

Chapter 1

INTRODUCTION

1.1 Motivations and Background

1.1.1 CO₂ Sequestration

The largely anthropogenic origins of the drivers of climate change over the last 100 years are, according to the fifth assessment report of the IPCC (Intergovernmental Panel on Climate Change), no longer in dispute. Among the anthropogenic sources that alter the earth's energy balance, the increase in the atmospheric concentration of CO₂ (primarily from fossil fuel emissions but also from net land use change emissions) has contributed the most and this contribution is accelerating. "It is *extremely likely* that more than half of the observed increase in global average surface temperature from 1951 to 2010 was caused by the anthropogenic increase in greenhouse gas concentrations and other anthropogenic forcings together", Stocker et al (2013). Based on direct measurements and remote sensing from satellites and other platforms, and on Paleoclimate reconstructions, some of the observed effects – warming of the atmosphere and the oceans through greenhouse gas effect, rising sea levels, ocean acidification, diminishing snow and ice, increased frequency of extreme weather events – have already exceeded levels not seen for over decades to millennia. Many of these effects are predicted to persist for hundreds of years to come even if all emissions ceased today. The objective of most climate change mitigation strategies is therefore not so much to reverse climate change but to stabilize it within a defined threshold by limiting future emissions.

Carbon Capture and Storage (CCS) is a method to reduce CO₂ emissions on scales necessary for global impact. It involves direct injection into subsurface saline aquifers, deep unminable coal beds, or depleted oil and gas reservoirs (Bromhal et al., 2005; Kavscek and Cakici, 2005; Orr, 2004; Bachu, 2003).

CO₂ injected into a saline aquifer may exist in four distinct forms: (i) as a bulk free phase, (ii) as a trapped residual free phase, (iii) as a dissolved aqueous species, and (iv) as a precipitated mineral. One of the main objectives of CO₂ injection design during CCS is to minimize storage of bulk free CO₂ because it poses possible risk of leakage, especially in the years following the end of injection. The proportion of the total injected CO₂ that will be trapped in any of the four forms will depend on the short and long term evolution behaviour of the free phase. This evolution will in turn be determined by CO₂ and brine properties (viscosity, IFT, density), the petrophysical properties of the brine bearing formation and the injection configuration.

CO₂ is less dense than brine under temperature and pressure conditions typical of saline aquifers and the evolution of CO₂ injected into brine is inherently unstable, the instability driven by gravity forces. CO₂ will therefore migrate upwards unless stopped by a low permeability barrier, such as a cap rock, beneath which it will accumulate and spread laterally. The gravity-driven rise of a lighter non-wetting phase injected into a denser wetting phase has been clearly shown by Birovljev et al (1994) and others (Ezeuko et al, 2010, McDougall and Mackay, 1998) to occur in two distinct stages. The first stage is characterised by a progressive elongation of a fingered CO₂-water interface through drainage displacement processes along the direction of the gravity gradient, with the gravitational bias increasing as the finger lengthens. This biased growth of CO₂ will continue as injection proceeds and the buoyancy forces acting on it increase. The second stage of gravity-driven flow consists of the spontaneous mobilization of CO₂ once buoyancy forces exceed the capillary entry thresholds of perimeter pores between the gaseous and aqueous phases. This stage is characterised by both drainage and imbibition processes. Imbibition – including snap-off and cooperative mechanisms – can lead to the fragmentation of CO₂ fingers into daughter clusters that may become trapped as a residual free phase. Note that in this second (*migratory*) stage, it is no longer necessary for the gas to have hydraulic connectivity with the injection source.

CO₂ injected for sequestration could exhibit both types of gravity-perturbed flow (Kumar et al, 2005) although most authors hold that migratory flow occurs only post-injection (Flett et al., 2004; Pruess et al., 2003). Regardless of when it starts to occur, the migratory regime is perhaps the most important flow regime during CO₂ sequestration because it is

governed by a set of mechanisms by which free CO₂ could be rendered permanently immobile as a residual phase by capillary forces. It has also proven to be the most difficult flow process to simulate by conventional field scale simulators because of the fast changing hydrodynamic discontinuities involved and the microscopic character of the capillary trapping processes, both of which are incompatible with the Darcian flow dynamics of most conventional field simulators (Cinar et al, 2009).

Inherent to Darcy's law is the assumption that flow through porous media occurs only by the application of an external pressure gradient along a hydraulically continuous phase. It is thus, in its classical form, ill-suited for describing buoyancy-driven or viscous-driven *discontinuous* migratory flow. Moreover, the assumption of uniform distributions of immiscible fluid phases within a gridblock regardless of the relative phase saturations is also inconsistent with the distinct saturation distribution patterns observed in experiments of gas injection in liquid-saturated porous media. The implications of this oversimplification for the calculation of gridblock to gridblock transmissibilities, as well as the surface area for mass transfer across immiscible phase boundaries, are not well understood. For Darcian simulators to make meaningful predictions about CO₂ storage capacity and security, the constitutive relations used to capture the microscopic features of multiphase flow in porous media, i.e. relative permeability and capillary pressure curves, would have to be refined somewhat (Meheust et al, 2002; Frette et al, 1994; Maloy et al, 1985).

Experiments to quantify residual CO₂ saturations during cyclic drainage and imbibition processes (El-Maghraby and Blunt, 2013; Herring et al, 2013; Andrew et al, 2013; El-Maghraby et al, 2011; Pentland et al, 2010; Suekane et al, 2008; Bachu and Bennion, 2007) and to gain further understanding of the effect of gravity and viscous forces on CO₂ evolution (Cinar et al, 2009) have been reported in the literature but these mainly focus on residual trapping. Moreover, no experiment on CO₂ injection at temperature and pressure conditions typical of saline aquifers and conducted at a scale large enough to support migratory flow behaviour has been reported. To date, the few pore network modelling (PNM) studies reported on CO₂ storage have mainly dealt with reducing uncertainties in the estimation of residual trapping capacity. Ferer et al (2001) studied the effects of viscosity ratio and capillary number on immiscible CO₂-water displacement in a

2D diamond lattice network and showed that CO₂ residual trapping could be enhanced by increasing CO₂ viscosity. Pentland et al (2012) used simulations on a reconstructed network to reproduce the experimental results of a displacement sequence involving CO₂ drainage followed by brine imbibition. They showed that the narrower the average pore throats in the network the greater the residual saturation, as could be expected.

The common feature of these studies is the assumption that residual and capillary trapping occur under capillary dominated flow processes in a two-stage sequence of displacement events – CO₂ drainage then brine imbibition – that follow each other in orderly and predetermined steps. Gravity forces are generally ignored to avoid unwanted complications or due to equipment limitations. However, in the large scale systems that these results are intended to model, gravity actually plays an important role. We shall see that by viewing the migratory process as a whole, the simultaneous evolution of the drainage and imbibition fronts creates characteristic cluster size distributions and trapping patterns that highlight the dynamic nature of these scale-dependent processes.

While PNMs are ideal tools for investigating specific microscopic features of migratory flow, such as residual trapping, this research shows that it can also be used to study the full sequence of migratory evolution at intermediate scales (1cm – 25cm). We shall see that by careful parameter selection and consistent scaling arguments, the full spectrum of CO₂ evolution regimes can be simulated. Results offer new insights into the processes that control the evolution of CO₂ injected in brine and also identify critical aspects of field scale models that may need to be modified to facilitate realistic simulation of CO₂ migratory processes at the larger scale. More generally, this treatment attempts to advance our understanding of the fundamental physical processes that govern CO₂ evolution in porous media.

In spite of the potential of CCS to significantly reduce future anthropogenic CO₂ emissions, the hope of its widespread implementation is vexed by the question of who is to pay for it. For CO₂ sequestration volumes to rise to an order of magnitude that is comparable to anticipated future emissions, it will be essential to develop sequestration technologies that use CO₂ as a primary feedstock for generating real economic value

rather than as an unwanted waste product. The utilization of CO₂ to improve oil recovery is an important example of such technologies.

1.1.2 Improved Oil Recovery

Even as oil demand in the developed world stagnates due to competition from renewable energy sources, anticipated growth in demand from the emerging markets is expected to keep prices high for the foreseeable future. So whilst production from otherwise marginal prospects such as heavy oil reservoirs and mature conventional oil reservoirs has become economically attractive, there is also a renewed interest in maximizing recovery from new discoveries which increasingly have to be produced from extreme environments. As the scope for improved oil recovery techniques expands, it becomes more vital to conduct critical studies of alternative options to determine their relative merits under given conditions. The focus here is on the pore to core scale mechanisms that drive CO₂ enhanced oil recovery (EOR) and engineered depressurization of oil reservoirs. CO₂ EOR and depressurization have, aside from their demonstrated effectiveness, the common feature of leaving behind relatively smaller environmental footprints than alternative methods of oil recovery such as thermal methods, waterflooding, hydraulic fracturing, etc. The utilization of CO₂ for EOR is generally recognised as one of the primary means by which CO₂ can be sequestered in order to mitigate global climate change.

1.1.2.1 Solution gas drive

Depressurization, also known as solution gas drive or blowdown, is probably the least energy intensive oil production strategy in use. Oil production is achieved by the expansion and subsequent evolution of solution gas following the pressure depletion that accompanies fluid withdrawal. Although commonly implemented as the last recovery phase after extended waterflooding, and just before abandonment and decommissioning, it has nevertheless attracted attention of late as a viable non-thermal means for producing heavy oil. In operational terms, depressurization is fairly straightforward and cheap to implement because it mostly involves repurposing of existing facilities. From a reservoir engineering point of view, however, it is one of the most difficult recovery techniques to predict and analyse.

The challenges of reconciling observed multi-phase flow physics with its representation in continuum-type simulators are even more acute when it comes to solution gas drive

processes simply because the exact nature of the interactions between the different pore level mechanisms are still being discovered. Visualization experiments using synthetic porous media have given fundamental insights into the mechanics of bubble nucleation and its dependence on depletion rate and pressure-dependent IFT, and how the interplay between capillary, gravity and viscous forces, and the pore structure leads to distinctive gas evolution patterns or regimes (Kennedy and Olsen, 1952; Stewart et al, 1952, 1954; Handy, 1958; Chatenever et al, 1959; Dumoré, 1970; Kortekaas and van Poelgeest, 1991; Mackay et al, 1998; Dominguez et al, 2000; etc). Efforts at extending these fundamental insights to the interpretation of depletion experiments on reservoir core samples have, however, often led to conflicting conclusions. Whilst some of the confusion can be attributed to differences in data interpretation approaches and the peculiarities of experimental set ups, it is primarily a reflection of just how little is currently understood about the complex web of interactions between rock mineralogy, wettability, pore size distribution, pressure-dependent fluid properties, saturation history, diffusive mass transfer, system scale, nucleation, and depletion rate. Pore network modelling provides a means for examining these issues from first principles. In this thesis, a refinement of a dynamic model of buoyancy-driven migration has been incorporated within a modelling framework originally developed by McDougall and co-workers (McDougall and Sorbie, 1999; McDougall and Mackay, 1998; Bondino et al., 2005b; Ezeuko, 2009) to facilitate the interpretation of depressurization experiments performed on heterogeneous reservoir rock samples.

1.1.2.2 *CO₂ enhanced oil recovery*

CO₂ is highly soluble in oil and its dissolution alters the phase behaviour of oil. Important phase behaviour changes that enhance oil mobility during CO₂ EOR include an increase in oil volume and a decrease in oil viscosity and CO₂-oil interfacial tension. Dissolution is a time-dependent diffusion process, that is, oil does not spontaneously become saturated upon coming into contact with CO₂. Dissolved CO₂ concentration builds up gradually, leading to correspondingly gradual changes in oil properties, which drive CO₂ EOR. CO₂ dissolution is therefore as much governed by the configuration of the contact surface of the solute (CO₂) and the solvent (oil) (which is a function of the flow regime and the geometrical structure of the host medium) as by the prevailing temperature and pressure conditions. This means that CO₂ dissolution rate as well as the dissolved CO₂

concentration distribution with time in bulk oil will be different from that in an equal volume of oil that resides within the constricted interstitial spaces of a porous medium. Unfortunately, most estimates of displacement efficiency during CO₂ EOR are based on flash calculations that use equilibrium solubility values to adjust relevant CO₂ property (e.g. viscosity) data. Uncertainties in CO₂ EOR performance evaluations can therefore be magnified when estimates of displacement efficiency take insufficient account of the impact of in situ porous media architecture on thermodynamic processes. As part of this thesis, a mechanistic approach to modelling gas dissolution in liquid is used to examine the impact of the time evolution of heavy oil viscosity due to non-equilibrium CO₂-oil mass transfer on CO₂ EOR displacement efficiency.

1.2 Objectives

The goal of this research is to explain gas flow behaviour through liquid-saturated porous media from a fundamental physical basis, with special emphasis on flow phenomena associated with CO₂ flow in brine and oil, as well as the evolution of solution gas following oil depressurization. Achieving this goal involves undertaking four interrelated tasks:

1. Develop a pore network simulator that incorporates the pertinent physics governing the motion of gas-liquid interfaces through porous media during external and internal drive processes.
2. Validate the simulator against experimental data.
3. Conduct parametric sensitivity studies to investigate the impact of various combinations of system variables (e.g. temperature- and pressure-dependent fluid properties, network size, pore size distribution, coordination number, etc) on gas flow regimes at the core scale and to explore the implications for the determination of petrophysical input data for reservoir scale simulators that use Darcian formulations.
4. To develop a theoretical framework within which to design and interpret future experimental and field development programmes.

1.3 Thesis outline

Chapter 2 introduces relevant literature on the three subject areas that are the focus of this thesis: pore network modelling, CO₂ sequestration, and depressurization. The chapter begins with an overview of the state of progress on the use of pore network modelling techniques for analysing multiphase flow in porous media – the historical development of pore network modelling is discussed in the light of advances in network construction techniques and in the methods for implementing fluid flow physics in the network. A discussion of the advantages and weaknesses of some predictive network construction techniques is followed by a review of basic concepts associated with multiphase flow physics in porous media. The generic approaches for implementing fluid flow physics on network models are then discussed, and the section closes with a review of experimental and network modelling studies of the effect of gravity on gas flow in porous media. The second section of the chapter focuses on the review of issues related to CO₂ sequestration in saline aquifers. An overview of the basic CO₂ trapping mechanisms is followed by a review of the strengths and limitations of available options for modelling CO₂ storage in saline aquifers, highlighting the need for the development of new modelling techniques in order to capture the subtleties associated with unstable gas flow in porous media. This is followed by a chronological review of experimental studies of CO₂-brine interactions in porous media. A review of network modelling of CO₂-brine interactions demonstrates the shortage of literature dealing with this subject. The last section of the chapter presents a review of depressurization-related literature covering previous experimental, theoretical, and modelling studies.

Chapter 3 presents a detailed description of the process modules that make up the pore network simulator developed during this research. A brief review of some essential computational details associated with pore space representation and clustering is followed by a detailed discussion of conceptual issues related to modelling gas-liquid interface movement (dynamic drainage and imbibition) and non-equilibrium mass transfer (supersaturation and undersaturation) at the pore scale, under two-phase and three-phase conditions. A breakdown of important pore scale phenomena constituting depressurization and gas injection processes – including bubble nucleation, spontaneous gas migration, and gas dissolution – into their discrete logical structures are presented along with corresponding implementation algorithms. The implementation details of

thermodynamic models of CO₂ compressibility factor, density, and solubility in brine are then presented.

In Chapter 4, an extensive investigation of the effects of pressure- and temperature-dependent fluid properties (IFT, density, solubility) as well as network parameters (mean pore radius, PSD variance, connectivity, height-scale) on gravity-destabilized gas flow is presented. First, a parametric sensitivity of the variables that define the microscopic Bond number is used to classify gravity-driven regime transitions. The impact of pore space architecture as represented by the pore size distribution variance and network coordination number, on regime transitions is then presented. A number of injection experiments are then reproduced and interpreted. This is followed by a comparative analysis of the flow behaviours of CO₂ and CH₄ during slow injection in water over a range of temperature and pressure conditions, including a detailed analysis of CO₂ solubility trapping. The chapter closes with a discussion of the implications of gravity-driven regime transitions for the parameterization of continuum models of fluid flow in porous media.

Chapter 5 examines the impact of the combined effects of capillary, gravity and viscous forces on injected gas flow regime transitions. In contrast to Chapter 4, flow behaviour at high injection rates (or Capillary numbers) is investigated. The chapter begins with a description of the pore level mechanisms that govern regime transitions at varying injection rates under both favourable and adverse viscosity ratios. The effect of injection rate on displacement behaviour for three different injection configurations – gravity destabilized, gravity-stabilized, and edge injection – is presented. This is followed by a discussion of the implications of a decreasing IFT in the presence of gravity and viscous forces. The application of the pore network model developed in this research to the evaluation of CO₂ EOR is demonstrated by an analysis of non-equilibrium mass transfer effects on the displacement efficiency of heavy oil by CO₂ under simulated laboratory conditions. A comparison of CO₂ and CH₂ flow regimes at varying injection rates and over two temperature and pressure conditions follows. Conceptual issues associated with scale-up are discussed with the aid of simulations at a range of capillary numbers with varying network sizes. A reproduction of a targeted set of micromodel displacement experiments by Lenormand et al (1988) is used to further validate the model.

Chapter 6 features applications of the model to the analysis of specific processes that are of special significance to the evaluation of CO₂ storage security in saline aquifers. First, the impact of the pore sizes ratios in a capping rock to that in an underlying reservoir on the capillary trapping capacity of a reservoir-caprock system is examined in the framework of changing macroscopic Bond number. A similar analysis is then made with respect to dissolved CO₂ trapping security. Next, the impact of microscopic and macroscopic heterogeneity features – in the form of laminae and stochastic shales, on capillary and residual trapping of CO₂ is investigated and the implications for CO₂ storage security at the reservoir scale explored. Finally, a model of two-phase relative permeability that accounts for discontinuous gas production during buoyancy-driven gas migration is developed and then used to propose a new hysteretic relative permeability model for the parameterization of continuum models for field-scale CO₂ storage simulation.

In chapter 7 attention turns to quantitative prediction in the context of pressure depletion. Chapter 7 presents the first part of a case study of a depressurization experiment on a waterflooded, naturally fractured North Sea chalk sample, and shows how the pore network model developed can be used as a surrogate for costly laboratory experiments to gain fundamental insight into fluid flow in porous media and to parameterize reservoir scale simulators. After building a petrophysically equivalent network model of the experimental core using an anchoring process that incorporates measured core and fluid data, an initial set of sensitivity studies are performed to assess how individual mechanisms constituting the depressurization process affect measurable quantities such as critical gas saturation and oil production. The impact of capillary/gravity force balance, length scale, interfacial tension, nucleation density, initial water saturation, and spreading coefficient on the depressurization process are all explored. These scoping runs are used to explain the fundamental pore scale mechanism underlying the depressurization process. Then a predictive 3D network is developed through a match of the experimental saturation profiles by varying nucleation and wettability parameters.

The second part of the interpretation and extrapolation of the depressurisation case study is presented in Chapter 8. The history matched model of the experimental core that

was built in Chapter 7 is used to make specific predictions regarding the effect of a wide range of operating and boundary conditions – depletion rate, initial water saturation, system scale, and fracture spacing – on critical gas saturation and the relative permeability function, to yield useful correlations. To better characterise the uncertainties associated with the determination of critical gas saturation and relative permeabilities, new sensitivity studies are performed to investigate the impact of additional factors related to fluid interfacial tensions and rock matrix architecture. A literature survey is also presented that discusses the specific results obtained in the context of other published depressurisation experiments.

Chapter 9 highlights the main findings from this research and discusses their practical significance. Some recommendations for future research direction in this area are then given.