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Appendix 4: Transport and Consolidation Properties of the Mercia Mudstone

Energy and Marine Geoscience Programme

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BRITISH GEOLOGICAL SURVEY

ENERGY AND MARINE GEOSCIENCE PROGRAMME

INTERNAL REPORT IR/14/070

Appendix 4: Transport and Consolidation Properties of the Mercia Mudstone

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The BGS reactive flow
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Summary

This report describes ongoing research at BGS, examining the transport properties of the Mercia Mudstone. This material represents one of a number of potential sealing lithologies of particular interest for carbon storage in both the Irish Sea and the southern North Sea. Observations presented are the initial findings of the study and additional analyses and testing will be reported elsewhere. The following report describes project rationale, the sample recovery process, the experimental approach and preliminary observations from consolidation and hydraulic testing. Finally the expected future direction of the test programme is described.

1 Introduction

A key component of a successful carbon storage scheme is a well-characterised caprock, assessed to have sufficient integrity to act as a final barrier against the migration of carbon dioxide, on timescales of the order of a thousand years. Factors which may affect seal integrity include:

- Lateral variations in sealing fraction (e.g., clay to non-clay, salt to silt)
- Cross-fault variations in sealing fraction (e.g., clay to non-clay, salt to silt)
- Faulting/fracture flow
- Regions of the caprock where the stress-state is currently close to the yield envelope (Harrington et al. 2011)
- Chemical diagenesis of the caprock (particularly in zones of prior weakness, such as faults and sand lenses)

In order to address such factors, a thorough understanding of the baseline mechanical and transport properties of a potential seal is fundamental to the assessment of seal integrity. A sound knowledge of these factors will provide:

- More refined capacity estimates based on potential for leakage
- Confidence for operator and regulator
- Operational limits to minimise potential risks

Whilst these properties may be inferred through a number of indirect techniques (see Section 3), only very limited data is available derived from direct experimental observation. Such data provides valuable additional information in relation to process understanding and the role of coupled phenomena (e.g. physic-chemico coupling). This study is focussed on examining the transport properties of the Mercia Mudstone, a formation with potential as a caprock for carbon storage sites both in the UK and Ireland. The primary aims are to conduct controlled laboratory experiments examining:

- baseline hydraulic properties
- multi-phase flow properties in the super-critical CO₂ window
- flow processes/mechanisms during injection of super-critical CO₂

The influence of burial depth on fluid flow properties have also been briefly investigated, though not the primary aim of this study. Findings will improve process understanding of the long-term hydromechanical and multi-phase flow behaviour of caprocks for CCS applications, as well as assessing the degree of coupled evolution between chemical and transport behaviour in caprocks subjected to flow of CO₂.

This report briefly describes the process of sample selection and recovery for testing (Section 2) before discussing relevant prior understanding and similar studies previously conducted in other sealing lithologies (Section 3). This is followed by a description of the experimental approach and progress to date (Sections 4 and 5 respectively). Finally, the expected progression of the ongoing test plan is given in Section 6.

2 Site/sample selection

2.1 PREMO-TRIASSIC CCS PROSPECTS IN THE IRISH SEA

Figure 1 gives an overview of potential CO₂ storage sites for Ireland and the UK. Offshore Ireland, the Permo-Triassic deposits of the Central Irish Sea and East Irish Sea Basins are of particular interest as prospective storage targets for captured carbon dioxide (Lewis et al. 2009a). Within the Permo-Trias, the storage potential of the Sherwood Sandstone Group (SSG) and sealing capability of the Mercia Mudstone Group (MMG) are clearly demonstrated by the established hydrocarbons industry within the East Irish Basin. There the Lower Triassic Sandstone group can be divided into two sub-units; the St Bees Sandstone and Orsmkirk Formations, which are made up of sequences of fluvial, Aeolian and playa deposits. The Orsmkirk Sandstone is present basin-wide and forms the reservoir for most the hydrocarbons found in this basin to date (Seedhouse&Racey, 1997). This reservoir formation is sealed by the Upper Triassic Mercia Mudstone Group. These mudstones were deposited in ephemeral lakes after Atlantic rifting ceased and are contain inter-bedded evaporites. The sequence of the MMG members varies across the basin, an in increase in sand content and pinching-out of the halite towards the margins of the basin.

Whilst the Mercia is considered as a regional caprock, the sealing unit within the group differs from the northern to the southern parts of the basin. The northern gas fields are directly overlain by the Flyde Halite Member, which forms the base of the MMG. This halite layer forms an excellent hydrocarbon seal. However, this unit thins towards the south, where the SSG is capped by a mudstone (Ansdell Mudstone Member). The Andsdell Mudstone is part of the Leyland Formation and has a notably more variable sealing capacity (Seedhouse&Racey, 1997). A general reduction in the thickness and number of evaporate beds in the upper part of the MMG, highlights the importance of careful assessment of the sealing characteristics of mudstones within the group.

The MMG is mainly comprised of red, reddish-brown mudstones with occasional grey and green mudstone and siltstone layers (Armitage et al., 2013). It is thickens in the East Irish Sea basin, due to its subsidence during the Mid-Late Triassic (Ziegler, 1990). Drilling wells indicate a maximum thickness of 2030 m and seismic reflection data indicates that up to 3200 m of the MMG are present in the northern part of the East Irish Sea Basin. The MMG was deposited in a low relief setting and three primary depositional processes are reported to be responsible for the MMG sediments: 1) silts and fine sand transported by flash floods; 2) settling-out of mud and silt in saline water bodies and 3) aeolian dust deposited on damp mudflats (Talbot et al., 1994; Warrington, 1992). Deposition of the MMG halted in the late Triassic when a sea level rise flooded the mudflats and deposited dark grey to black marine muds which are known as the Westbury Formation (Talbot et al., 1994).

Hobbs et al. (2002) provide a detailed account of mineralogical analyses of the Mercia Mudstone Group (MMG) available within the literature. They divide these findings into clay and non-clay fractions. Primary non-clay minerals observed include quartz, calcium and magnesium carbonates, calcium sulphates, micas, iron oxides and halite. Feldspar and some very small quantities of heavy minerals may also be present. The clay fraction within the Mercia Mudstone is primarily composed of illite, chlorite and mixed layer clays (illite-smectite, chlorite-smectite), though pure smectite may also be present in some horizons.



Figure 1. Potential CO₂ storage sites for Ireland and parts of the UK. (Lewis et al., 2009b)

2.2 SAMPLE RECOVERY AND PRESERVATION

2.2.1 Preservation of argillaceous materials

High quality, well-preserved caprock is rarely available. Historically, such material was rarely kept during exploration, but was likely to be in the form of chips, often contaminated by drilling fluid. Where caprock core has been kept, storage conditions are generally detrimental to core condition. Storage at room temperatures and without attempts to isolate core from ambient air conditions, argillaceous materials are very quickly damaged by drying/desiccation processes, which fundamentally alter the physical properties of the rock. Such core is likely to provide erroneous data as a result (Desbois et al. 2014).

From previous experience, it is imperative that every effort be made to preserve the core in as near pristine condition as is physically possible. Attention must be paid to:

1. de-stressing damage
2. mud invasion
3. oxidation
4. dehydration
5. microbiological degradation
6. storage temperature

In general, the larger the diameter of the core the better it is for all aspects of testing. It is then possible to sub-sample so as to avoid surface damage caused by drilling and sampling. There are sampling protocols that minimise de-stressing damage and the use of the preservation cell (P-cell) should be used for all high value cores. Mud invasion should be minimized through the use

of appropriate core barrels and consideration should be given to this aspect of sample handling prior to the commencement of drilling. To minimize microbiological degradation core should be stored at 4°C.

2.2.2 Recovery of test material

Significant efforts were made in order to find suitably well-preserved material, large enough for the purposes of this study, including from within the BGS on- and offshore borehole collection. However, this combined with sample concerns in relation to the high degree of fine-scale heterogeneity within the MMG made use of pre-existing material an unsuitable option. Instead, fresh material was collected during excavation of a new drift at a commercial salt mine in Northern Ireland (within the Larne Basin). This represented a unique opportunity to collect fresh material from the MMG, at depth and below the weathered zone, in advance of the permanent grouting of the rockwall.

As described in the previous section, it is imperative that cores are not allowed to dehydrate. During recovery of test material, all samples were collected following a strict preservation protocol to guard against this, yielding good quality test material. Recovered rock was wrapped in cling-film and vacuum-packed in thick foil, sealed using heating tongs. The foil packages were then sealed in heavily padded crates for transport to the UK. The collected mudstone is stored in an on-site refrigerated core-store designed to minimise core degradation.

Large blocks were collected predominantly from a depth of 57 m (36 m into the Upper Mercia Mudstone Group (UMMG)). A number of additional blocks were collected from higher in the UMMG (with depths ranging between 21 m and 57 m). The collected material ranges from silty to very fine grained in nature and varies from relatively homogeneous, to a more laminated/heterogeneous fabric. Zones of gypsum veining are also common in the succession and are often coincident with bleaching due to reduction. Well preserved, unweathered core is exceptionally rare and the collected material represents a significant resource for testing physical properties generally impacted by such processes. A transport test is due to start on the first core this month and will give an insight into the multi-phase flow properties of the Mercia mudstone and its sealing capacity. Figure 2 shows an example of the recovered Mercia Mudstone, displaying characteristic bleached zones associated with reduction. Petrological characterisation of this material is underway, though the results are not available at this time.

2.3 IN SITU CONDITIONS

In order to examine baseline properties, appropriate *in situ* conditions must be applied during flow testing. Test conditions were selected based on an approximate depth to top of reservoir of 1 km. A confining pressure, P_c , of 23 MPa was therefore selected (equivalent to 1020 m depth, based on an overburden density of 2.3 g/cm³) and an applied pore-water pressure, P_w , of 10 MPa, resulting in an applied effective stress, σ_{eff} of 13 MPa. For reactive flow testing, a temperature of 38°C was selected. The resulting pressure and temperature conditions are well within the super-critical CO₂ window. In the reactive flow test, two preliminary stress increments ($P_c = 19, 21$ MPa) were applied up to the target P_c (23 MPa), so as to confirm whether any consolidation might take place on the approach to the selected *in situ* conditions (see section 5.3.1). For the detailed consolidation testing, effective stress was varied more widely in order to illicit the material response across a range of conditions (see section 5.3.2).

The influence of pore fluid composition is expected to be of importance during reactive flow testing, but is also crucial during non-reactive transport experiments on clay-rich materials, as small differences in fluid chemistry can cause sample swelling. In the absence of pore-fluid composition data, a salt-saturated solution was made using crushed halite from close in the succession to the mudstone sampling location. No evidence of any adverse effects due to discrepancies in fluid chemistry have been observed during testing to date; such changes are generally apparent almost immediately.



Figure 2. Sample material collected from the Upper Mercia Mudstone Group.

3 Caprock sealing and flow

A significant body of work is available in the literature in relation to caprock sealing properties and the controls on seal integrity. However, there remains a limited amount of directly measured data available in relation to the physical properties of caprock materials at *in situ* conditions. In this section, we describe some of the key studies in relation to the mechanical and transport properties of the MMG (sections 3.1, 3.2 and 3.3). Due to the absence of reactive flow studies conducted on the MMG subsection 3.3, which briefly discusses current understanding of multi-phase fluid flow, also highlights a number of experimental studies conducted on other caprock materials.

3.1 MECHANICAL AND GEOTECHNICAL PROPERTIES OF THE MMG

The onshore geotechnical properties of the Mercia Mudstone Group have been well characterised, due to its importance in the engineering geology in the UK. An extensive study conducted by BGS, provides both new data and a detailed summary of information available in the literature (Hobbs et al. 2002). They report values for bulk density and particle density in the range of 1.47-2.47 Mg/m³ and 2.42-2.86 Mg/m³, respectively. Other mechanical and geotechnical properties are less trivial to summarise, given significant spatial disparity in their reported values. This high degree of sequence variability, both laterally and with depth, results primarily from the presence of sandy horizons, and the influence of diagenesis. Handling such heterogeneity remains a significant challenge for site characterisation, though this is not the subject of this project.

Of particular interest to this study is the consolidation state of the Mercia and the influence of burial on associated physical properties. Transport properties are intrinsically interlinked with clay fabric and porosity, which are directly impacted by burial and exhumation history, particularly in weaker materials such as mudstone. As sediment is buried, the resulting increase in effective stress leads to consolidation, by way of compaction and dewatering processes, and a reduction in porosity. Considerable effort has gone into investigating the relationship between porosity and depth of burial in clay rich materials, with a number of early studies being summarised by Rieke and Chilingarian (1974). In its simplest form the effects of burial on porosity, ϕ , can be approximated, as follows:

$$\varphi = n_0 e^{(-cz)}$$

for a depth, z , below surface. The parameters n_0 and c are functions of several contributing factors, such as position within the sedimentary basin, regional tectonic stresses, mineralogy and formation age. In reality, degree of variability in these parameters means that it has not proved possible to construct a reliable master curve of porosity versus depth (or effective stress), which encompasses all sediments. Instead, experimental data examining the relationship between void ratio and applied effective stress for a given caprock, allow predictions of the influence of depth on mechanical and transport properties to be made.

Most available information relating to the consolidation properties of the Mercia Mudstone is derived from the engineering geology sector, where it is described as ‘heavily overconsolidated’. Chandler (1969). However, standard laboratory consolidation testing in this sector is not designed to simulate sufficient stress levels to measure the over-consolidation ratio or fully characterise the consolidation behaviour, of well-preserved, intact and unweathered Mercia Mudstone (Hobbs et al. 2002). Additional consolidation data would provide an improved understanding of the mechanical response of the Mercia at burial depths appropriate to CCS targets in Ireland and the UK.

3.2 HYDRAULIC FLOW

Direct measurement of hydraulic permeability in tight, clay-rich lithologies is non-trivial (Yang and Aplin et al. 2007), due to the exceptionally small flow rates expected at realistic *in situ* conditions. Achieving steady-state flow can be time consuming, especially for larger, more representative sample volumes. As a result, availability of direct permeability measurements in tight mudstones and shales is limited and values are often inferred from petrophysical properties. The authors of this report are unaware of any studies within the literature providing direct hydraulic permeability measurements for the Mercia Mudstone. However, field observations highlight the influence of sandy layers within the MMG to increase the ability of the material to yield water (Hobbs et al. 2002), indicating that mineralogical variations within the group are likely to yield significant deviations in hydraulic properties.

3.3 MULTI-PHASE FLUID FLOW IN GEOLOGICAL SEALS

The multi-phase migration of fluid in low permeability porous media can result from a number of mechanisms, as described by Marschall et al. 2005 (Fig. 3). The dominance of one mechanism, as preferred to another, is strongly dependent upon the associated properties of the material involved (Rodwell, 1999). For a water-saturated, porous material, fluid transport may occur by dissolution and diffusion through the pore-space. In contrast, hydrofracture may lead to rapid migration of an additional phase, along the path of fracture propagation. Two additional mechanisms may allow two-phase fluid flow to occur, by way of advection; (i) visco-capillary flow (Hildenbrand et al. 2004; Marschall et al. 2005) and (ii) dilatant pathway formation (Marschall et al. 2005; Cuss et al. 2014). The former requires capillary forces to be overwhelmed, allowing the displacement of pore-water and the ingress of the second phase and is, therefore, directly related to the pore-throat radii within the porous material. The latter is expected to occur in argillaceous material where the pore-throats are too narrow to allow such displacement to occur and, instead, a network of local pathways accommodate the second phase, by way of transient dilatancy (Marschall et al. 2005).

In cases where visco-capillary flow behaviour is expected, the response of the caprock can be estimated by assessment of the pore-throat properties of the material. A number of techniques are regularly utilised to examine these characteristics, for example, Mercury Injection Porosimetry (MIP). However, there are limitations in such an approach including, (i) the potential for sample damage through drying, (ii) the possibility of measuring damaged material due to preparation of a sample of inappropriate volume (not representative of bulk behaviour). Additionally, it may also be necessary to first assess the assumption that advective two-phase

flow will not occur by dilatancy under the relevant conditions. In order to assess the performance of a caprock, an improved understanding of the dominant flow mechanism, under appropriate injection and long-term storage conditions, is therefore desirable.

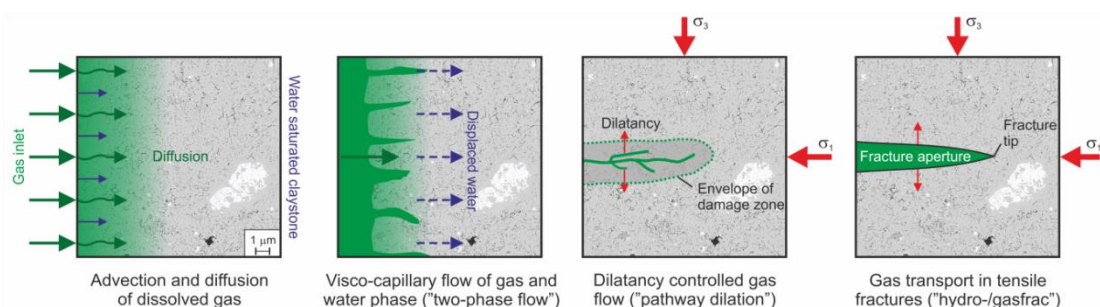


Figure 3. Schematic summary of multi-phase flow mechanisms in low permeability materials (after Marschall et al. 2005).

Whilst a significant body of work is available in relation to the multi-phase fluid flow properties of a range of geological seals from clays (Harrington and Horseman 1999; Donohew et al. 2000; Graham et al. 2012; Harrington et al. 2012) through to shales (Angeli et al. 2009; Cuss, et al. 2014), there are very few studies providing direct evidence of the behaviour of such materials when injected with super-critical CO₂. Hildenbrand et al. (2004) carried out gas breakthrough tests for a number of low to intermediate-permeability pelitic rocks, using N₂, CH₄ and CO₂ as permeants. Reservoir comparable effective stresses were simulated in a triaxial flow cell for the N₂ and CO₂ tests. They applied an instantaneous high pressure gradient across the sample and monitored the subsequent pressure fluctuations in a downstream reservoir and the residual pressure difference remaining between upstream and downstream reservoirs. In the CO₂ penetration experiments, testing was conducted significantly above the critical temperature (at 50°C). Effective permeability coefficients on identical samples were observed to be higher for N₂ than CO₂. Residual differential pressures were determined as ranging from 0.1-6.7 MPa, 0.1-4.9 MPa and 0.1-3.6 MPa for N₂, CO₂ and CH₄ breakthrough tests respectively. A notable inverse correlation between capillary displacement pressure and effective or absolute permeability was shown for all three gases. Capillary displacement pressures were also shown to generally be higher for N₂ than for CO₂ and CH₄.

The residual pressure difference approach was also utilised by Wollenweber et al. (2009). They conducted gas breakthrough and diffusion tests on marlstone and limestone, for helium and supercritical CO₂. Diffusion testing was unsuccessful for the limestone sample, but an effective diffusion coefficient of $7.8 \times 10^{-11} \text{ m}^2$ was reported for the marlstone. Breakthrough experiments were carried out in a triaxial fluid flow cell with applied temperatures ranging from 21 to 45°C. Maximum effective permeabilities were also determined for both sample types, ranging between $0.1\text{--}4.0 \times 10^{-21} \text{ m}^2$ for helium and $0.4\text{--}2.9 \times 10^{-21} \text{ m}^2$ for CO₂, and were observed to increase upon repeat testing. Cyclic gas breakthrough testing with CO₂ was observed to lead to a decrease in residual capillary pressures and in increase in effective gas permeabilities with successive experiments, which the authors attribute directly to sample exposure to CO₂. The absolute permeability for a single phase, before and after CO₂ breakthrough and diffusion tests, was also found to have increased.

Li et al. (2006) carried out CO₂ breakthrough tests for samples of Weyburn Midale evaporate, a major caprock in the Weyburn reservoir. All testing was conducted at a temperature of 59°C; a comparable value to that expected *in situ* at the Weyburn reservoir. Initial hydraulic permeabilities of the samples tested were found to range $\sim 1 \times 10^{-19} \text{ m}^2$ to $1 \times 10^{-22} \text{ m}^2$. As well as obtaining the breakthrough pressures for CO₂, obtained by incremental stepping of injection pressure, the gas absolute and effective permeabilities were determined using nitrogen and CO₂ respectively. Their observations indicate that the Weyburn Midale Evaporite seal rock is a highly effective geological seal to nitrogen. However, the authors also note that the

breakthrough pressure for a CO₂/brine system is considerably reduced compared with that for a CH₄/brine system and, as such, argue that sealing units within depleted reservoirs should not be expected to remain secure at conditions comparable to the original reservoir pressure.

In another study, Springer et al. (2006) carried out transport testing of Nordland Shale (also under reservoir conditions), for both N₂, CO₂ and super-critical CO₂. In both the N₂ and CO₂ tests, the capillary entry pressure was determined by applying stepwise increases to the upstream pressure whilst maintain a constant effective stress (by simultaneous increase of confining pressure). An electronic balance was connected to the downstream fluid outlet in order to ascertain the moment of gas entry. Unfortunately, the coarseness of pressure stepping during these tests did not allow for any noticeable difference in capillary entry pressures to be observed, for N₂ as compared to CO₂ (2.1-4.1 MPa and 2.8-3.5 MPa respectively). During testing with super-critical CO₂ the point of fluid entry was determined to occur at a pressure of 1.7 MPa (significantly lower than the average measured for gaseous CO₂) and the authors attribute this solely to the expected difference in interfacial tension for the two phases. They also note that, whilst this value implies entry of super-critical CO₂ into the Nordland shale is unlikely, these results are dependent upon regional variability of grain size within the caprock.

Scarce information is available in the literature relating to the mechanisms involved in CO₂ migration through argillaceous materials. However, gas breakthrough testing conducted by Harrington et al. (2009), indicates that standard visco-capillary flow concepts may not fully described two-phase flow behaviour in the Nordland Shale. Initial hydraulic testing of two shale samples yielded comparable intrinsic permeabilities of around $4 \times 10^{-19} \text{ m}^2$ for both specimens. This was then followed with nitrogen injection, to assess gas transport properties by way of multistep constant pressure test programme. Their observations indicate gas entry and breakthrough pressures under initially water-saturated conditions of 3.0 and 3.1 MPa, respectively. After gas entry was achieved, flow rate through the specimen was varied to examine the underlying flow law. They used a standard two-phase flow code (TOUGH2) to numerically model the test observations. However, they found that whilst fitting to the pressure data was possible, the magnitude of the flux through the sample could not be matched using this approach. The authors argue that this finding, coupled with their experimental observations, indicates that standard visco-capillary two-phase flow concepts are not adequately representative of the processes involved for the Nordland Shale. Instead, they suggest their findings are more satisfactorily explained by localised gas migration through dilatant pathways.

Nevertheless, the experiments of Harrington et al. (2009) and co-workers were conducted using a non-reactive permeant. However, a carefully instrumented experiment conducted by Angeli et al. (2009) provides additional insight into breakthrough behaviour for super-critical CO₂, in one potential CCS target seal lithology. They applied an increasing pressure gradient across a Draupne shale sample, by maintaining a constant backpressure and incrementally increasing the pore pressure at the upstream side, whilst monitoring entry and exit volumes using two syringe pumps. Piezoelectric transducers were also used to monitor changes in the axial ultrasonic P-wave velocity (V_p) of the material, whilst additional transducers measured axial and radial strain. This integrated approach allowed clear identification of the point of super-critical CO₂ entry and sample breakthrough, which occurred at differential pressures of 3.5 MPa and 3.6-4.0 MPa respectively. Strain data also indicated sample dilation from the onset of gas entry, providing strong evidence for the opening of pathways within the material, along which super-critical CO₂ migrated. The onset of fluid breakthrough was also observed to correlate with a significant reduction in V_p , which the authors attributed to sample infiltration by CO₂ and, potentially, the formation of fractures caused by breakthrough. In addition, the exit pore-fluid from the shale was found to be primarily pure CO₂ (96%), while the post-test sample was found to have maintained a high water content, implying a relatively localised migration of CO₂ along only a few pathways within the material. Their findings provide compelling evidence for migration of CO₂ by dilatant pathway formation within the Draupne seal.

Whilst quantification of diffusive transport properties is not the primary focus of this study, findings reported by Busch et al. (2008), point to the potential for reactive processes to alter multi-phase fluid flow behaviour in shales. The authors investigated the diffusive properties of the Muderong Shale (an Australian caprock with intrinsic permeability $\sim 10^{-21} \text{m}^2$), exposed to CO_2 under reservoir conditions. They observed a slight increase in the effective diffusion coefficient (from 3.08 and $4.81 \times 10^{-11} \text{m}^2/\text{s}$) with successive testing and suggest this may be due to changes in the pore network as a result of mineral alteration. They also carried out gas sorption experiments on crushed samples of the shale and specific clay minerals, which demonstrated the high CO_2 sorption capacities of the material. Constructing a likely CO_2 storage scenario with a Muderong Shale seal, they estimate that diffusive gas breakthrough will occur after $\sim 0.3 \text{MYrs}$. This is for a relatively thin seal and suggests that the storage times for such a scenario may be reasonably acceptable. However, the results of this study also indicate that the porosity of the shale may be significantly changed by geochemical reactions and the authors suggest that seal integrity could be notably reduced by interactions between CO_2 , water and the caprock. They call for further research on the potential for such interactions to impact the transport properties of caprocks.

Whilst the sealing potential for the Mercia Mudstone Group in and around the Irish Sea is demonstrated by the presence of previous hydrocarbon discoveries, there is a paucity of data examining the influence of permeant (e.g., CH_4 versus CO_2) on seal integrity. An improved understanding of the likely mechanisms for multi-phase migration, as well as additional data quantifying the conditions necessary for seal failure, would also be beneficial for full assessment of the MMG. It is the intention that transport testing within this project will seek to address these issues.

4 Experimental approach

This section describes the approach to sample preparation and two apparatus used to conduct flow testing; a standard isotropic permeameter and a reactive flow apparatus.

4.1 SAMPLE PREPARATION

Samples are prepared by dry-drilling with a diamond-tipped core. As water cannot be used as drilling fluid for such materials, friction effects are reduced by use of compressed air. Finally cylindrical samples are honed to the chosen diameter by lathe-turning and the ends are faced-off perpendicular to the cylinder length. Care was taken to work as quickly as possible, in order to reduce the impact of sample drying. Samples to-date have been machined, such that flow is perpendicular to bedding within the mudstone. Final samples have a diameter $\approx 50 \text{mm}$ and aspect ratio $\approx 1:1$. These dimensions ensure bulk properties (as opposed to damaged material) are measured during flow testing. Offcuts taken during sample preparation were weighed immediately, then placed in an oven and exposed to a temperature of 106°C for greater than one day (following standard geotechnical procedures), before re-weighing. The resulting calculated moisture contents for the pre-test material fell within the range 10-14%. Oven drying of the post-test samples will provide additional geotechnical data, including void ratio, dry and bulk density and water saturation.

4.2 ISOTROPIC PERMEAMETRY

The primary focus of this project is reactive flow testing of the Mercia mudstone under chosen *in situ* conditions (see section 2.3) and the experimental set-up for this is described in section 4.3. However, we also report here additional consolidation testing which provides insight into the influence of depth on the hydraulic properties of Mercia Mudstone. The experimental approach

for this additional testing is described here and is based around a simpler isotropic permeameter apparatus (Figure. 4). The basic permeameter is described in some detail by Harrington and Horseman (1999) and consists of five main components: (1) a specimen assembly, (2) a 70 MPa rated pressure vessel and associated confining pressure system, (3) a fluid injection system, (4) a backpressure system, and (5) a National Instruments data acquisition system. The specimen is subject to an isotropic confining stress. The permeant can be changed at any time during an experiment. Independent pore pressure transducers are placed on the injection and backpressure lines to allow the system to be monitored for drift.

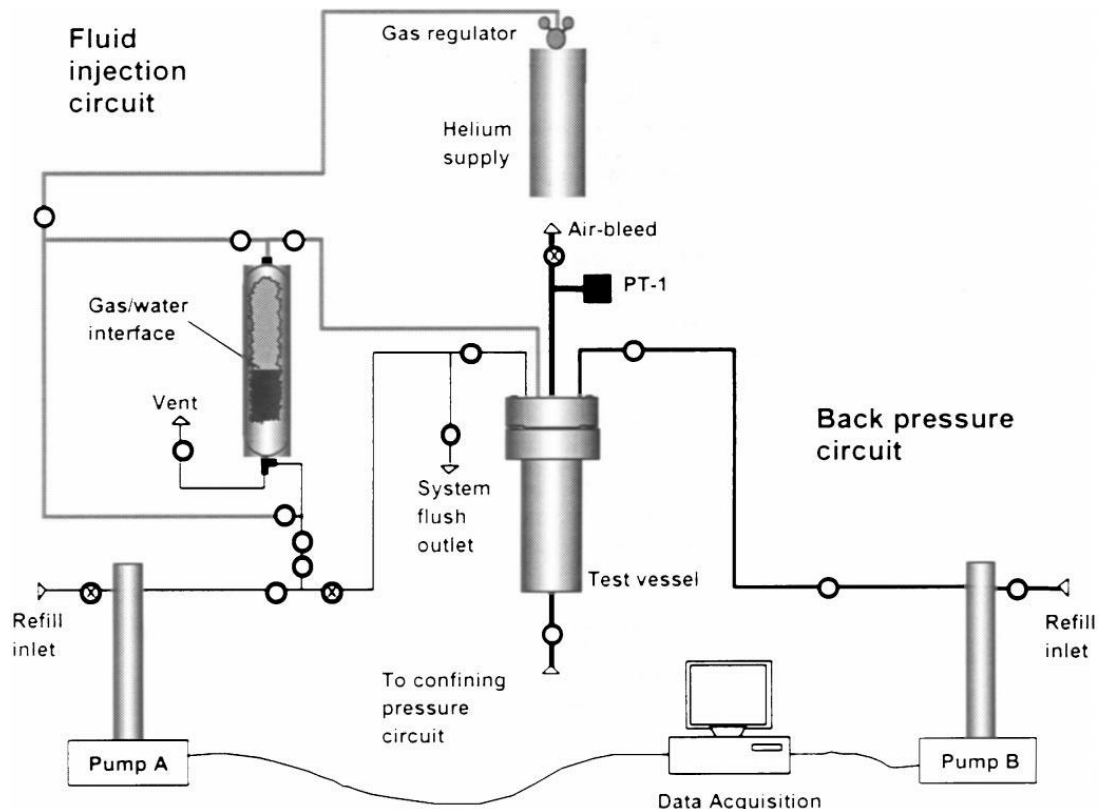


Figure 4. Schematic of a standard BGS isotropic permeameter apparatus.

The cylindrical rock specimen is sandwiched between two end-caps and jacketed in heat-shrink Teflon to exclude confining fluid. A unique ‘lock-ring’ arrangement (Fig. 5) is then placed over the jacketed specimen, so as to provide a leak-tight seal. The inlet and outlet zones for permeant flow through the specimen are provided by porous filter discs 50 mm in diameter which are recessed into the bearing surface of the end-caps. During hydraulic testing, all the filters are saturated with an aqueous porewater solution suited to the given rock chemistry (section 2.3).

Volumetric flow rates are controlled or monitored using a pair of high-precision ISCO syringe pumps, operated by two digital control units. These pumps are calibrated in advance of testing, using a Druck PTX610 pressure transmitter. The ISCO pump controller has an RS232 serial port that allows volume and pressure data to be transmitted to a high specification National Instruments data acquisition. All pump data, as well as data from the independent pore-pressure transducers is logged at an appropriate sample interval (this is generally two minutes for shales, but a higher rate is used for more permeable material).

Non-reactive testing is performed in an air-conditioned laboratory at a temperature of 20 ± 0.3 °C. This approach reduces environmental impacts on flow data and allows exceptionally small flows to be measured within leak-tight apparatuses. A typical test history comprises a sequence of test stages, each designed to examine a particular flow response.

During an equilibrium (EQ) stage, all the porous filters are saturated with the aqueous porewater solution and held at fixed pressure equal to the specified backpressure. This test stage is used to fully saturate the rock and to allow the specimen to reach hydraulic equilibrium with the applied stress and porewater pressure. Consolidation behaviour is tested by maintain a constant pore water pressure and increasing confining stress incrementally. The resulting measured outflows from the up and downstream pumps can then be used to quantify the resulting changes in sample porosity and other physical properties. In addition, by maintaining a constant confining pressure with an additional ISCO syringe pump, it may also be possible to monitor for any associated strains during consolidation of the sample.

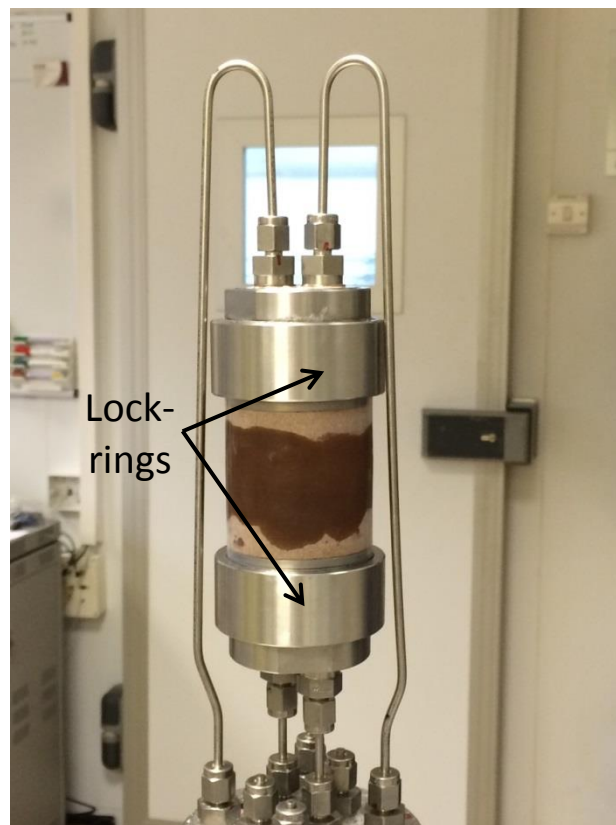


Figure 5. Isotropic test assembly, containing a sample of Mercia Mudstone.

4.3 REACTIVE FLOW APPARATUS

For the purposes of this project, a new bespoke reactive flow apparatus has been designed and constructed by BGS (Figure 6). This flow rig is based on a simpler isotropic permeameter concept, but has been adapted to allow multi-phase fluid flow testing across the CO₂ phase space (excluding hydrate), under likely reservoir conditions. The apparatus is housed in a Binder (FED400) oven, allowing tests to be conducted up to 150°C. All internal pipework and connections are made from grade II titanium, so as to negate the potential for corrosive behaviour to impact any reaction chemistry. Two interface vessels were constructed as part of the up and downstream pressure systems, to allow water and CO₂ to equilibrate at the selected test temperature, prior to injection. In order to have the option of simulating conditions in deeper reservoirs, these vessels and the sample pressure vessel were designed to provide a maximum rating of 1.3 kBar. This required the introduction of high-pressure cone-and-thread fittings and exceptionally thick walls to the interface vessels, which are sealed with gold mechanical seals. The resulting apparatus provides an experimental capability to conduct flow testing with a range of permeants (water, gaseous CO₂, liquid CO₂, super-critical CO₂ or CO₂-saturated solution), under representative in-situ stresses and conditions for Irish and UK potential CCS targets.



Figure 6. The BGS reactive flow apparatus.

Two primary approaches can be conducted using an isotropic permeameter to illicit the hydraulic and multi-phase transport properties of a test sample. In both cases a constant hydraulic backpressure is maintained by way of the downstream pressure system, in order to simulate a constant hydration condition (as would be expected in the saturated zone and at depth). At the upstream filter, permeant can be injected at a constant flow rate (CFR), leading to an increase in pressure with time (for gas this is predicted by the ideal gas law). At some pressure, an outflow will be detected at the downstream filter, which most likely indicates transit of the injectate through the sample has occurred. Nevertheless, a number of experimental artefacts can mimic this response and care must be taken to ensure steady-state flow has been achieved. In many argillaceous materials, the response of the material may be time-dependent and for this reason it may be advantageous to adopt a second approach. Instead of using a constant flow rate, a constant pressure (CP or head) is applied at the upstream filter and then regularly incremented until a corresponding outflow is detected at the downstream end. Both methodologies have merits and the appropriate method is dependent on the expected material response.

5 Progress to date

This section describes progress to date, from preparation and calibration of the apparatus, to laboratory testing. Initial findings are described in relation to consolidation and hydraulic testing. However, it should be noted that availability of geotechnical data and petrological analysis will aide final interpretation of test observations after decommissioning of the current experiments.

5.1 LEAK TESTING/CALIBRATION

A rigorous understanding of the leakage behaviour of a permeameter system is crucial for the sound measurement of transport properties in low and ultra-low permeability. Exceptionally small leaks, which would generally be significantly smaller than measured flows in higher permeability materials, limit the magnitude of flow that can be resolved, potentially masking any outflow response. Generally, leakage rates on standard BGS permeameters are reduced to sub $0.1 \mu\text{l/h}$ in order to maximise the potential to detect exceptionally small flows. However, leakage reduction proved non-trivial for the non-reactive flow apparatus for a number of reasons. Firstly the sealing arrangement utilised in the interface vessels proved exceptionally sensitive to changes in oven temperature, resulting on variable leakage rates at different applied

temperatures. This problem was resolved, by redesign of the sealing arrangement to reduce the influence of expansion and contraction of the gaskets and surrounding housings. Secondly, whilst selected for steady temperature control, small-scale fluctuations in the temperature of the oven lead to additional noise in the monitored flow rates. Finally, diurnal temperature variations within the laboratory were observed to influence the pump responses, leading to additional fluctuation in flow measurements.

As a result, significant effort was made to reduce the leakage behaviour of the system, which was carefully monitored for both water and CO₂ at a range of temperatures. For example, the final baseline leakage rate for the injection circuit was estimated to be $\approx 0.13 \mu\text{l/h}$. However, continued temperature fluctuations introduce additional noise, meaning that flow responses cannot be easily detected below a level of $\sim 1 \mu\text{l/h}$. Nevertheless, these values are still exceptionally low and sufficient to allow measurement of permeabilities in the 10's of nDarcy's range.

5.2 P-T CALIBRATION

To allow for changes instrument sensitivity to changes in pressure and temperature, it was necessary for the pressure response of the piston pumps and the independent transducers to be calibrated in advance of testing. Calibration was conducted for the confining, backpressure and injection circuits from atmospheric conditions up to a maximum pressure of 24 MPa, for temperatures of 20, 30 and 50°C. The first calibration (20°C) represents the ambient laboratory temperature. Above this temperature, calibration was conducted by setting the oven to the relevant temperature and allowed to equilibrate. The oven has a heating rate of 1.75°C/min and cooling rate of 4.65°C/min. Once the oven temperature was considered stable the calibration was repeated. To calibrate the system the pumps were individually connected to a portable pressure indicator (Druck PTX610). The pressure in the pump was raised in increments of 2 MPa from 0 to 24 MPa and then reduced in 2 MPa increments back to atmospheric, to check for hysteresis in the system. At each step the pressure was allowed to equilibrate and continuous readings taken by the logging system. At the same time, data from the relevant pressure transducers was recorded. Once the calibration was completed the data was analysed for each pump and pressure transducer, with respect to the known applied values recorded by the pressure indicator.

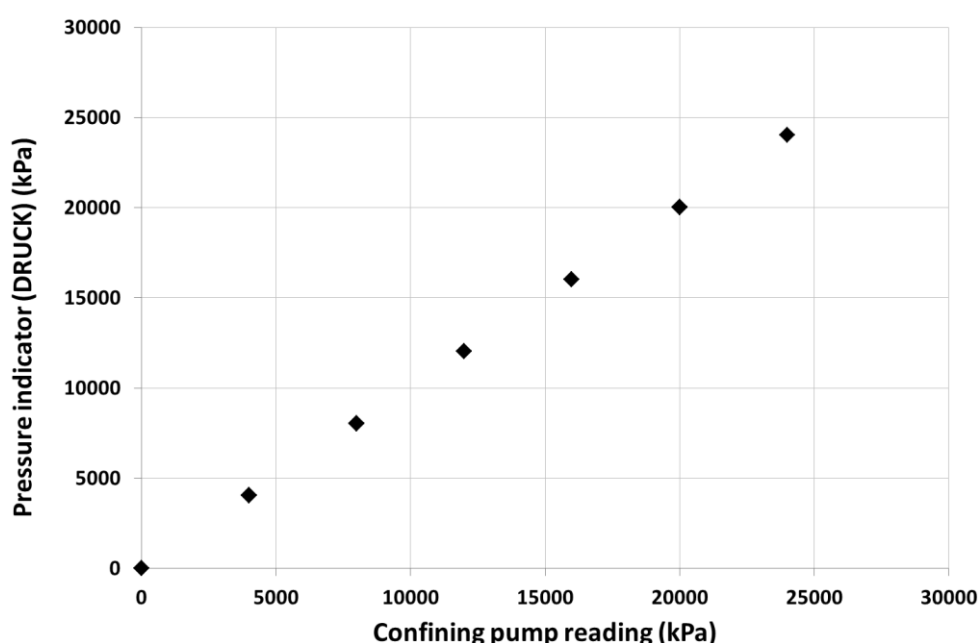


Figure 7. Confining pump calibration at 20 °C

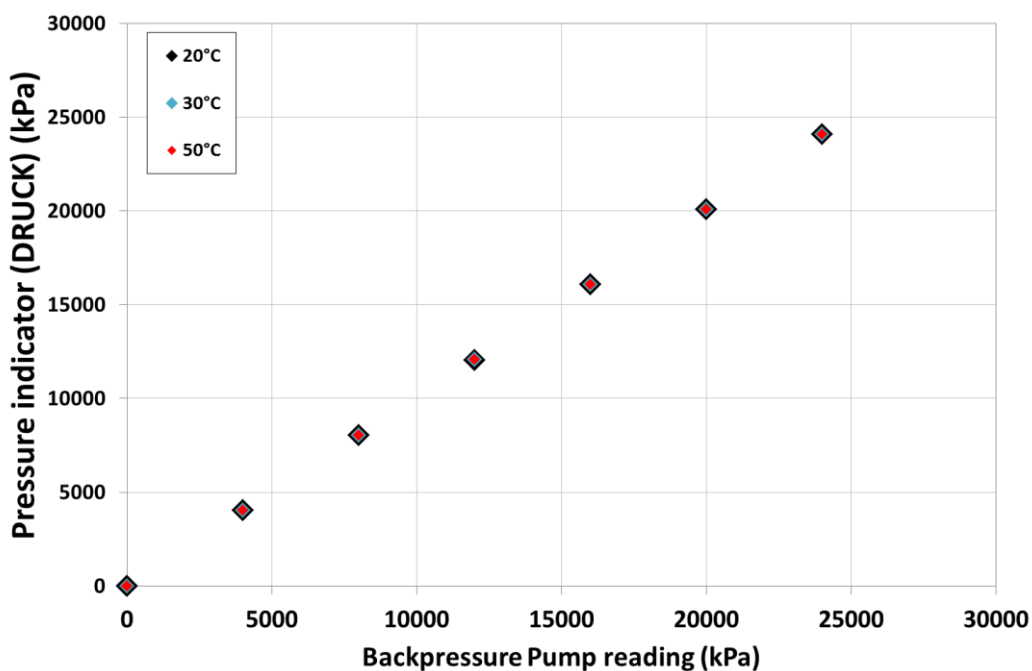


Figure 8. Backpressure pump calibration for 20, 30 and 50 °C

Measured calibration curves showed no significant evidence of hysteresis for any of the three pumps (see Figures 7 to 9). This was also true at higher temperatures and no significant impact to calibration values was observed due to temperature elevation. The average calibration values are given below in Table 1.

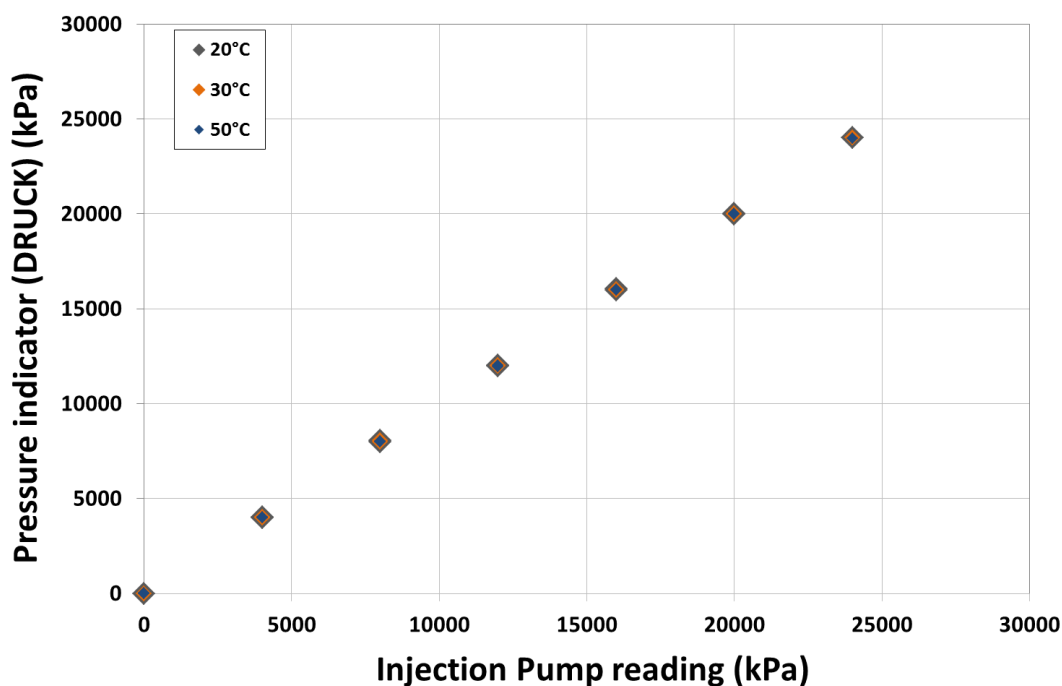


Figure 9. Injection pump calibration for 20, 30 and 50 °C

Pump	Slope (m)	Off set (b)
Injection	1.0028	+ 3.304
Backpressure	1.0086	+ 2.722
Confining	0.9994	- 2.869

Table 1. Calibration values for the three system pumps

5.3 HYDRATION AND CONSOLIDATION BEHAVIOUR

5.3.1 Reaction flow cell

Testing was initiated by applying a confining pressure of 9 MPa. Both upstream and downstream sample filters were then flushed with synthetic pore solution, in order to remove residual air. A pore pressure of 1 MPa was then applied to the sample and confining pressure increased to 10 MPa. The sample was left to equilibrate at a temperature of 38°C overnight, before being stepped up to target conditions of $P_c = 19$ MPa and $P_w = 10$ MPa. During hydration of the sample, a seal failure on the injection pump lead to a small leak in the pore fluid circuit. Pore pressure was not affected and the sample was isolated whilst the seal was replaced. However, the hydration response of the sample was masked during this time. Inflow data at the downstream filter are shown in Figure 10. Notable inflections in the curve are visible resulting from brief thermal fluctuations, as the oven doors were opened during investigation of the upstream leak. Nevertheless, inflows to the sample had stabilised after approximately 14 days, indicating that the sample was fully resaturated by this time.

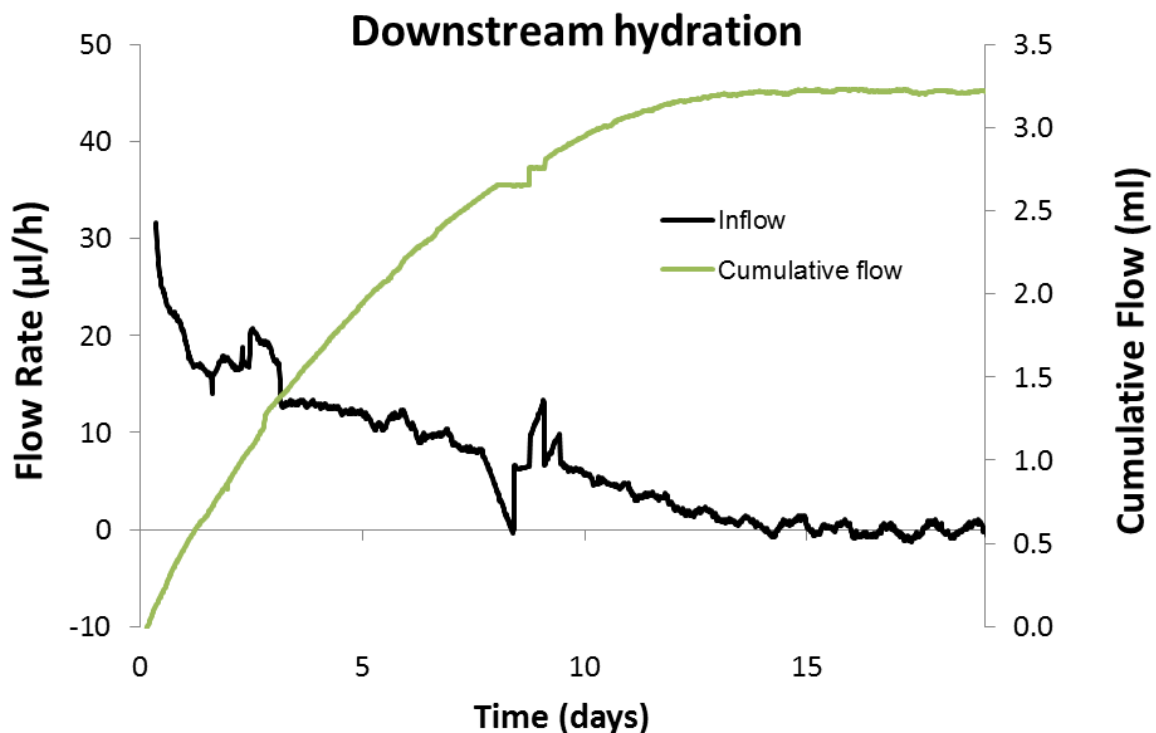


Figure 10. Hydration phase in reactive flow apparatus. Inflow had stabilised after two weeks exposed to synthetic porewater at constant pressure.

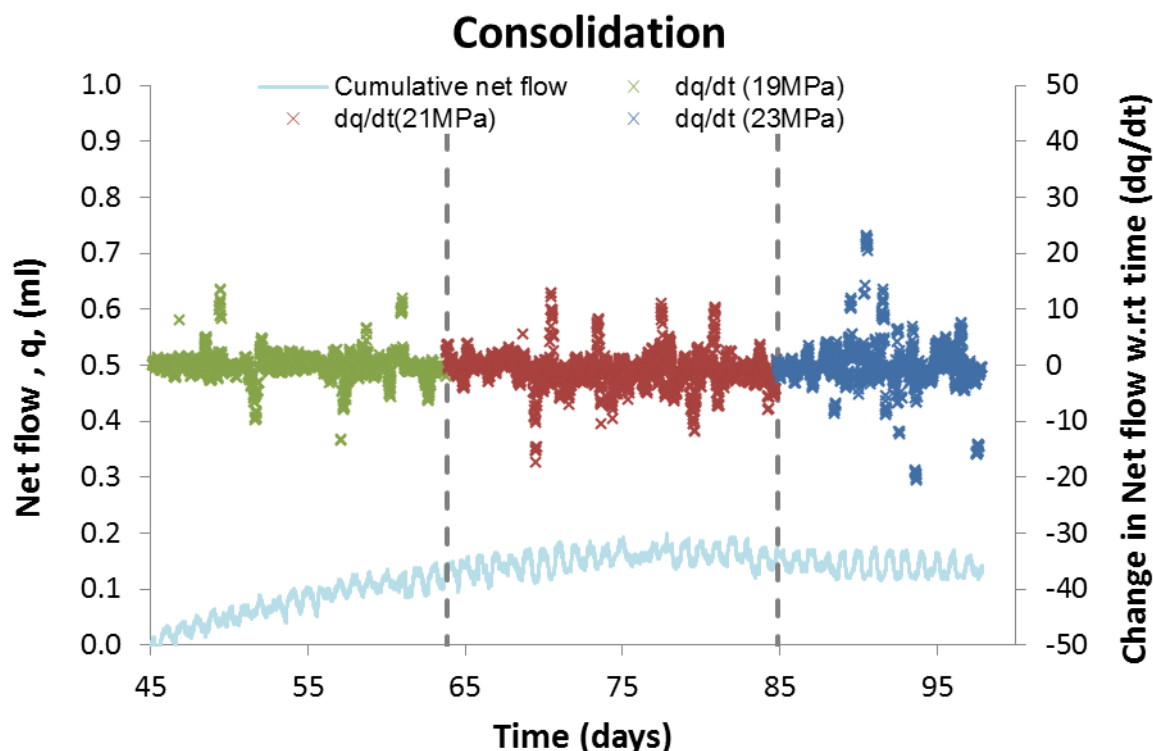


Figure 11. Net flow response of sample on incremental loading ($P_c = 19\text{MPa}$, 21MPa , 23MPa).

As described in section 2.3, the applied confining stress was then increased in incremental 2 MPa steps (allowing time to equilibrate) up to the target value of 23 MPa. Net flow was monitored during this period and is shown in Figure 11. A small cumulative inflow is observed over the $P_c=19\text{ MPa}$ step (days 45 to 65), potentially resulting from very slight sample swelling (and continued hydration) in response to the return to *in situ* conditions. A very small outflow was noted at the onset of the 23 MPa step. However, this corresponds with the onset of a further small leak on the injection pump circuit. After isolating the pressure vessel and replacement of an additional seal on the pump piston assembly, this outflow was no longer observed. During the period of sample elevation to target confining pressure a cumulative net inflow of approximately 0.15ml was observed, indicating that the sample was fully hydrated and that no significant consolidation occurred during pressurisation. This indicates that the test material has previously been exposed to effective stresses of greater than 9 MPa, as is to be expected. However, it should be noted that the complex diagenetic history of the Mercia Mudstone may well also influence the mechanical behaviour of the material.

5.3.2 Isotropic permeameter

Additional consolidation testing has been conducted on another Mercia Mudstone sample to investigate the influence of effective stress at higher pressures. A constant pore water pressure was applied to the sample, which was then exposed to a series of increasing steps in confining pressure, simulating the influence of burial. Two additional unload/reload steps were also applied to examine any potential hysteresis. The resultant changes in outflow were then monitored and used to calculate the reduction in void ratio, e , as a function of applied effective stress (Figure. 12). A number of techniques are available to determine the point of yield in e -log P_{eff} space. However, visual inspection suggests that yield in this sample of Mercia Mudstone occurs around $P_{\text{eff}} = 30\text{ MPa}$. This is consistent with previous observations detecting no evidence for yield at effective pressures significantly below this value (Hobbs et al. 2002). This data can be used to construct a failure envelope, providing an indication of potential limits for injection strategies where the Mercia Mudstone is considered to be the primary sealing lithology.

The test data also give evidence of the influence of effective stress on specific storage and Young's modulus, which will be reported after additional analysis.

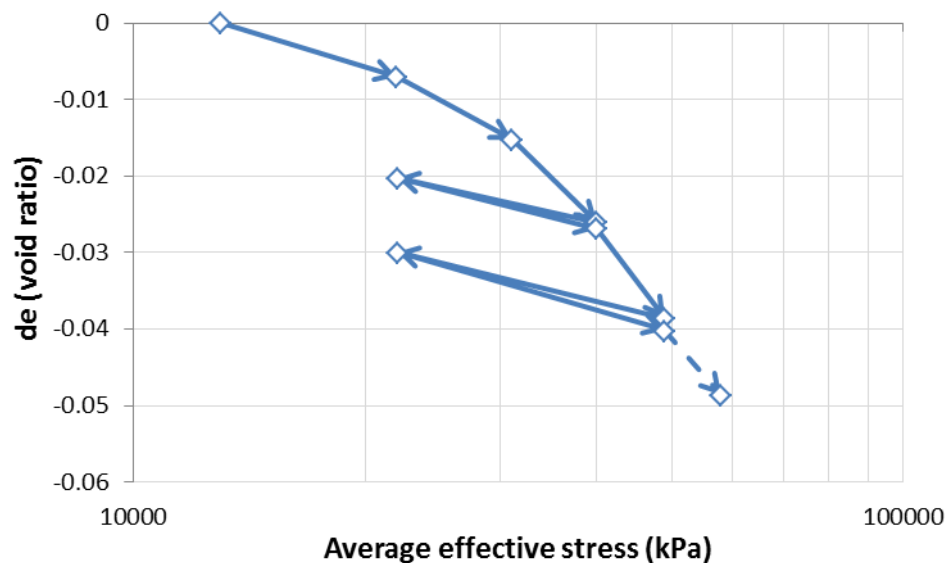


Figure 12. Change in void ratio with log P_{eff} , during consolidation testing in the isotropic permeameter.

5.4 HYDRAULIC TESTING

Hydraulic testing has been conducted in both the reactive flow cell and the standard isotropic permeameter (prior to consolidation testing). For the latter, a cross-flow was initially observed in the initial stages of sample resaturation (between the up- and downstream filters), suggesting interconnected permeability. To solve this issue, it was decided to bypass (hydraulically connect) the up- and downstream circuits and to interpret the data, post-testing by numerical analysis of the bulk consolidation transients. Numerical modelling is currently ongoing to quantify the flows observed and the consequent findings will be reported at a later date.

Hydraulic testing in the reactive flow cell indicates a relatively low sample permeability for a geological seal. This phase of testing was initiated under the selected *in situ* conditions ($P_c = 23$ MPa, backpressure $P_w = 10$ MPa). Based on an initial estimate of hydraulic permeability, injection of synthetic pore solution was initiated at the upstream filter by applying a constant flow rate (CFR) of 11 $\mu\text{l/h}$. The result was a rapidly increasing upstream pressure, with no detectable response at the downstream end. Injection had to be halted in order to ensure the confining pressure value was not approached. Reducing flow rate proved unsuccessful in eliciting flow, indicating relatively low sample permeability.

To check for any potential system blockage, the CFR test was repeated, instead injecting to the downstream filter. The same response was observed as a result and constant flow was halted and switched to an applied constant pressure (CP) of 13344 kPa at day 107. In order to allow for time-dependent effects, this pressure step was held for ~ 4 days, during which time no detectable flow as observed. The constant head was then incrementally increased by 2 MPa twice, each time allowing the system time to equilibrate, with no evidence of hydraulic flow occurring. Hydraulic testing is currently ongoing (see section 6). However, assuming potential for Darcian flow just below the detection level of the apparatus gives a maximum hydraulic permeability, with flow perpendicular to bedding, of $1.3 \times 10^{-21} \text{ m}^2$. The differing hydraulic responses observed during testing in the isotropic permeameter and the reactive flow cell indicate that there may potentially be variability in the physical properties of the Mercia Mudstone, even over a relatively small depth range. Such differences may be the result of mineralogical variations in lithology during deposition, or could relate to secondary mineralisation during diagenesis.

Petrological and geotechnical analysis of the post-test samples will provide further insight into these observations, in addition to findings from numerical modelling.

6 Test progression

As described in the previous section, testing to-date has included system optimisation, hydration, consolidation and hydraulic measurements. The reactive flow test is currently ongoing and progression of the experiment may vary, depending on material response. However, the current intention is to continue as follows:

1. Hydraulic testing. Additional constant head increments will be applied to the sample, in order to encourage hydraulic flow. If steady-state flow is established, the baseline hydraulic conductivity of the sample will be directly measured. Specific storage will also be calculated from analysis of the pressure/flow transients. If flow cannot be established under the currently selected *in situ* conditions, the sample will be exposed to pressure representative of a greater equivalent depth and hydraulic testing repeated. Findings from consolidation testing indicate that sample damage will not occur until $P_{\text{eff}} \sim 30$ MPa. As such, given a 10 MPa applied pore water pressure, this provides an opportunity to induce flow at greater confining pressures whilst avoiding the occurrence of sample yield.
2. Reactive flow testing. Prior to the start of multi-phase flow testing a pressure ‘recovery’ stage will be applied in order to dissipate any residual porewater pressures within the sample following hydraulic testing. Super-critical CO₂ will then be introduced to the upstream, whilst a constant hydration condition will be maintained with synthetic porewater at the downstream filter. Given hydraulic observations to-date, CO₂ injection will most likely be conducted by the application of a series of pressure gradients across the sample, in order to define the gas breakthrough pressure. If system resolution allows, gas entry pressure may also be determined. If stable gas flow is achieved, flow rate/pressure gradient can be varied to examine the gas permeability function. The intention is to maintain flow for a reasonable period in order to encourage the probability of observing any geochemical changes, post-testing. Once flow testing is complete, injected fluid pressures can be allowed to decay to measure the apparent threshold capillary pressure i.e. the point at which gas ceases to be mobile in the system.
3. Supporting analyses. Appropriate numerical modelling will be undertaken to support analysis of the data. Mineralogical and petrological analysis of post-test sample will be conducted to establish the degree of geochemical changes which may have occurred during flow.

7 Conclusion

Whilst the multi-phase transport characteristics of Mercia Mudstone have been indirectly inferred in a limited number of studies (Seedhouse and Racey, 1997; Armitage et al., 2013), the authors of this report are unaware of any direct measurement of CO₂ transport properties for this material, under realistic *in situ* conditions. It is the intention of this study to address this by conducting the first direct measurement of transport properties in the Mercia Mudstone and to expand the highly limited data-set of reactive flow tests in caprock currently available (Hildenbrand et al. 2004; Angeli et al. 2009). The test programme emphasis is on improving process understanding, the results of which can be applied to performance assessment of long-term caprock sealing capability.

There is also a paucity of data available in relation to the hydraulic properties of the Mercia Mudstone. Initial findings from this ongoing study indicate that there may be significant

variation in the hydraulic response of this material, though good sealing properties (sub- $1 \times 10^{-21} \text{ m}^2$) do occur in some material. However, the question of natural variability cannot be addressed without additional testing. The influence of burial depth on physical properties has also been investigated and further analysis will provide data on the influence of such changes on the hydraulic flow properties of the Mercia. Consolidation data will also allow the construction of the yield envelope for the Mercia Mudstone from the Larne Basin, providing insight into the influence of stress conditions on the potential for yield and, the likely associated failure mode (brittle/ductile) for a given stress path. Such data can be used to select suitable injection strategies to maximise capacity, whilst maintaining seal integrity.

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