest for general modeling of structural mechanics problems [487]. The poroelasticity node allows for coupling between solid mechanics and fluid flow physics interfaces. The main dependent variable solved from this interface is the displacement field (u_i) . Eq. 5.1 is solved using this interface where

the swelling stress is added as the body force source term. It is noted that in COMSOL tensile stress is taken as positive. Also, all mechanical stress profiles presented in subsequent sections are effective stresses (σ').

5.2.4.2. Porous media and subsurface flow (PMSF) module

The Darcy's Law physics interface under the PMSF module is commonly used to model low-velocity flow or flow in porous media where the porosity or permeability is small [487]. Hence, this is most appropriate for modeling water and gas flow in porous rocks as required by the constitutive theory. Two separate Darcy's Law interfaces can be set up to model two-phase flow. The main dependent variable solved by this interface is the phase pressure (p_w , p_g). Eqs. 5.2 and 5.3 are implemented using this interface where the phase coupling coefficients $M_{\alpha/\beta}$ are incorporated using the Storage Model interface.

5.2.4.3. Chemical species transport (CPT) module

The CPT module contains the Transport of Diluted Species in Porous Media interface which is solved for the concentration field of a solute in a solvent [487]. The interface can model both diffusion and advection and hence can couple fluid flow (Darcy's Law interface) with solute transport. The dependent variable in this interface is the solute molar concentration (C^c). Eq. 5.4 is solved directly using this interface without needing any extra source terms.

5.2.4.4. Mathematics module

The Mathematics module contains the Coefficient Form PDE physics interface which allows custom equation-based modelling. Custom user-defined partial differential equations (PDEs), ordinary differential equations (ODEs), and algebraic equations can be solved using this interface. This interface was used to model the damage evolution equation where the dependent variable was the damage variable *D*:

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$$\dot{D} = \frac{2(1-D)\bar{C}^{c}\Delta C^{c}}{S_{w}\omega^{0}(C^{c})^{2}}$$
(5.9)

5.2.5. Finite element discretization

A finite element mesh is created using mapped quadrilateral elements. The entire 2D geometry is divided into 5600 quad elements with the element-area ratio of 0.1. The mesh was refined near the shale-fracture interface to accurately capture the imbibed waterfronts at early times. The mesh is shown in Figure 5.1. The scatter/line plots of numerical solutions presented subsequently are plotted along the yellow horizontal line along the X-direction of the REV as shown in Figure 5.1. The simulation time was 500 hours which is around 20 days, within the well shut-in durations post hydraulic fracturing. The above field equations (using the respective physics interfaces in COMSOL) are solved in a fully coupled way.

5.3. Numerical examples

The details of the variables involved in the above field equations have been discussed in Chapter-3. For the numerical simulation in COMSOL, certain inputs are required which are tabulated below (Table *5-1*). The numerical simulation capability of the developed constitutive theory is first assessed by running a base case for the complete two-phase, damage chemo-poroelastic model. Then, the following different scenarios are studied and compared: (i) the effect of the absence of damage on two-phase chemo-poroelasticity, (ii) the effect of the absence of chemical effects in two-phase poroelasticity, and (iii) sensitivities of the main influencing parameters.

Table 5-1 Input parameters for simulation

Parameter	Value [Units]	Description
E	10.05 [GPa]	Young's modulus [148]

ν	0.33	Poisson's ratio [148]
α	0.8	Biot's coefficient [515]
ω^0	1 [MPa]	Swelling coefficient
D _e	3.3e-14 [m ² /s]	Solute diffusion coefficient
		[516]
k	1.0e-16 [m ²]	Absolute Permeability
ϕ	0.1	porosity
C _{smean}	0.3 [mol/m ³]	Mean solute concentration
$ ho_w$	1000 [kg/m ³]	Density, water
$ au_w$	1e-3 [Pa.s]	Dynamic viscosity, water
$ ho_g$	120 [kg/m ³]	Density, gas [517]
$ au_g$	2.5e-5 [Pa.s]	Dynamic viscosity, gas [518]
$K_{f,g}$	0.5 [MPa]	Gas bulk modulus [517]
D_f	2.8	Fractal dimension
σ_{xx}	50 [MPa]	X-direction (Minimum
		horizontal stress)
σ_{yy}	75 [MPa]	Y-direction (Overburden
		stress)
Simulation time	500 [hours]	

5.3.1. Base case: Two-phase, damage chemo-poroelastic simulation

In this base case, the complete capability of the constitutive theory is numerically assessed by solving the two-phase, damage chemo-poroelastic model. In this scenario, the effect of micro-structural alteration of the matrix on the poroelastic response is included. The effect of such micro-structural alteration is to cause reduction in the rock's strength as discussed in Chapter-4.3.

Firstly, the results for water-gas flow with associated solute transport are presented. Validations of poroelasticity and two-phase flow are presented in Appendix-D. The pressure diffusion and consequent waterfront movement into the matrix is expected to be slow due to the low permeability of the shale (Figure 5.2 (a) and (c)). After 500 hours (of shut-in), the water imbibition length is around 2 mm or 13.3% of the REV length (Figure 5.2 (c)). It is noted that the water flow follows piston-like displacement which is typical for low-velocity spontaneous imbibition process. Furthermore, no dispersion or mixing is expected when water imbibes into a gas-saturated porous medium [519]. From 1D scatter plots (plotted along the yellow line in Figure 5.1) shown in Figure 5.2 (b) and (d), it is clear that based on the pressure-pressure two-phase formulation, the water saturation profiles (S_w) follows the water pore pressure (p_w) profiles. It is recalled that in such a two-phase formulation, the main dependent variables are the phases pore pressures which are solved at each time step. Using the phase pressures, S_w is calculated at each time step using the auxiliary equations presented above. The gas pore pressure profiles are shown in Figure 5.3 (a) and (b) for early and late times, respectively. It is seen that gas flows out almost instantly under the imposed pressure drop and stabilizes across the matrix very quickly. This is in line with the spontaneous imbibition process of water into a gas saturated porous media where pressure equilibration in the gas phase is almost instantaneous i.e. negligible pressure gradient in the gas saturated region [84,316]. It is noted that this is specifically valid for capillary-dominated spontaneous imbibition processes where the displaced fluid has a very low viscosity compared to the displacing fluid. During gas production stages, the pressure drawdown in the gas saturated region will be significant and must be accounted for. It is also noted that the two-phase flow pressure-pressure formulation causes water pore pressure in the matrix to be negative due to the storage term $\frac{1}{M_{W/q}}$. This is a common mathematical consequence of the boundary

conditions imposed on such a formulation, especially for spontaneous imbibition twophase flow process as reported by previous studies [520]. Discussion on two-phase spontaneous imbibition boundary conditions is not elaborated here as there is an abundance of well-documented literature which the readers are referred to (c.f. [521– 523]).



Figure 5.2 (a) Water pore pressure snapshot at t = 500h, (b) water pore pressure profiles at different times, (c) water saturation snapshot at t=500h, and (d) Water saturation

profiles at different times



Figure 5.3 Gas pore pressure profiles at early times and (b) pressure stabilization at later times

The chemical effects are incorporated using the solute transport equation. The coupling of two-phase flow and solute transport with geomechanics is one-way such that the stress equation is affected by the water and gas pressures (poroelasticity) and by the change in solute concentration (i.e. swelling stress, $\omega^o > 0$), but the phase pressures and solute concentration are not affected by the change in stress conditions. This is presented in the formulations in Chapter-3 where the terms $\alpha_w \dot{\epsilon}_{kk}$, and $\alpha_g \dot{\epsilon}_{kk}$ were assumed negligible in the respective field equations (Eqs. 3.78-3.79). There was also no coupling term in the solute transfer field equation with stress (Eq. 3.85).

It is seen that the time to equalize the solute concentrations in the matrix and fracturing fluid (external water) is very long. Even after 500 hours, the solute outflow reached only <2 mm (Figure 5.4 (a)). It is also seen that outward solute transport follows closely with the water saturation (compare Figure 5.2 (c) and Figure 5.4 (b)). This is obvious as per the assumptions of the developed constitutive theory. The assumption was that only the

imbibed water favors solute transport and there is no solute transport in the gas saturated region of the matrix.

The swelling stress (σ_{swell}) generated in the matrix according to the developed theory is shown in Figure 5.4 (c)-(d). As seen, the maximum swelling stress is around 0.42 MPa (59.5 psi) corresponding to the maximum difference in the solute concentration between the matrix and fracturing fluid. With the progress of solute transport, the region of the matrix experiencing chemical swelling expands. It is worth noting that the generated swelling stress is too low to overcome the high magnitudes of confining stresses. Hence, a macro-scale impact of such stresses is not manifested through, for example, the creation of large micro-fractures with significant plastic strains. This was indeed seen in microscale experiments in Chapter-2. Moreover, no swelling stress was generated in the gas saturated region since there is no change in solute concentration and the water is still at irreducible water saturation.



Figure 5.4 (a) Solute concentration snapshot at t=500h (scaled-up X-axis), (b) solute concentration profiles at different times, (c) swelling stress snapshot at t=500h (scaled-

up X-axis, and (d) swelling stress profiles at different times

With water and solute transport occurring in the shale matrix, the stress state inside the rock changes due to different pore pressures of water and gas giving rise to unique poroelastic responses for water and gas saturated regions. This unique response is challenging to observe with other two-phase formulations [199,201] highlighting the significance of the theory developed in this dissertation. This is because, as discussed in

detail earlier, the averaged pressure formulation or pressure-saturation formulations cannot accurately incorporate respective water and gas-dependent coupled processes [513,524,525].

The stress distribution for the complete two-phase, damage chemo-poroelastic scenario (base case) is shown at different times in Figure 5.5. The unique poroelastic response in water and gas saturated regions of the rock is evident. The transition between the two regions is characterized by what is referred to in this dissertation as 'poroelastic response interface' (PRI). The PRI diffuses further into the matrix with time. As the water-gas interface moves further into the matrix, the PRI also expands. Since there is negligible change in gas phase pressure due to the well shut-in simulation, there is no change in stresses in the gas saturated region.



Figure 5.5 (a) σ'_{xx} and (b) σ'_{yy} stress profiles at different times

The damage variable profiles give insight into the evolution of damage in the watersaturated region. The damage variable evolution is independent of the confining conditions. It is seen that after 5 hours of water imbibition, damage variable (D_{chem}) reached a maximum of 0.13 at the fracture-matrix interface and diffusively reduces further into the matrix before neutralizing in the gas saturated region (Figure 5.6 (a)). The value of D_{chem} is always highest at the fracture-matrix interface due to the maximum difference in solute concentrations. At 50 hours, D_{chem} increased to 0.28 and by 500 hours has already reached the theoretical limit of 0.3 amounting to complete failure or localization of micro-structural alteration. The permeability in the water-saturated increases significantly with time due to damage evolution while the permeability in the gas saturated region remains constant (Figure 5.6 (b)). Permeability is seen to increase ~5.5 times after 500 hours of water imbibition. It is noted that since the permeability is increased only in the water-saturated region, the water pore pressure and saturation curves are not affected by such permeability alteration.



Figure 5.6 (a) Damage variable profile and (b) corresponding permeability evolution profile at different times

5.3.2. Case 2: Effect of neglecting damage in two-phase, damage chemoporoelasticity

In the previous section, the complete two-phase, damage chemo-poroelastic case was solved serving as the base case. In this section, the effect of neglecting micro-structural deterioration due to chemical effects is studied (i.e. D = 0 in Eq. 5.1).

When damage is neglected (solid lines in Figure 5.7), the two-phase chemo-poroelastic behaviour is significantly different. It is seen that while the stress in the gas saturated region remains unchanged (Figure 5.7), the stresses in the water-saturated region change significantly due to neglecting the damage-induced permeability evolution in the watersaturated region. When damage is neglected, the stresses in the damaged region are grossly overestimated (compare the difference between dashed and solid lines in Figure 5.7). The difference in stress due to damage and without damage increases with time as the water-saturated region experiences increasing micro-structural deterioration i.e. the rock is weakened due to damage evolution. For example, the difference in σ_{xx} with and without damage was ~7 MPa after 5 hours of damage, ~14 MPa after 50 hours of damage, and ~15 MPa after 500 hours of damage. Moving into the undamaged gas region, the stress responses merges signifying the effect of damage is only in the water-saturated region. The results obtained from the constitutive theory are in qualitative agreement with a similar experimental observation made by David et al. [526] where mechanical instability (including damage visualized by computed tomography) was found to be associated only with regions that imbibed water. This experimental observation corroborates the developed theory.



Figure 5.7 Comparison of (a) σ'_{xx} and (b) σ'_{yy} stress responses with damage (dashed lines) and without damage (solid lines)

5.3.3. Case 3: Effect of neglecting damage and chemical effects (simple two-phase poroelasticity)

In this section, both damage and chemical effects are omitted from the constitutive theory (i.e. D = 0 and $\omega^0 = 0$). When chemical swelling stress effects are neglected, it is seen that the stresses are marginally higher only in the water-saturated region (solid lines in Figure 5.8). The response in the gas saturated region does not change due to the absence of solute flow. The increment in stress is caused because of the absence of neglecting the tensile swelling stresses that oppose the applied compressive in-situ stresses. Since damage is also neglected, there is no damage-induced permeability evolution and hence the variable profiles other than stresses are not affected.



Figure 5.8 Comparison of (a) σ'_{xx} and (b) σ'_{yy} stress responses with chemical effects (dashed lines) and without chemical effects (solid lines)

5.3.4. Sensitivity analysis

The apparent sensitivities (stress state, chemical swelling coefficient, damage) have been covered in the previous discussion through comparison of two-phase poroelastic, twophase chemo-poroelastic, and two-phase chemo-poroelastic with damage scenarios. However, two parameters sensitize all coupled multi-physics phenomena. These are the solute diffusion coefficient (D_e) on which the damage evolution is based, and the damage permeability coefficient (α_D) which controls the permeability evolution due to damage. In this section, the effect of these two parameters is discussed in detail in addition to the effect of stress anisotropy.

5.3.4.1. Sensitivity of solute diffusion coefficient (D_e)

The value of the solute effective diffusion coefficient can be low due to the high tortuosity of the shale rocks [527]. Changing the value of D_e inherently implies altering the tortuosity of the matrix. It is seen from Figure 5.9 (a) that as the value of D_e is decreased, damage variable evolves much slower due to hindered solute transport. At 5 hours, the damaged area for $D_e = 3.3x10^{-16} \text{ m}^2/\text{s}$ is significantly lower compared with the damaged area for $D_e = 3.3x10^{-14} \text{ m}^2/\text{s}$. Similarly, at 50 and 500 hours, the damaged area was lower for a lower solute diffusivity coefficient. Plotting the damage variable evolution at a point in the water-saturated region close to the fracture-matrix interface, (x,y) = (0.02,7.5), shows clearly that with a decrease in diffusivity coefficient the critical limit of 0.3 is reached much slower leading to delayed micro-fracturing of the rock. This implies that micro-fracturing of rock due to chemical damage is delayed significantly in highly tortuous rocks.



Figure 5.9 Effect of solute diffusion coefficient on (a) damage variable profile (solid line: $D_e = 3.3 \times 10^{-14} \ m^2/s$, dashed line: $D_e = 3.3 \times 10^{-16} \ m^2/s$) and (b) damage evolution with time at point (0.02,7.5)

Since the gradient of the solute concentration between the pore water and fracturing fluid is the chemical driving force causing micro-structural alteration of the matrix, the permeability evolution is also significantly slower. At 500 hours, both values of D_e lead to a ~5.5 times increase in permeability. However, at 50 hours, while permeability increased ~4.9 times for $D_e = 3.3x10^{-14} \text{ m}^2/\text{s}$, it increased ~3.9 times for $D_e = 3.3x10^{-16} \text{ m}^2/\text{s}$. Similarly, at 5 hours, permeability with $D_e = 3.3x10^{-14} \text{ m}^2/\text{s}$ increased ~2.3 times whereas it increased ~1.7 times for $D_e = 3.3x10^{-16} \text{ m}^2/\text{s}$. Such a manifold increase in permeability during the well shut-in periods can cause water entrapment in the micro-structurally altered matrix which cannot be flowed back due to strong wettability forces. These insights highlight the importance of having a multiphysical constitutive theory as ignoring important physical phenomena can obscure actual causes of water loss in the shale matrix.



Figure 5.10 Permeability profiles at $D_e = 3.3 \times 10^{-14} m^2/s$ (solid lines) and $D_e = 3.3 \times 10^{-16} m^2/s$ (dashed lines)

5.3.4.2. Sensitivity of damage permeability coefficient (α_D)

The damage permeability coefficient (α_D) is an experimentally determined parameter. It critically controls the extent of permeability enhancement with damage evolution. Sensitivity of (α_D) shows that a slight increase or decrease in value can cause significant

alteration of permeability (Figure 5.11). In the preceding discussions, $\alpha_D = 5$ was used. When α_D is increased to 7 (dotted lines in Figure 5.11), permeability evolves rapidly with damage with almost an order of magnitude increase in permeability value and a significant increase in damaged area. On the other hand, when α_D is reduced to 2 (dashed lines in Figure 5.11), the damaged area is significantly reduced and there is no substantial increase in permeability values. The continuum damage mechanics theory is almost always supported by experiments to characterize the damage variables [528–530]. A purely theoretical approach is seldom used. Complex experiments to validate constitutive theories especially for two-phase tight porous systems such as shales remain a challenge to be realized.



Figure 5.11 Effect of α_D on damage-dependent permeability (solid lines: $\alpha_D = 5$, dotted lines: $\alpha_D = 2$, dashed lines: $\alpha_D = 7$, $D_e = 3.3 \times 10^{-14} m^2/s$)

5.3.4.3. Sensitivity of stress anisotropy

The varying states of in-situ stresses acting on the matrix can affect the poroelastic response of the water and gas saturated regions. To study the effect of stress anisotropy,

two further cases are compared with the base case ($\sigma_{yy} = 1.5\sigma_{xx}$). These are (i) $\sigma_{yy} = \sigma_{xx}$ and (ii) $\sigma_{yy} = 2\sigma_{xx}$. The effect of stress anisotropy on the complete two-phase, damage chemo-poroelastic scenario is compared only between base case ($\sigma_{yy} = 1.5\sigma_{xx}$) and $\sigma_{yy} = 2\sigma_{xx}$ as there is no significant micro-structural deterioration of the matrix under isotropic confinement (discussed in detail in earlier chapters e.g. Chapter-2 and Chapter-4.1).

For the damage chemo-poroelastic scenario, a comparison of effective stresses (Figure 5.12) shows that the chemo-poroelastic and damage chemo-poroelastic responses for different anisotropic conditions are similar except that the magnitudes of effective stresses are shifted. The shift in magnitude is seen only in the vertical direction (σ'_{yy}) as the applied horizontal stress (σ_{xx}) remained constant. As observed, when anisotropic stress is increased ($\sigma_{yy} = 2 \sigma_{xx}$), σ'_{yy} , after 500 hours increased by ~1.5 times to 50.5 MPa with consideration of damage (dashed lines in Figure 5.12 (d)). A similar increase in magnitudes is observed at 5 and 50 hours. When only chemical effects are considered without damage, it is seen that σ'_{yy} increases by ~1.5 times irrespective of the time (solid lines in Figure 5.12 (d)). The difference in σ'_{yy} with and without damage consideration is time-dependent due to the fact that the damage variable (D_{chem}) continuously evolves with time.

For the scenario, when both damage and chemical effects are neglected (solid lines in Figure 5.13), all three cases are compared ($\sigma_{yy} = \sigma_{xx}, \sigma_{yy} = 1.5 \sigma_{xx}$, and $\sigma_{yy} = 2 \sigma_{xx}$). Stress response with chemical effects but without damage consideration are plotted together for comparison (dashed lines in Figure 5.13). It is seen that a similar shift in magnitude is seen in the vertical direction (σ'_{yy}) when anisotropic confinement is increased (Figure 5.13 (b)) or decreased (Figure 5.13 (f)) from the base case (Figure 5.13)

(d)). For instance, σ'_{yy} increases by ~1.5 times for $\sigma_{yy} = 2 \sigma_{xx}$ and decreased by almost the same amount for $\sigma_{yy} = \sigma_{xx}$. Again, no change in magnitudes of σ'_{xx} because the applied stress (σ_{xx}) does not change and only the vertical stress (σ_{yy}) is altered to study the anisotropy.



Figure 5.12 Comparison of σ'_{xx} and σ'_{yy} stress responses with damage (dashed lines) and without damage (solid lines) for different anisotropic conditions



Figure 5.13 Comparison of σ'_{xx} and σ'_{yy} stress responses with chemical effects (dashed lines) and without chemical effects (solid lines) for different anisotropic conditions

5.4. Conclusions

The developed constitutive equations were solved using the finite element-based COMSOL Multiphysics platform. The base case assessed the capability of the complete two-phase, damage chemo-poroelasticity theory. It was seen that a unique poroelastic response interface (PRI) defines the separate poromechanical behavior of the water and gas saturated regions of the rock. The results indicate that even when chemical swelling stresses are small, the time-dependent micro-structural deterioration of the matrix due to chemical effects can be significant that causes a reduction in the rock's strength subsequently aiding water loss. This highlights the importance of considering micro-

structural deterioration of the matrix in the constitutive theory inspired from the principles of continuum damage mechanics. Clearly, distinct damage chemo-poroelastic response is seen for the water and gas saturated regions. This was the direct advantage of developing an inclusive multi-physical constitutive theory which allowed for easy coupling of twophase flow with other physics. For shales with low chemical swelling coefficients, no substantial difference was seen in the stress distribution of the matrix with inclusion and exclusion of chemical effects. This implies that chemical effects alone are not significant, it is the micro-structural deterioration (damage) that they cause which is significant.

The PRI interface was defined to signify that the poromechanical behavior on either side of the interface is unique and separate. The PRI for the complete two-phase, damage chemo-poroelastic case depends on both water saturation and solute concentration as formulated in the damage function. The numerical observations provide new insights into the damage chemo-poroelastic behavior of the shale rock which can explain fracturing fluid loss in shales. Sensitivity studies showed that damage is enhanced with faster solute diffusion. This can be significant in shales with a high concentration of in-situ salts. Also, the permeability evolution can be significant if the damage permeability coefficient (α_D) is high, the range of which can be determined through properly designed damage characterization experiments for specific shales. This signifies that unless there is substantial permeability enhancement of the matrix, significant water uptake (and loss) should not be expected by (in) the matrix. In such a case, it may seem that entrapment of water in micro-fractures could be the main contributor to fracturing fluid loss into shale matrix. Understanding such behavior is critical for mitigating and predicting the amount of water loss in the shale matrix. Quantitative assessment of the shale water loss can be further performed using appropriate upscaling of simulation results.

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Chapter 6. Conclusions and future work

6.1. Conclusions

Hydraulic fracturing (HF) along with horizontal drilling has been responsible for bringing the shale revolution to many parts of the world. Well shut-in periods after a typical HF operation are standard and unavoidable. Low amounts of water-based fracturing fluid recovery post this shut-in period gives rise to the water loss problem in shales. The interactions of the shale matrix with the fracturing fluid under the action of in-situ stresses give further rise to critical multi-physical phenomena that are responsible for considerable amounts of water loss in shales. Understanding the coupled action of these phenomena and understanding their extent is critical for providing answers to the many intriguing questions. This can be achieved through a combination of laboratory experiments and development and numerical solution of novel multi-physical theories. This dissertation thus systemically investigated the water loss problem in shale matrix through the development of a new two-phase, damage chemo-poroelastic constitutive theory guided by experiments and solved using finite element method (FEM).

Initially, a micro-scale multi-physical investigation was performed using a novel shear cell that critically explained the micro-macro link between HF and various multi-physical processes occurring at the shale-fracture interface. Specifically, it was found that hydration stresses generated even by highly clay-reactive fluids such as de-ionized water are insufficient to cause micro-structural alteration and consequent permeability evolution on their own. This inability to cause micro-structural alteration is further enhanced with the application of isotropic stresses on the shale. The dominant factor that causes micro-structural alteration of rock's shear strength brought about by water exposure.

The micro-scale understanding was used to develop continuum-scale constitutive theory 245

to explain water loss in shales. Using non-equilibrium thermodynamics and principles of continuum mechanics, a fully coupled two-phase, damage chemo-poroelastic constitutive theory was developed. To enable coupling of critical processes, a pressure-pressure two-phase formulation was used. Important inputs to the theoretical model were then obtained through laboratory experiments. Some experimental observations were also used to assess the extent of different phenomena for the specific shale used in this dissertation (IRCM shale), to aid in numerical simulation.

In the first set of experiments, hydration-induced deformation under stress was investigated using experimental and digital methods. This investigation specifically reconciled the reported contradictions in the literature regarding shale wettability using spontaneous imbibition (SI) and contact angle (CA) tests. To achieve this, X-ray microcomputed-tomography (micro-CT or µ-CT) and environmental scanning electron microscopy (ESEM) was used. It was shown that the affinity of shale for a particular liquid, based on SI, is strongly dependent on the chemistries of the in-situ rock constituents and of the fracturing fluid. This chemistry-based dependence influencing the wettability judgment is insignificant in CA tests. Based on this, SI was found to be a suitable yardstick for estimating the liquid wettability of shales. Moreover, it was found that SI needs to be performed at confined conditions to eliminate micro-fracture initiation that cause wettability judgement bias by overestimating the liquid uptake capacity of shales. Theoretical calculations using the Poisson-Boltzmann equation revealed that hydration stresses are low in magnitude and cannot overcome the confinement pressure to cause micro-fracture evolution irrespective of the swellable smectite composition of shales.

The wettability judgement bias between SI and CA was further investigated using a combination of X-ray and neutron imaging along with small-angle X-ray scattering 246

(SAXS) and focused ion beam scanning electron microscopy (FIB-SEM). It was found that shales always imbibe more water in the matrix due to the easy pore accessibility of the smaller water molecules compared to oil molecules. Such pore inaccessibility causes significant anomaly in theoretically predicted liquid uptake volumes. It was concluded that hydrocarbon liquids diffuse faster into the matrix when the oil-wet organic matter content is high. If the oil-wet pores in the inorganic matter are in the order of nanometres, then capillary uptake is limited due to the pore inaccessibility of larger oil molecules. Water molecules can still diffuse into much smaller pores because of their size and assistance of osmotic forces. Hence, the fewer the micro- or nano-pores in the shale, the higher the rate of oil diffusion will be. The water used in the fracturing fluid often contains solutes. Regarding solute diffusion in the IRCM shale, pore pressure transmission tests (PPTT) on the IRCM shale sample assessed the membrane efficiency of the shale to be low (almost zero). Hence, chemo-osmotic effects were not significant and were omitted from the developed constitutive theory.

The pressure-pressure two-phase formulation of the developed constitutive theory requires characterization of the flow parameters such as capillary pressure and relative permeability. While capillary pressures are easy to obtain using mercury intrusion (MICP), estimating the relative permeability of clay-rich rocks is a significant challenge. To overcome such a challenge, fractal-based models have gained popularity. Such models, however, did not account for clay swelling effects which are prominent in shales. Hence, a MICP-based an improved fractal formulation was developed to estimate clay-affected capillary pressures. Good agreement between experimental and model-corrected capillary pressures was obtained. After such a comprehensive petrophysical investigation and validation, the proposed model was used to obtain the capillary pressure – water saturation relationship to solve the two-phase flow component of the developed

constitutive theory.

Finally, with the required inputs and simplifications, the two-phase, damage chemoporoelastic constitutive model was solved using the finite element method-based COMSOL Multiphysics platform. The numerical results indicate that for shales with insignificant chemo-poroelastic effects, chemical coupling does not substantially affect the stress distribution in the matrix. This implies that the chemical and mechanical (or poromechanical) components of the model could be solved in a decoupled manner saving time in large-scale simulations. However, when micro-structural alteration (damage) is considered to cause weakness of the rock matrix due to chemical effects, there is a significant decrease in effective stresses in the water-saturated region of the matrix. This implies that solute transport and consequent swelling as such do not significantly contribute to water loss in the shale matrix. It is the chemically driven micro-structural alteration caused by solute-water-shale interaction that causes loss in stiffness and degradation of the matrix leading to an increase in storage capacity of the matrix that can contribute to water loss in the shale matrix. Also, unless there is substantial permeability enhancement of the matrix, significant water loss should not be expected in the matrix, as shown by the sensitivity studies. In such a case, entrapment of water in micro-fractures may be the main contributor to fracturing fluid loss especially when shearing stresses exist.

The results revealed water and gas saturated regions have unique responses to chemical and poromechanical loadings. The chemo-poroelastic and damage chemo-poroelastic responses of the water and gas saturated regions are characterized by what is termed in this dissertation as poroelastic response interface (PRI). Such a two-phase, damage chemo-poroelastic constitutive model is a fresh development for shales and highlights the importance of incorporating critical physical processes in the constitutive theory to accurately characterize the water-gas damage poromechanical behaviour of clay-rich rocks. The developed theoretical framework can be easily extended to investigate borehole instability problems, CO₂ storage in underground rocks, nuclear disposal, soil behaviour, tunneling, and other civil engineering avenues.

6.2. Future work

Based on the comprehensive experimental, theoretical, and numerical research presented in this dissertation, the following recommendations for future works are listed below:

- (i) The linear elasto-damage assumption can be extended to account for plastic, elasto-plastic, and visco-plastic effects. This can be significant where mechanical damage plays a critical role in addition to chemical damage.
- (ii) A more comprehensive damage variable can be derived to include a more representative coupling of permeability alteration due to both effects of deviatoric stresses (shearing) and chemical effects.
- (iii) The theory and simulation can be extended beyond shut-in periods to account for early and late production times. With the substantial time-dependent flow of gas and water, the damage chemo-poroelastic behaviour is expected to change significantly.
- (iv) Gas adsorption effects can be included in the constitutive theory including damage related to adsorption-induced micro-structural alteration. As a further advancement, thermal effects on adsorption can be included.
- (v) The constitutive theory can be advanced by considering local chemical nonequilibrium including the effect of interactions between water and gas phases at high pressures.
- (vi) Dynamic capillary pressure models can be incorporated to advance the constitutive theory to account for the change in in-situ capillary pressures due 249

to micro-structural alteration (damage) of the matrix.

- (vii) Mineral heterogeneity effects can be included in the constitutive theory by considering tensorial inputs of permeability and diffusion coefficients. The capillary and solute diffusion coefficients can be modified to account for poresize dependent configuration diffusion of water in shales.
- (viii) Dual continua flow related to unique fractures and matrix flow regimes can be included by modifying the representative elementary volume (REV) assumed initially for theoretical development. This can give insights into simultaneous poromechanical responses of both matrix and micro-fractures (both natural and hydraulically induced).
- (ix) Experimental validation of complex constitutive theories remains a challenge and novel design and setups can be established to validate the developed theory at laboratory scale for two-phase tight porous systems.
- (x) Like many other constitutive models, the limitation of field-scale applicability and verification remains a significant challenge. This requires several complex up-scaling techniques that can be utilized in future works. Comparison of water loss estimation from the constitutive model with that of field reported data will significantly enhance the applicability of the constitutive model.

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Appendix-A

A.1 Spontaneous imbibition experiments

Spontaneous imbibition is the displacement of the non-wetting phase by the wetting phase as a result of the capillary force between them [531]. Such a process is important for oil recovery from water-wet and/or fractured reservoirs [532]. Imbibition can occur either co-currently or counter-currently [533,534]. When wetting and non-wetting fluids flow in the same direction the process is co-current imbibition and when they flow in the opposite direction it is counter-current. However, counter-current imbibition is the most possible displacement phenomenon occurring in reservoirs where water and oil flow through opposite directions e.g. imbibition of water into the matrix through water-filled fractures [535,536]. Therefore, our experiments were designed to mimic the counter-current imbibition process.

Several small cubic rock samples (10x10x5mm) were cut from a larger rock sample and oven-dried at 105 °C for 24 hours. After measuring their dry weights, the cubic samples were saturated with oil using the vacuum-saturation method. Oil-saturated samples were weighed again to calculate the pore volume and porosity. Spontaneous imbibition (water displacing oil) experiments were performed by submerging the oil-saturated samples in formation brine under an analytical weighing balance with 0.0001g accuracy (Figure A.1). The change in weight was recorded until equilibrium is reached. The change in weight was converted to the volume of oil expelled (recovered) from the sample. Pore volume material balance calculations were performed after each test to ensure the validity of the experiments. During the experiments, brine was free to enter the sample from all the faces representing an all-faces-open (AFO) boundary condition. It is noted that the effect of different boundary conditions is pronounced only on the rate of imbibition and not on the ultimate oil recovery [537–540].


Figure A.1 Spontaneous imbibition experimental setup

A.2 Numerical simulation

A.2.1 Oil-water capillary pressure from MICP (corrected for clay bound water)

Oil-water capillary pressures can be calculated from mercury intrusion capillary pressure (MICP) data using the oil-water interfacial tension and contact angles. These oil-water capillary pressures are henceforth referred to as MICP-based capillary pressures. However, due to the high amount of clay minerals often present in low permeability rocks, a significant amount of bound water is present which is essentially immobile. Therefore, when oil-water capillary pressure is of interest in these rocks, the contribution of such bound water to water saturation in relative permeability behaviour should be identified and minimised. With such correction, more accurate oil-water capillary pressure curves are obtained from routine core analysis i.e. such as from MICP results. In order to implement this correction, the correlation derived by Hill et al. [541] was used. In this approach, $1 - \frac{\phi_E}{\phi_T} (= \frac{V_s}{V_p}) = (0.084C_o^{-1/2} + 0.22)Q_v$; where $Q_v = CEC(\frac{meq}{100g}) \times \frac{\rho_{bulk}}{\frac{\phi_T}{100}}$.

The terms ϕ_E , ϕ_T , V_s , V_p and C_o respectively are effective porosity, total porosity, bound water volume, free water volume, and in situ pore fluid concentration in eq/l. CEC is the cation exchange capacity and ρ_{bulk} is the rock bulk density. Therefore, according to Hill et al. [541], $(P_c)_{o-w}$ can be calculated from the following equation and mercury capillary pressure data:

$$\frac{(P_c)_{Hg-a}}{(P_c)_{o-w}} = \frac{\sigma_{Hg-a}\cos\theta_{Hg}}{\sigma_{o-w}\cos\theta_{o-w}} (1 - \frac{V_s}{V_p})^{1/2}$$
(A.1)

In addition, the oil saturation is calculated as:

$$S_o = S_{Hg} [1 - (0.084C_o^{-1/2} + 0.22)(Q_v)]$$
(A.2)

In order to calculate the oil-water capillary pressure data, the original MICP data along with oil-water interfacial tension, oil-water contact angles, and CEC were used i.e. $\theta_{Hg} = 140^{o}$, $\sigma_{Hg-a} = 485.5(mN/m)$ and $C_{o} = 0.6041(eq/l)$ (from given ion concentrations). Corrected oil-water capillary pressure data is shown in Figure A.2.



Figure A.2 Plot of clay-corrected P_{cow} (MICP-based) vs. S_o (non-wetting phase) for samples (a) S1, (b) S2, and (c) S3

A.2.2 Fractal dimension and relative permeability estimation

To calculate any of the petrophysical or hydraulic properties of porous media, the fractal dimension (D_f) needs to be estimated. In this study, D_f was calculated using the MICP

data based on wetting phase saturation, the derivation of which is widely published [426,439,458,542,543]. Thus, to obtain the fractal dimension, $log S_w$ is plotted versus $log P_c$ according to [426]:

$$\log S_w = (3 - D_f) \log P_{cmin} + (D_f - 3) \log P_c$$
(A.3)

The main inputs in numerical simulation of spontaneous imbibition experiments are MICP-based capillary pressure data and fractal-based relative permeability data. To obtain the latter, first, the fractal dimension is estimated from the $log(S_w)$ vs. $log(P_c)$ plot. All other input parameters were experimentally obtained. Since the MICP-based capillary pressure data give a straight line on the $log(S_w)$ vs. $log(P_c)$ plot, it is evidenced that porous media of the three low permeability sandstone samples studied are fractals (Figure A.3). The fractal dimensions were calculated from this straight-line region. The extracted D_f values using Eq. A.3 for each sample are presented in Figure A.3 and listed in Table A-1.



Figure A.3 Plot of log (S_w) vs. log (P_c) to calculate fractal dimension (D_f) for samples (a) S1, (b) S2, and (c) S3

Sample #	D_{f}	\mathbb{R}^2	\mathbf{S}_{wi}	Pc _{min} (psi)
S1	2.805	0.992	0.37	1.1826
S2	2.911	0.996	0.73	11.8556
S 3	2.928	0.985	0.68	2.6718

Table-A.1: Extracted D values for all samples along with S_{wi} and permeability

Next, the relative permeability of the wetting and non-wetting phase can be calculated based on S' (effective wetting phase saturation) as below [426].

$$S' = \frac{S_w - S_{wi}}{1 - S_{wi}}$$
(A.4)

$$K_{rw} = S'^2 S'^{\frac{5-D}{3-D}} = S'^{\frac{11-D}{3-D}}$$
(A.5)

$$K_{rnw} = (1 - S')^2 (1 - S'^{\frac{5-D}{3-D}})$$
(A.6)

The resulting relative permeability curves for all samples calculated using Eqs. A.4-6 are presented in Figure A.4 showing high connate water saturation and narrow two-phase flow area as expected. The data are plotted on both Cartesian and semi-log plot.



Figure A.4 Oil-water relative permeability curves for samples (Cartesian and semi-log) (a)-(b) S1, (c)-(d) S2, and (e)-(f) S3 calculated using Eqns. (5), (6) and (7)

A.2.3 Numerical simulation methodology

Laboratory scale numerical simulation of the already performed spontaneous imbibition experiments was carried out using a commercial reservoir black-oil simulator (Schlumberger Eclipse (E100) v2015) which solves the flow equations using the fully implicit scheme. The choice of the simulator is arbitrary as all commercial conventional reservoir simulators work on the same basic principle of material balance. A cartesian grid model representing the cubic rock sample surrounded by a large water reservoir was built. The total grid system was divided into 20 grids in the x-direction, 20 grids in the ydirection and 10 grids in the z-direction respectively (Figure A.5(a)). At the centre of the overall grid, a 10x10x4 local grid was assigned properties of the respective rock sample (porosity, permeability, etc.) to represent the cubic sample immersed in brine. Initial water saturation was zero ($S_{wi} = 0$) in the rock sample grid system while it was 1 in the surrounding grids i.e. representing a water reservoir or beaker as in the experiments (Figure A.5(b)). The surrounding grids (representing the water reservoir) were enclosed in a no-flow (closed) boundary. The initial and boundary conditions for the simulation were chosen such that they represent purely capillary-driven flow with no viscous effects. Initial conditions for inside the grids representing the cubic sample are thus:

$$S_w(x, y, z, t = 0) = S_{wi} = 0$$
 (A.7)

$$p_o(x, y, z, t = 0) = 0$$
 (A.8)

$$\mathbf{p}_{\mathbf{w}} = -\mathbf{P}_{\mathbf{c}}(\mathbf{S}_{\mathbf{w}\mathbf{i}}) \tag{A.9}$$

Where S_w is water saturation inside the sample at any time t, S_{wi} is the initial water saturation, p_o is oil-phase pressure, p_w is water-phase pressure and x, y, z are coordinate axes. For all the grids representing the water reservoir surrounding the sample, the initial and continuing condition (i.e. at all times) is:

$$S_w = 1, @t = 0, t = 0^+$$
 (A.10)

The boundary conditions at the interface of the cubic sample and the water reservoir are:

$$S_w(x, y, z, t) = 1$$
 (A.11)

$$p_o(x, y, z, t) = p_w = 0$$
 (A.12)

The above condition (Eq. A.12) implies that the water pressure inside the grids representing cubic sample is less than the water pressure at its interface with the water reservoir. It is in fact this difference that drives the imbibition of water from the reservoir into to the cubic sample which is purely a capillary phenomenon. Lastly, the no-flow boundary condition enclosing the water reservoir implies zero flowrate (q) of oil or water at this boundary:

$$q_0(x, y, z, t) = q_w = 0$$
 (A.13)

The above-mentioned conditions are also schematically represented in Figure A.6. The abovementioned mathematical expressions are not unique but are presented for readers' clarity regarding the approach to numerically simulate a spontaneous imbibition experiment. The efficiency of commercial simulators of the likes used in this study (Eclipse v100) to predict counter-current imbibition processes has been proven in earlier studies [355,521,544]. Experimentally determined rock and fluid properties, oil-water capillary pressure, and fractal-estimated relative permeability curves were used as input in the simulation that was run for the same number of hours as the experiments took to reach equilibrium. It must be noted that the fractal-estimated relative permeability input curves are based on counter-current phenomena as its estimation is based on mercury-intrusion data which itself is a counter-current process where mercury displaces the air in the sample at incremental pressures from all directions. The comparison of experimental and simulation results is discussed in Section 4.3.3.1 of Chapter-4.3. The simulation parameters are tabulated in Table A-2.

Table A-2:	Simulation	parameters
------------	------------	------------

Global grid	
No. of grids in X	20
No. of grids in Y	20
No. of grids in Z	10
S _{wi}	1.0

Local sub-grid (represe	enting sample)
No. of grids in X	10
No. of grids in Y	10
No. of grids in Y	4
S _{wi}	0.0





Figure A.5 (a) Cartesian grid system used in numerical simulation and (b) Z-direction slicing of the grid showing the central part representing the rock sample



Figure A.6 Initial and boundary conditions shown schematically

Appendix-B

For illustrations of how clay swelling affects the pore network, the samples were exposed to the prepared brine for over 24 hours and before-after environmental SEM (ESEM) images were captured of the same spots. For e.g., in Figure B.1, clear closure of micropores is visible due to clay swelling (encircled by red).





Figure B.1 ESEM images showing pore structural changes due to clay swelling at different scales where left image is before exposure and right image is after exposure of three different spots i.e. (a)-(b) are one set, (c)-(d) are higher magnification of (a)-(b),

(e)-(f) are second set, (g)-(h) are third set

Appendix-C

C.1 Procedure for estimating k_{ϕ}

The parameter k_{ϕ} in Eq. 4.49 is estimated through iterative minimization of the sum of squares of errors (SSE) between each subsequent MICP-corrected capillary data-sets for various values of k_{ϕ} . The value where the error stops decreasing was chosen for further calculations. The SSE is plotted against various values of k_{ϕ} (Figure C.1). It was inferred that beyond a value of $k_{\phi} \approx 2.5$ for all samples, there is no change in SSE i.e. no more improvement in the MICP-based data. Physically, it implies that pores have a maximum swellable tendency thereafter no more swelling is possible and the processes that caused the swelling have attained equilibrium. This fact is also apparent through plotting different capillary pressure data sets on $log(S_w) - log(P_c)$ plot (Figure C.2 (a)-(c)) where it was seen that further improvement of the MICP-based data beyond a certain point is ceased.



Figure C.1 SSE vs k_φ for all samples



Figure C.2 Iterative plots for improved MICP-based data sets (green dots) for samples (a) S1, (b) S2, and (c) S3

Appendix-D

D.1. Examples and validation

Here, examples of decoupled physics modules are solved and presented to demonstrate the application of the constitutive theory developed in Chapter-3 and solved in Chapter-5. Validation of decoupled physical parts of the system is provided by comparison with either analytical or previous literature data.

D.1.1 Validation of poroelasticity

The poroelasticity physics is validated through the reproduction of the example by Zheng et al. [498,545] for a rock sample undergoing uniaxial compression (i.e. a drained uniaxial single-phase poroelastic case is solved). This example consists of a 2m x 3m 2D porous medium fully saturated with oil where only the top boundary is open for fluid flow (Figure D.1). A 4 MPa uniform load is applied on the top boundary while the other sides have roller constraints. The input data used is shown in Table D-1



Figure D.1. Schematic of the domain used in the example

Young's modulus	1.44x10 ⁴ MPa
Poisson ratio	0.2
Biot's coefficient	0.79
Biot's modulus	1.23x10 ⁴ MPa
(Storage)	
Rock density	2000 kg/m ³
Oil density	940 kg/m ³
Porosity	0.2
Permeability	$2x10^{-13} \text{ m}^2$
Kinematic viscosity	1.3x10 ⁻⁴ m ² /s
Initial pore pressure	1.64 MPa
Outflow pressure	0 MPa

Table D-1: Input parameters for poroelastic example

The transient pore pressure and vertical displacement profiles are shown in Figure D.1 for different times. The results are an excellent match with the analytical and numerical results presented by Zheng et al. [545] and Freeman et al. [498]. Furthermore, the effective stress is plotted in Figure D.2 which shows that with time, the effective stress approaches the applied load as the pore pressure dissipates.



Figure D.2. (a) Pore pressure and (b) vertical displacement profiles at different times



Figure D.3. Effective stress profile at different times

D.1.2 Validation of two-phase flow

In this section, the analytical solution for counter-current spontaneous imbibition is presented and compared with the solution given by COMSOL. The boundary conditions, input parameters, and simulation geometry and domain are the same as those presented in Chapter-5. It is noted that the analytical solution is limited to infinite-acting solutions i.e. before water saturation reaches the boundary at the other end of the REV. The analytical solution is actually 'semi-analytical' in the sense that it is an integral solution

requiring trivial iterations to arrive at the solution. The solution was developed by Schmid et al. [546] inspired from the work of McWhorter and Sunada [547]. The solution was made open source by the authors in the form of a spreadsheet and is readily available online [548]. The details of the solution are not provided here for which the readers can refer to the above references. The main part of the solution is that the water saturation S_w scales with the similarity variable ω such that the solutions are found only as a function of ω :

$$\omega = \frac{x}{\sqrt{t}}, S_w = S_w(\omega) \tag{D.1}$$

Since a given saturation value travels a distance proportional to \sqrt{t} , the water flux scales as $1/\sqrt{t}$ with a proportionality constant *C* which has units of m/\sqrt{s} . The magnitude of *C* determines the speed of spontaneous imbibition and hence is analogous to the diffusion capillary coefficient (*D*). The solution is arrived at by introducing a new fractional-flow function *F* [549] such that:

$$\omega(S_w) = \frac{2C}{\emptyset} F'(S_w) \tag{D.2}$$

It is noted that F here is distinct from the Buckley-Leverett fractional flow, although is inspired from it. The final equation which is solved is a second-order ordinary differential equation for F:

$$FF'' = -\frac{\phi}{2C}D\tag{D.3}$$

Apart from porosity, permeability, water/gas viscosities, the required inputs are S_{wi} , S_{or} , k_{rw} , k_{rg} , and P_c which are provided through fractal theory – the same inputs as used in the simulation in Chapter-5. The water saturation profiles obtained from the simulation in Chapter-5 merge into one curve when scaled by x/\sqrt{t} . This scaled curve is then

matched with the water saturation versus similarity variable (ω) curve obtained from the analytical solution. It can be seen (Figure D.4) that an excellent match is obtained between simulated and analytical profiles. The value of *C* obtained after iterations was $6.03x10^{-9} m/\sqrt{s}$. This validation endorses the accuracy of the two-phase flow simulation performed in Chapter-5.



Figure D.4 Comparison profiles of simulated and analytical water saturation (S_w) versus similarity variable (ω)

D.1.3 Validation of solute transport

The validation of solute transport equation is provided through comparing the solute mass fraction profiles from COMSOL with those from Heidug and Wong [172]. For this the geometry and boundary conditions enacted by Heidug and Wong [172] are used (Figure D.5). The geometry consists of a 2D rectangular domain where the left side of the

saturated sample is exposed to a distilled water containing 0.35 mass fraction $(C_{x=0}^c)$ of some salt. The inside of the sample is initially saturated with distilled water without any salt $(C_{t=0}^c = 0)$. It is noted that C^c here represents the solute mass fraction, instead of solute concentration, which is unitless. Other parameters used in the simulation are tabulated in Table D-2. The solute mass fraction response in the sample at different times is compared.





Wong [172]

Table D-1: Input parameters for solute transport	

Young's modulus	2 GPa
Poisson ratio	0.3
Porosity	0.082

Permeability	$4x10^{-15}$ mm ²
Kinematic viscosity	0.798 mPa.s
Solute mass fraction at boundary	0.35
Diffusion coefficient	$1 \times 10^{-4} \text{ mm}^2/\text{s}$

The results are plotted in Figure D.6 which are along any line parallel to the X-direction. The solute mass fraction profiles obtained from COMSOL simulation are represented by solid lines whereas those from Heidug and Wong [172] are represented by dashed lines. It can be seen that solute mass fraction profiles obtained from COMSOL simulation at different times are very close to those reported by Heidug and Wong [172]. The apparent differences in the curves can be attributed to the linearization of the relationship between solute chemical potential (μ^c) and solute concentration (or mass fraction) in this study. On the other hand, the relation between μ^c and C^c was logarithmic in the study by Heidug and Wong [172]. Nonetheless, as can be seen the differences are minimal. This validation approves the accuracy of the solute transport equation solved in Chapter-5.



Figure D.6 Comparison of solute mass fraction profiles obtained from COMSOL (solid lines) with those from Heidug and Wong [172] (dashed lines)

Appendix-E

The basic workflow for COMSOL Multiphysics simulations is presented below in Figure

E.1.



Figure E.1 Basic workflow for COMSOL Multiphysics simulations