

Efficiency of Carbon Dioxide Storage and Enhanced Methane Recovery in a High Rank Coal

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4 **1 Efficiency of carbon dioxide storage and enhanced methane**
5 **2 recovery in a high rank coal**
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4 **16 Abstract**

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6 17 High affinity and adsorption capacity of coal to carbon dioxide provides alternative approach for
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8 18 the enhanced recovery of methane from unminable coalfields (CO₂-ECBM) by which a potential
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10 19 solution for long-term CO₂ sequestration in deep geological formations can also be achieved.
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12 20 However, due to chemo-mechanical effects induced by the interactions between CO₂ and coal, the
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14 21 effective methane production and carbon dioxide storage can be degraded which has caused
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16 22 uncertainties about the techno-economic feasibility of the CO₂-ECBM process. This study presents
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18 23 an experimental investigation that aims to address key knowledge gaps related to the efficiency of
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20 24 CO₂ storage and CH₄ recovery in high rank coals for which comprehensive experimental data set
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22 25 and analysis are largely missing. Competitive displacements of CH₄ with N₂ or CO₂ in an
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24 26 anthracite coal sample from South Wales coalfield have been studied, based on a series of core
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26 27 flooding experiments.

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28 28 The results show that the N₂ breakthrough time (the time at which 1% of the total gas injected was
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30 29 recovered) was almost spontaneous whereas a considerably delayed breakthrough time was
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32 30 observed for the case of CO₂-ECBM experiment. In addition it was observed that for the CO₂-
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34 31 ECBM experiment, the ratios of CH₄ recovery with respect to the total amount of gas injected and
35
36 32 gas stored were higher by factors of 10 and 2.4, respectively. The results also show that 90% of the
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38 33 total N₂ injected was produced in the outflow gas, whereas for the case of the CO₂ experiment, only
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40 34 63% of the total injected CO₂ was produced. Presence of high amount of N₂ in the outflow may
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42 35 lead to additional challenges in order to separate N₂ from CH₄ and thus affects the efficiency of the
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44 36 N₂-ECBM method. Under the conditions of the experiments, the total CH₄ displacement ratio and
45
46 37 breakthrough for the case CO₂-ECBM were found to be more favorable compared to those obtained
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48 38 from N₂-ECBM. This study provides new insights into the efficiency of CO₂-ECBM process and
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50 39 offers a comprehensive experimental data set that can be used for testing the accuracy of predictive
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52 40 models.

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41 **Keywords:** *CO₂ sequestration, enhanced coalbed methane recovery (ECBM), anthracite coal, core*
42 *flooding, gas permeability, gas sorption, South Wales coalfield.*
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1. Introduction

The process of coalbed methane (CBM) production from unminable coal fields usually involves the pressure depletion in the coal reservoir by pumping out the naturally existing formation water. However, the pressure depletion only allows a limited amount of in-place-gas (CH_4) to be produced because the methane is adsorbed on the coal even at low pressures (White et al., 2005). As a result, approximately 30 to 70% of the in-place-gas in coal cannot be recovered using the conventional pressure depletion method (Puri and Yee, 1990). Enhanced coalbed methane (ECBM) recovery is a process by which N_2 or CO_2 (or a mixture of both) is injected into the coal seam to enhance the recovery of coalbed methane (White et al., 2005). In N_2 -ECBM, N_2 first displaces the free CH_4 from the seam and reduces the partial pressure of methane in the reservoir that enables further methane in the adsorbed phase (in coal matrix) to be released (Shi and Durucan, 2005). However, rapid breakthrough of N_2 during the production of methane has been reported to be the major issue in the field projects (Perera and Ranjith, 2015). Alternatively, CO_2 has been suggested to enhance the coalbed methane recovery (CO_2 -ECBM) due to the higher affinity of coal to adsorb carbon dioxide compared to methane that may result in larger amount of coalbed methane production. In addition, the potential long term sequestration of CO_2 in deep unminable coal seams during the process of CO_2 -ECBM is an advantage over the N_2 -ECBM process (Shi and Durucan, 2005). Permeability evolution in coal as the result of changes in effective stress and sorption-induced swelling and shrinkage during ECBM process has been extensively studied by researchers, through laboratory investigation and numerical modeling, *e.g.* Feng et al. (2017), Hadi Mosleh et al. (2017), Liu and Harpalani (2013), Ma et al. (2011). Experimental studies show that coal can exhibit shrinkage or swelling during interaction with different gas species, *e.g.* Mazumder et al. (2006), Mazzotti et al. (2009), Hadi Mosleh (2014). Therefore, the uptake or release of CO_2 and CH_4 is a combination of adsorption/desorption

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4 68 processes and coal swelling/shrinkage that can affect the permeability of the coal, resulting in the
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6 69 overall rate and efficiency of methane recovery and carbon dioxide storage.
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8 70 Observations from limited pilot tests of carbon sequestration in coal seams that have been reported
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10 71 in the literature (Japan, Poland and China) indicate the reduction in the injectivity of carbon dioxide
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12 72 as the result of reduction in coal permeability induced by swelling (Reeves and Oudinot, 2005;
13
14 73 Yamaguchi et al. 2006; van Bergen et al. 2006). However, the outcomes of the field tests reported
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16 74 have largely remained inconclusive (Pan and Connell, 2012). A limited number of lab-scale
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18 75 experimental studies have also been reported on processes related to enhanced coalbed methane
19
20 76 recovery nitrogen and carbon dioxide, *e.g.* van Hemert et al. (2012), Wang et al. (2010), Mazumder
21
22 77 and Wolf (2008), Yu et al. (2008). The experimental approach adopted in majority of these studies
23
24 78 is based on core flooding test in which a core sample of coal is first saturated with CH₄ and then N₂
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26 79 or CO₂ (or a mixture if gas) is injected into the sample. The composition of the outflow gas is
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28 80 monitored during the test to evaluate the breakthrough time of the injected gas, displacement of
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30 81 gases and the rate of gas storage/recovery. Wang et al. (2010) carried out a series of gas storage and
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32 82 recovery experiments on highly volatile bituminous coal and showed that for the example
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34 83 considered, the amount of the adsorbed CO₂ was two orders of magnitude larger as compared to the
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36 84 amount of desorbed CH₄. Yu et al. (2008) has reported gas storage and recovery experiments on
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38 85 coal samples originated from Qinshui basin in China. The results show that initially the CO₂
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40 86 fraction in the outflow gas was very small compared to the CH₄ and the initial CH₄ displacement
41
42 87 with CO₂ was not associated with the CO₂ release. They have also shown that with an increase of
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44 88 the volume of replaced CH₄, the discharge capacity of CO₂ has slowly increased.
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46 89 Compared to the extensive experimental investigations carried out on adsorption/desorption
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48 90 characteristics and permeability properties of coal to gas species, the laboratory scale experimental
49
50 91 studies on the process of N₂-ECBM and CO₂-ECBM are very limited and comparative assessment
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52 92 of the efficiency of enhanced methane recovery by N₂ and CO₂ is still lacking. In the last decade
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54 93 several conceptual models have been developed to account for the flow of gas in coal and fractured
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4 94 rock (*e.g.* Shi and Durucan, 2003; Salimzadeh and Khalili, 2015; Hosking, 2014). These models are
5
6 95 usually based on mechanistic approaches that require appropriate constitutive relationships (*e.g.*
7
8 96 gas permeability model) and experimental data for testing. Data sets generated from laboratory
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10 97 scale experiments on N₂-ECBM and CO₂-ECBM are critical bench marks for testing such
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12 98 numerical models that can be used for simulation and design of the process at field scale.
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14 99 However, the experimental studies that contain adequate material properties and provide
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16 100 constitutive relationships for numerical modeling are scarce, especially for high rank coals, *i.e.*
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18 101 anthracite. In this work, we aim to address i) gaps in knowledge related to the response of a high
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20 102 rank coal to gas injection, displacement and storage during ECBM process, and ii) the lack of
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22 103 adequate and comprehensive experimental dataset required for testing the predictive models. In this
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24 104 paper, an experimental investigation on the process of N₂-ECBM and CO₂-ECBM in a high rank
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26 105 coal from South Wales coalfield is presented and comparative assessment of the efficiency based
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28 106 on gas recovery and storage for both N₂-ECBM and CO₂-ECBM is discussed. Core flooding
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30 107 experiments have been conducted in which N₂ and CO₂ were injected into the CH₄-saturated coal
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32 108 sample to evaluate the competitive displacement of CH₄ with N₂ and CO₂ under simulated
33
34 109 underground conditions. The displacement process, gas breakthrough, and recovery ratios are also
35
36 110 discussed.

111 **2. Material and methods**

112 The anthracite coal sample used in this work was obtained from the Six Feet coal seam, at the
113 Unity coal mine located in South Wales, UK (Hadi Mosleh et al., 2017). Blocks of coal with
114 dimensions of approximately 0.5×0.5×0.5m were collected from the depth of approximately 550m.
115 Prior to core flooding experiments, a series of coal characterisation tests including the Proximate
116 and Ultimate Analyses (BS 1016-104 and BS 1016-106) were conducted on crushed samples in
117 order to determine key properties of moisture content, ash content, and volatile matter as well as
118 elemental composition such as sulphur and carbon contents. Table 1 presents a summary of the
119 physical and chemical properties of the coal used.

120 **2.1. Preparation of core samples**

121 The core sample used was drilled from a large block of coal using a diamond core drill bit with
122 70mm internal diameter. The core sample was then cut into the required length using a diamond
123 saw. Special care was taken during the coring and cutting processes to minimise breakage or
124 damage to the coal structure. Any small breakage especially around the edges could potentially
125 damage or puncture the rubber membrane during triaxial core flooding tests and under the high
126 confining pressures and therefore had to be removed. In order to prevent breakage of the coal
127 samples under high stress conditions, the ends of the specimens were ground and made parallel to
128 each other using a fine sand paper. This allowed a uniform distribution of the axial stresses to both
129 ends of the sample. In order to remove any residual moisture, the core sample was then air-dried
130 for 24hr before it was placed in the triaxial cell for the tests.

131 **2.2. Triaxial core flooding setup**

132 Triaxial core flooding setup was designed and developed by Hadi Mosleh (2014). The experimental
133 setup comprises i) a high pressure triaxial core flooding system, ii) a pressure control system, iii) a
134 temperature control system, and iv) an ancillary system including gas supply and analysing units. A
135 schematic diagram of the developed laboratory facility is presented in Figure 1 (Hadi Mosleh et al.,
136 2017).

137 The core sample sits within a 1.5mm thick silicone rubber sleeve and the gas passes through a
138 porous plate at the bottom of the sample, then it leaves the cell through a similar arrangement at the
139 top after having passed through the test core. A Mass Flow Meter capable of measuring high flow
140 rates up to $17 \times 10^{-6} \text{m}^3/\text{s}$ (1L/min) is connected to the outlet which is capable of working under both
141 subcritical and supercritical conditions, with pressures up to 20MPa.

142 The pressure control system includes a pressure/volume controller to control the confining pressure
143 and a high pressure regulator with a needle valve to control the gas pore pressure. Two 32MPa in-
144 line pore pressure transducers were selected to measure the inlet and the outlet gas pressures. The
145 confining system consists of a 32MPa pressure/volume controller with a $2 \times 10^{-4} \text{m}^3$ (200mL) oil

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4 146 reservoir. Volume changes can be measured and displayed to $1 \times 10^{-9} \text{m}^3$ (0.001mL). The confining
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6 147 pressure is provided by silicone oil 350 (Polydimethylsiloxane) and a hydraulic pump. The
7
8 148 composition of the outflow gases was determined using an Emerson X-Stream general purpose gas
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10 149 analyser (standard 19"/3HU version) with the optimum gas flow rate of $1.7 \times 10^{-5} \text{m}^3/\text{s}$ (1L/min) and
11
12 150 $\pm 0.01\%$ accuracy of Full Range Output (FRO). More details of the design and development of the
13
14 151 laboratory setup can be found in Hadi Mosleh et al. (2017).
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17 152 **2.3. Experimental procedure**

18
19 153 The core sample of 70mm diameter and 100mm length was carefully wrapped with a thick PTFE
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21 154 tape before being placed in the silicone rubber sleeve. The displacement transducers, two axial and
22
23 155 one radial, and three thermocouples were then attached to the sample. The top cap was placed on
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25 156 the base pedestal and the cell was filled with the silicone oil. The temperature of the system was
26
27 157 adjusted to 25°C (the corresponding temperature of the depth at which the sample was taken), using
28
29 158 four heating elements attached to the cell's body and a programmable controller. The temperature
30
31 159 was kept constant throughout the test. A confining pressure of 1MPa was applied and the sample
32
33 160 was subjected to vacuum for 24 hours to remove the residual moisture and gases from the pore
34
35 161 space. Prior to each core flooding test, the core sample was saturated with the chosen gas.
36

37 162 The steady-state method has been used to estimate permeability of the coal sample (Carles et al.,
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39 163 2007). For the initial permeability measurements, the confining pressure was maintained at the
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41 164 desired pressure and increased stepwise. Once the steady-state flow rate was achieved at each step,
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43 165 the differential gas pressures and gas flow rates were recorded. The permeability of the coal sample
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45 166 was calculated using Darcy's law (Carman, 1956), given as:

$$46$$
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$$48 \quad k_g = \frac{2Q_0\mu_g LP_0}{A(P_{up}^2 - P_{down}^2)} \quad (1)$$
$$49$$
$$50$$
$$51$$

52 167 where, k_g is the gas permeability coefficient (m^2), Q_0 is the volumetric rate of flow (m^3/s), μ_g is the
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54 168 viscosity of the gas (Pa.s), L is the sample length (m) and P_0 refers to the reference pressure (Pa)
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4 169 which in this study was atmospheric pressure, *i.e.* 1×10^5 Pa. A is the cross-sectional area of the
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6 170 sample (m^2), P_{up} is the upstream gas pressure (Pa), and P_{down} is the downstream gas pressure (Pa).
7
8 171 The viscosity of gases (μ_g) was calculated as function of temperature, using the Sutherland formula
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10 172 (Smits and Dussauge, 2006).

11
12 173 The experimental tests carried out based on the steps summarised in Figure 2:

14 15 174 **Stage 1: Flow characterisation of the coal sample**

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17 175 Since helium is a non-adsorptive/non-reactive gas it was used to characterise the coal sample for its
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19 176 intrinsic permeability and to investigate the mechanical effect of stresses on permeability of coal
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21 177 during gas injection and depletion processes. The intrinsic permeability to helium has been used as
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23 178 a key material property to compare gas flow behaviour of the coal sample used in this study with
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25 179 those from previous studies, *i.e.* Hadi Mosleh (2014), and also to evaluate the changes in
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27 180 permeability of the same coal sample with respect to gas species. The permeability of the coal
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29 181 sample to helium was estimated for a range of gas injection pressures (up to 5.5MPa) and at several
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31 182 confining pressures (up to 6MPa). In order to evaluate the effects of confining pressure on the gas
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33 183 flow properties of the coal sample, the confining pressure was first increased stepwise up to 6MPa
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35 184 while gas injection pressure was kept constant at 3.5MPa. To assess the effect of pore pressure
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37 185 changes on gas flow and permeability of the coal sample, gas pressure was increased gradually to
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39 186 5.5MPa while the confining pressure was kept constant (6MPa). The coal sample was then
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41 187 subjected to vacuum for 24 hours and saturated with CH_4 at 5MPa injection pressure and 6MPa
42
43 188 confining pressure. The permeability of the coal to CH_4 was measured by performing a CH_4
44
45 189 flooding experiment under a range of gas injection pressures from 3.5 to 5.5MPa.

46 47 48 190 **Stage 2: N_2 - and CO_2 -ECBM experiments**

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50 191 The coal sample was re-saturated with CH_4 at 5MPa injection pressure and 6MPa confining
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52 192 pressure. N_2 gas was then injected into the CH_4 -saturated at 5MPa injection pressure while the
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54 193 downstream valve was at atmospheric pressure, *i.e.* 0.1MPa. The composition of the outflow gas
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4 194 was analysed during the experiment using the gas analyser. After the N₂-ECBM experiment, the
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6 195 residual gas was removed from the sample by applying vacuum. The sample was purged with CH₄
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8 196 While the composition of outflow gas was monitored using the gas analyser until no residual N₂
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10 197 was present in the outflow. The sample was then re-saturated with CH₄, and CO₂ subsequently was
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12 198 injected at 5 MPa. The confining pressure was kept constant throughout at 6MPa. The composition
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14 199 of the outflow gas was monitored continuously and the test was continued until CH₄ was mostly
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16 200 displaced with CO₂. Figure 3 presents a schematic diagram of the experimental conditions applied
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18 201 for the N₂- and CO₂-ECBM experiments.

202 **3. Results and discussions**

203 **3.1. Helium flooding experiment**

204 For low permeability coals, the flow behaviour is highly dependent on the effective stress (Huy et
25
26 205 al., 2010). For incompressible fluid such as water, the effective stress is defined as the difference
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28 206 between the confining pressure and linear mean gas pressure across the sample (Harpalani and
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30 207 Chen, 1997):

$$31 \quad \sigma_{eff} = P_c - \frac{P_{up} + P_{down}}{2} \quad (2)$$

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37 208 where, σ_{eff} is the effective stress and P_c is the confining pressure.

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40 209 Since gas is compressible, its bulk density varies greatly which in turn has a significant effect on
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42 210 gas transport within the porous medium. Therefore unlike incompressible fluids, variation of gas
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44 211 pore pressure across sample length is not expected to be linear. In this study, the analytical solution
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46 212 presented by Wu et al. (1998) has been used to estimate the changes in gas pore pressure across the
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48 213 sample at steady-state flow conditions:

$$49 \quad P(x) = -b + \sqrt{b^2 + P_L^2 + 2bP_L + 2q_m \mu(L-x)/k_\infty \beta} \quad (3)$$

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51
52
53 214 where, $P(x)$ is the gas pressure (Pa) at linear distance x (m), b is the Klinkenberg coefficient, P_L is
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55 215 the gas pressure at outlet boundaries of linear flow systems (Pa), q_m is the gas mass injection or

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4 216 pumping flux (kg/s.m^2), L is the length of linear flow systems or thickness of unsaturated zone (m),
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6 217 k_{co} is the absolute permeability (m^2), and β is the compressibility factor; μ viscosity (Pa.s).

7
8 218 The length of the sample was divided into 7 sections of 0.02m long, and for each section the
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10 219 average pore pressure was estimated using Eq. (3). In general, the average pore pressure within the
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12 220 coal sample obtained from Eq. (3) was found to be approximately 26-28% higher than average pore
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14 221 pressure obtained from linear approximation method. The mean gas pore pressure obtained from
15
16 222 Eq. (3) was then used to estimate the effective stress, using Eq. (2).

17
18 223 The variations of permeability of the coal sample to helium with effective stress are presented in
19
20 224 Figure 4a. Based on the results, the permeability of the coal sample ranges between 0.15 and
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22 225 $0.45 \times 10^{-15} \text{m}^2$ over the range of applied pressures and confining stresses applied. Variations in
23
24 226 confining pressure and gas pore pressure showed slightly different effects on permeability
25
26 227 evolution of the coal sample, however the overall trends of permeability behaviour as a result of
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28 228 changes in confining pressure and gas pore pressure were similar, *i.e.* the coal permeability to
29
30 229 helium was reduced with increase in effective stress. These results are consistent with the results of
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32 230 another series of core flooding experiments performed by Hadi Mosleh (2014) on a similar coal
33
34 231 sample (sister sample) obtained from same block of coal (Figure 4b). Coal permeability variations
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36 232 with effective stress can be attributed to the expansion or closure of the internal fractures and
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38 233 microfractures (Vishal et al., 2013). Non-linear evolution of coal permeability to gases with
39
40 234 effective stress has been reported by other researchers (*e.g.* Feng et al., 2016; Mitra et al., 2012).

41 42 43 235 **3.2. CH₄ flooding experiment**

44
45 236 The CH₄ core flooding experiment was performed to evaluate the initial permeability of the coal
46
47 237 sample to CH₄ before introducing CO₂ during the gas storage and recovery experiments and its
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49 238 consequent swelling effect on gas flow properties of coal. The results of the coal permeability to
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51 239 CH₄ versus effective stress are presented in Figure 5. The coal permeability to CH₄ was found to
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53 240 vary between $0.03 \times 10^{-15} \text{m}^2$ and $0.14 \times 10^{-15} \text{m}^2$ under the applied stresses. In general, the
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55 241 permeability of the coal sample to CH₄ was found to be one order of magnitude lower than that to

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4 242 helium which can be mainly related to their differences in molecular size. The effect of gas
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6 243 sorption-induced permeability evolution of coal should also be taken into account when
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8 244 interpreting such results. The range of permeability evolution of coal reported in the literature as
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10 245 the result of CH₄ interaction with coal matrix varies greatly. For instance, Harpalani and Mitra
11
12 246 (2010) have reported a CH₄ permeability reduction of approximately 25% compared to the original
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14 247 value, whereas in a study conducted by Milewska-Duda et al. (2000), the effect of CH₄ on coal
15
16 248 matrix swelling and permeability reduction was found to be negligible, compared to highly reactive
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18 249 gases such as CO₂.

19
20 250 Once the evaluation of the initial properties of the coal sample was completed, the coal sample was
21
22 251 re-saturated with CH₄ at injection pressure of 5MPa and confining pressure of 6MPa.

252 3.3. N₂ - ECBM recovery

253 The results of the gas displacement process during the N₂-ECBM experiment are presented in
254 Figure 6. The results present the variation of the gas composition in the outflow with time. It can be
255 observed that an early breakthrough of the injected N₂ has occurred shortly after the injection
256 process was started. The definition of the breakthrough time of the injected gas varies in the
257 literature. A common definition for the breakthrough in work related to gas storage and recovery
258 processes has been considered here which is described as the time at which 1% of the total gas
259 injected is recovered (van Hemert et al., 2012; Mazumder and Wolf, 2008; Ross, 2007). In this
260 case, the breakthrough time was less than 100s.

261 The breakthrough time reported in the literature might vary greatly ranging from several minutes to
262 several days depending on the coal type, sample size, permeability, gas injection pressure, injection
263 rate and effective stresses, *e.g.* Connell et al. (2011), Shi et al. (2008), Yu et al. (2008). The early
264 breakthrough observed in the N₂-ECBM experiment and relatively fast displacements of CH₄ are
265 primarily related to the displacement of the free gas existing within the coal cleats/microfractures
266 rather than the free gas in the coal matrix. This is related to the experimental conditions in which a
267 relatively high injection pressure has been applied under low effective stress on the sample.

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4 268 The results presented in Figure 6 show that within the first half an hour of the experiment, more
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6 269 than 95% of the production gas consisted of N₂. Rapid changes in N₂ and CH₄ fractions at this stage
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8 270 of the experiment can be attributed to the displacement of the free or weakly adsorbed CH₄
9
10 271 molecules with N₂. Therefore, the dominant gas exchange process at this stage was the differences
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12 272 in the partial pressures of N₂ and CH₄ within the coal cleats and microfractures. As the experiment
13
14 273 continued, the rate of changes in the fraction of CH₄ in the production gas became very slow and
15
16 274 remained steady and continuous. This can be related to the slow diffusion of N₂ and CH₄ in the coal
17
18 275 matrix (Cui et al., 2004), which is the dominant gas exchange process at this stage of the
19
20 276 experiment. As a result, the diffusion of N₂ into the coal matrix gradually reduces the partial
21
22 277 pressure of CH₄ in the coal matrix and eventually leads to CH₄ desorption.

24 278 **3.4. CO₂ - ECBM recovery**

26 279 The experimental results of the gas displacement process during the CO₂-ECBM experiment are
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28 280 presented in Figure 7 which shows the variations of gas composition in the production gas with
29
30 281 time as a result of CH₄ displacement with CO₂. The small spikes on the graph are related to the
31
32 282 minor fluctuations in the injection pressure generated as a result of simultaneous operation of the
33
34 283 gas booster.

36 284 From the results presented, it is apparent that the breakthrough time of CO₂ is two times slower
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38 285 than the N₂-ECBM experiment that can be attributed to a combination of gas diffusion process in
39
40 286 the coal and the effects of coal matrix swelling induced by the CO₂ adsorption. Although, the
41
42 287 volumetric deformation has not been directly measured in the experiments presented here,
43
44 288 reduction in the mass flow rate of outflow gas during the CO₂-ECBM experiment demonstrate the
45
46 289 significance of the effect of coal swelling on the flow process. The mass flow rates recorded at
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48 290 downstream of the sample reduced from 14g/h to 1g/h during the course of CO₂-ECBM experiment
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50 291 (more than 5 hours), whereas for the case of N₂-ECBM experiment, the recorded mass-flow rates
51
52 292 remained relatively steady throughout the experiment, *i.e.* 28-34g/h.

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4 293 With its relatively smaller kinetic diameter, CO₂ molecules can penetrate into the micro-pores of
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6 294 coal which are inaccessible or less accessible to CH₄ and N₂ molecules that have larger kinetic
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8 295 diameters. This can result in one or two orders of magnitude higher diffusivity of CO₂ in the coal
9
10 296 matrix compared with N₂ and CH₄ (Cui et al., 2004). Hence, the higher diffusion of CO₂ than that
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12 297 for CH₄ and N₂ may limit its breakthrough in the production gas through faster diffusion into the
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14 298 coal matrix. Moreover, the effect of the coal swelling induced by CO₂ adsorption can also result in
15
16 299 slower rate of gas flow in the cleat and consequently increases the time of the breakthrough.

17
18 300 The results of the gas storage and recovery experiments show that, the overall rate of CO₂
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20 301 displacement with CH₄ is much slower compared to case for N₂. For the N₂ experiment, more than
21
22 302 95% of CH₄ has been displaced within less than 30 minutes, whereas for the case of CO₂
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24 303 experiment, the fraction of displaced CH₄ has almost reached 90% after 3 hours of continuous CO₂
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26 304 injection. As stated earlier, higher diffusion rate of CO₂ and the effect of sorption-induced swelling
27
28 305 on coal matrix during the CO₂-ECBM process can together govern the slower gas displacement
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30 306 rates observed. Whereas, in the N₂-ECBM process, the slower rate of N₂ diffusion into the coal
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32 307 matrix leads to relatively higher partial pressure of N₂ gas within the coal cleats and therefore faster
33
34 308 gas displacement rate and N₂ breakthrough is observed.

309 **3.5. Gas storage and recovery in coal**

38
39 310 Based on the experimental data of gas flow rates at upstream and downstream obtained from two
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41 311 mass flow meters, and the composition of the outflow gas obtained from gas analyser, the upstream
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43 312 and downstream mass flow rates were estimated and converted to mole per second (mol/s). The
44
45 313 cumulative amounts of gas injected, recovered and stored in the coal sample were then calculated
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47 314 for each experiment. It should be mentioned that the gas storage here implies the total amount of
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49 315 gas adsorbed to the coal matrix as well as the free gas stored in cleats/microfractures and matrix
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51 316 pore volume. Figures 8 and 9 present the cumulative amounts of gas injected, recovered and stored
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53 317 in the coal sample during N₂- and CO₂-ECBM experiments, respectively.

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4 318 The results presented in Figures 8 and 9 show that for the same duration of the experiment and
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6 319 under similar experimental conditions, the total amount of injected N_2 was 11 times higher than
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8 320 that for CO_2 injection. In addition, the results show that 90% of the total injected N_2 was in the
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10 321 production gas, whereas in the case of the CO_2 experiment, only 63% of the total injected CO_2 was
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12 322 in the production gas. Therefore 36% of the injected CO_2 has been retained within the coal sample.

13
14 323 In another study conducted by Hadi Mosleh (2014), the maximum adsorption capacity of the same
15
16 324 coal to CO_2 was estimated 1.21mol/kg. By assuming the total amount of stored CO_2 during CO_2 -
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18 325 ECBM experiment as adsorbed gas, it can be postulated that only 20% of the adsorption capacity of
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20 326 coal sample to CO_2 was utilised. This can be related to several factors:

- 21
22 327 • Effect of gas diffusion rate: the gas adsorption isotherms were measured on powdered coal
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24 328 samples and over 24 to 48 hours, when the equilibrium state was observed (Hadi Mosleh, 2014),
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26 329 whereas the experiments of this study have been conducted on intact 70mm core samples, and
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28 330 over shorter durations (~4hr). Therefore, much longer time was needed for the gas to diffuse
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30 331 into the coal matrix and to achieve equilibrium state.
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32 332 • Effect of coal swelling: coal swells when it comes into contact with CO_2 , this resulted in
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34 333 reduction of coal permeability under confined conditions and therefore a reduction in the
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36 334 accessibility of the coal matrix to more CO_2 gas.
- 37
38 335 • Effect of effective stress on coal permeability: in gas adsorption measurements by Hadi Mosleh
39
40 336 (2014), powdered coal was placed in a high pressure cell without confining pressure applied to
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42 337 coal sample. Whereas in this study, the results of helium and CH_4 flooding experiments have
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44 338 shown that permeability of the coal decreases as effective stress increases. This is related to
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46 339 compression of fractures and microfractures and therefore reduction in accessibility of coal
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48 340 matrix to gas.

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52 341 **3.6. Efficiency of CH_4 recovery**
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4 342 Figure 10 shows the cumulative amounts of CH₄ recovered during the N₂-ECBM and CO₂-ECBM
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6 343 experiments. From the results, it may be suggested that the total amounts of CH₄ recovered in N₂-
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8 344 and CO₂-ECBM experiments are almost equal (0.187mol and 183mol, respectively) and therefore
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10 345 both methods can be equally effective in terms of CH₄ recovery. However the rate of CH₄ recovery,
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12 346 which is an important factor affecting the success of ECBM application, should be taken into
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14 347 account when interpreting such results. The results presented in Figure 10 show that the rate of CH₄
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16 348 recovery for the case of N₂ injection was significantly higher at the early stages of the experiment
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18 349 and reduced considerably for much of the experiment's duration; whereas for the case of CO₂
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20 350 injection, the rate of CH₄ was found to be more or less steady throughout the experiment. Similar
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22 351 observations have been reported by Yu et al. (2008) based on the core flooding experiments
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24 352 conducted on coal samples from Qinshui basin in North China.

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28 354 In addition, the efficiency of CH₄ recovery from coal can be related to other factors including: i)
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30 355 the amount of gas required for the injection, ii) the fraction of injected gas in the production gas
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32 356 which needs to be separated from CH₄, and iii) the amount of gas that can be stored in coal which
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34 357 is particularly important for the case of CO₂ sequestration process. Figures 11 and 12 present the
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36 358 ratio of CH₄ recovery with respect to the amount of gas injected and stored, respectively, during
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38 359 both N₂ and CO₂ experiments.

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41 360 The results of CH₄ recovery versus injected gas (Figure 11) indicate that the CO₂ injection lead to a
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43 361 higher ratio of CH₄ recovery throughout the experiment (up to 10 times higher than that obtained
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45 362 by N₂ injection). This is mainly related to the higher amounts of N₂ injected under similar
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47 363 experimental conditions, *i.e.* gas injection pressure and confining pressure. The amount of the CH₄
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49 364 recovery for both experiments decreased sharply in the first hour of the experiments. The rate of
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51 365 CH₄ recovery, however, remained almost steady for the N₂ experiment after the first hour, whereas
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53 366 for the CO₂ experiment, it decreased gradually over time. This behaviour can be attributed to the
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55 367 effect of coal matrix swelling on gas permeability and flow as described previously.

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4 368 The results of CH₄ recovery versus stored gas (Figure 12) also show that storage of CO₂ lead to
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6 369 higher ratio of CH₄ recovery (on average 2.4 times higher than that obtained by N₂ injection). In
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8 370 other words, for every mole of CO₂ stored in the coal sample 1.2mol of CH₄ was recovered. Higher
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10 371 ratios have also been reported in the literature, *e.g.* a ratio of 2 to 1 (Tsotsis et al., 2004) which can
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12 372 be related to the differences in coal type (different sorption capacities and gas flow and mechanical
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14 373 properties) and the experimental conditions.

15 16 17 374 **4. Conclusions**

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19 375 The results of gas storage and recovery from a series of experiments conducted on the CH₄
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21 376 saturated coal sample were presented on a high rank coal from South Wales coalfield. N₂ and CO₂
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23 377 were injected at the upstream of the sample and composition of outflow gas was monitored. The
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25 378 results of both experiments were assessed and compared in terms of breakthrough time, gas
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27 379 displacement rate, and efficiency of gas storage and recovery.

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30 380 The results showed that the N₂ breakthrough time was almost spontaneous whereas for the case of
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32 381 CO₂, the breakthrough time was delayed by a factor of two. Similarly, the gas displacement rate
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34 382 observed in both experiments varied greatly which was mostly related to differences between
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36 383 diffusivity of N₂ and CO₂ as well as higher affinity of the coal to CO₂. The latter effect also
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38 384 resulted in storage of 36% of injected CO₂ in coal. The results of CH₄ recovery showed that with
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40 385 respect to both injected and stored gas, the ratios of CH₄ recovered during CO₂ experiment were
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42 386 higher than those for N₂ experiment.

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44 387 This study has shown that early N₂ breakthrough and higher rate of N₂ production may lead to
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46 388 additional challenges in order to separate N₂ from CH₄ and thus affects the efficiency of the N₂-
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48 389 ECBM method. For the case of CO₂, the total CH₄ recovery, displacement ratio, breakthrough and
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50 390 CO₂ storage are more favourable. In general, the displacement ratio, CO₂ breakthrough time and
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52 391 CO₂ storage are important parameters affecting the success of carbon sequestration application and

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4 392 the results of this study provide new insights into the efficiency of gas recovery and storage in
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6 393 anthracite coal using carbon dioxide and under the experimental conditions applied.
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10
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23

24 401 **References**

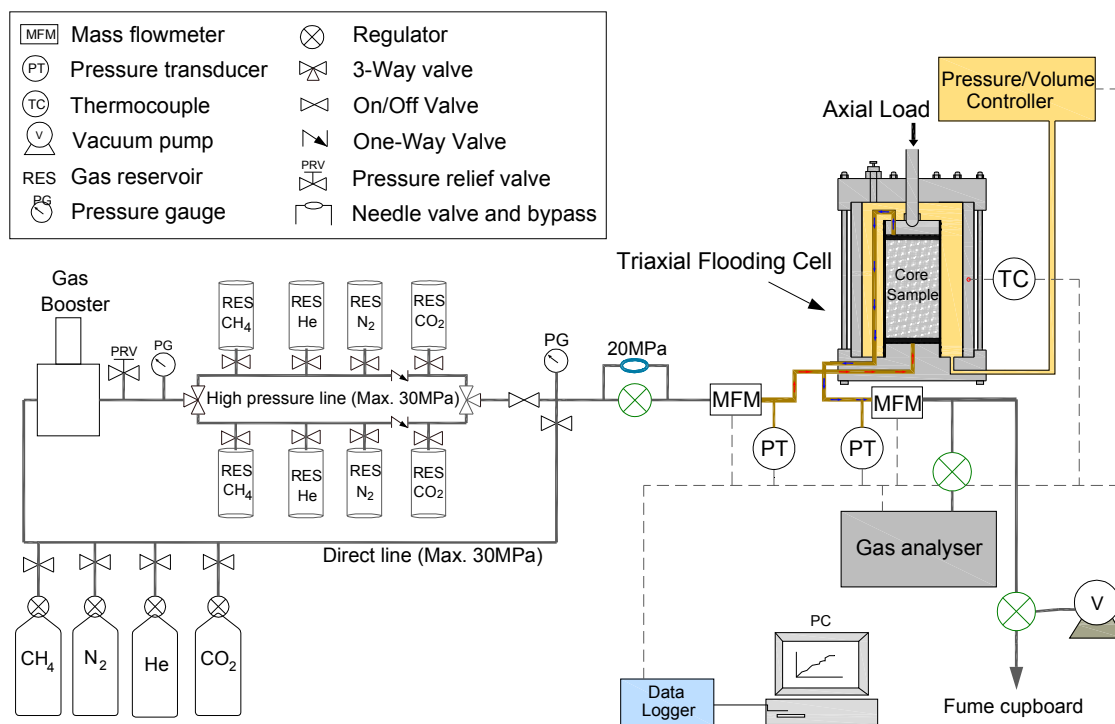
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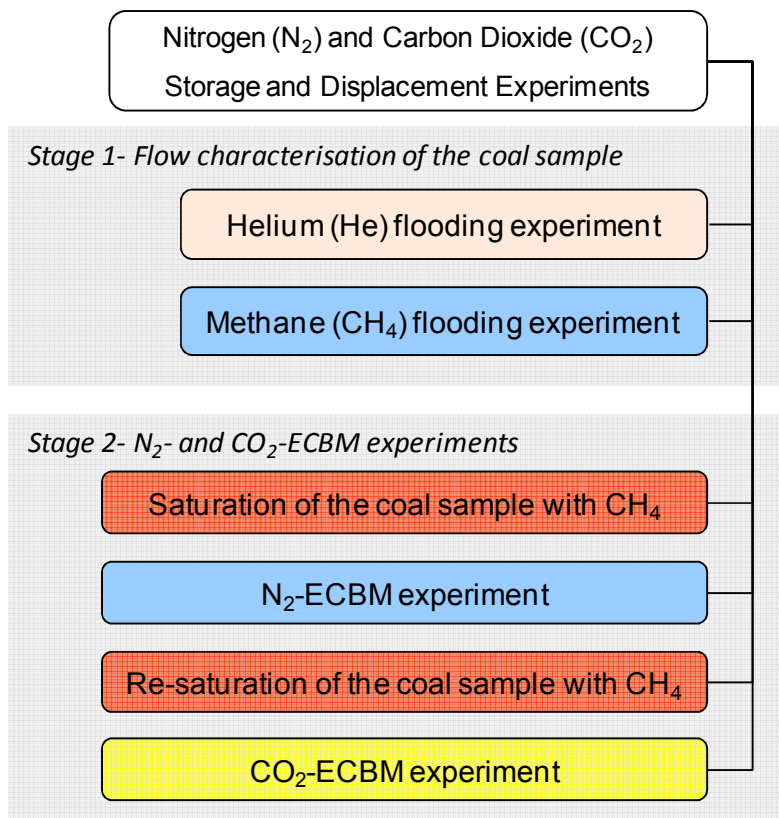
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Table 1. Physical and chemical properties of the coal sample.

Moisture (wt%)	1.2	Carbon (%)	86.4
Sample diameter (<i>mm</i>)	70	Volatile matter (%)	9.7
Sample length (<i>mm</i>)	120	Fixed carbon (%)	84.4
Bulk density (kg/m ³)	1398	Sulphur (%)	0.8
Porosity (-)	0.05	Ash (%)	4.9



27 **Figure 1.** A schematic diagram of the developed laboratory facility (Hadi Mosleh et al., 2017).



30 **Figure 2.** The order of experimental studies carried out.
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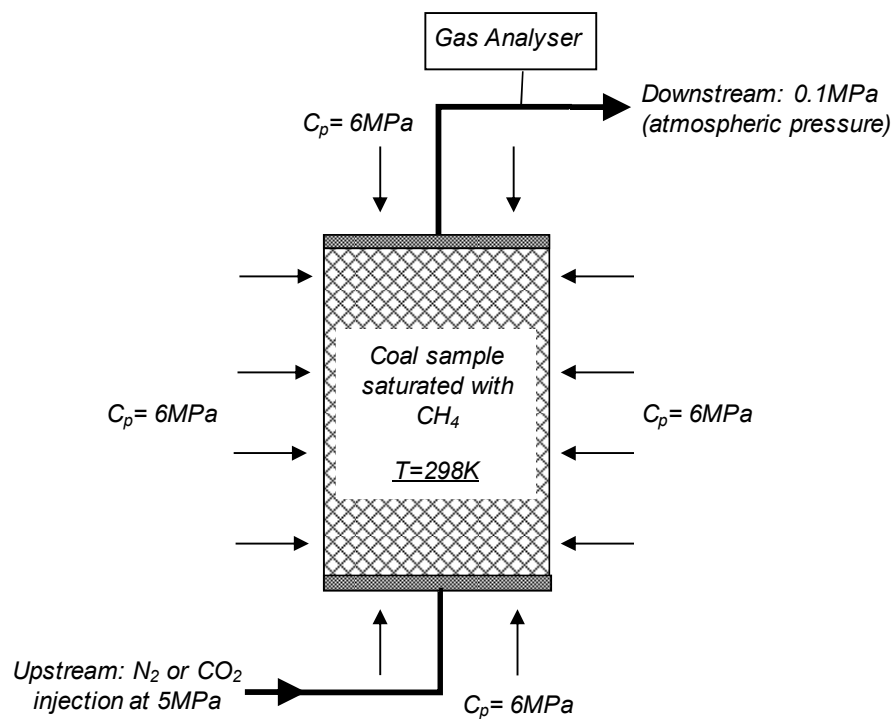


Figure 3. Schematic diagram of the experimental conditions applied for the N₂ and CO₂ ECBM experiments, C_p is the confining pressure.

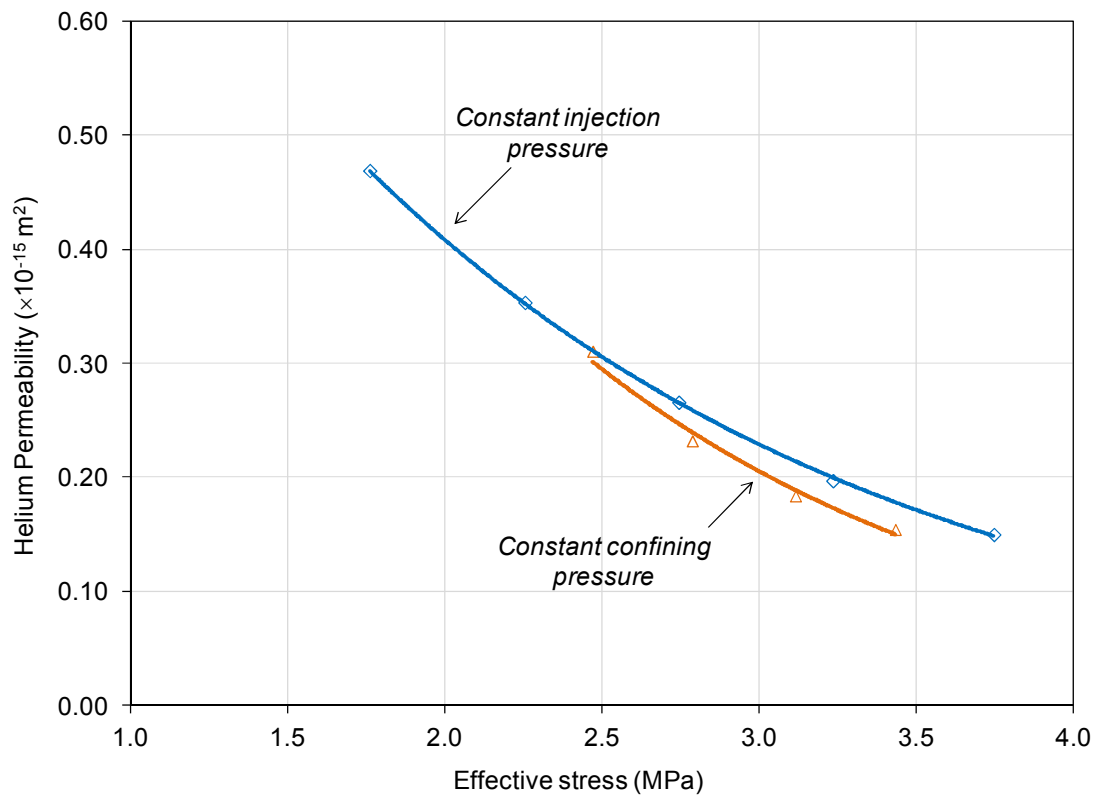


Figure 4a. Variations of the coal permeability to helium with effective stress under constant injection pressure and constant confining pressure.

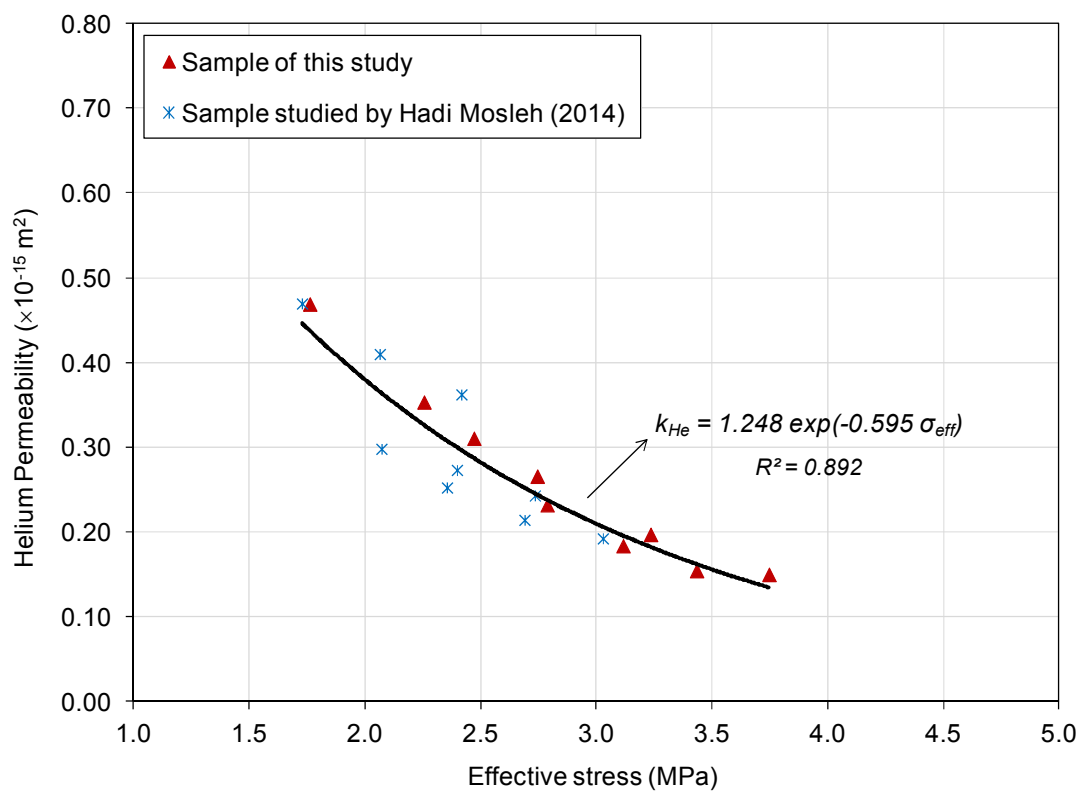
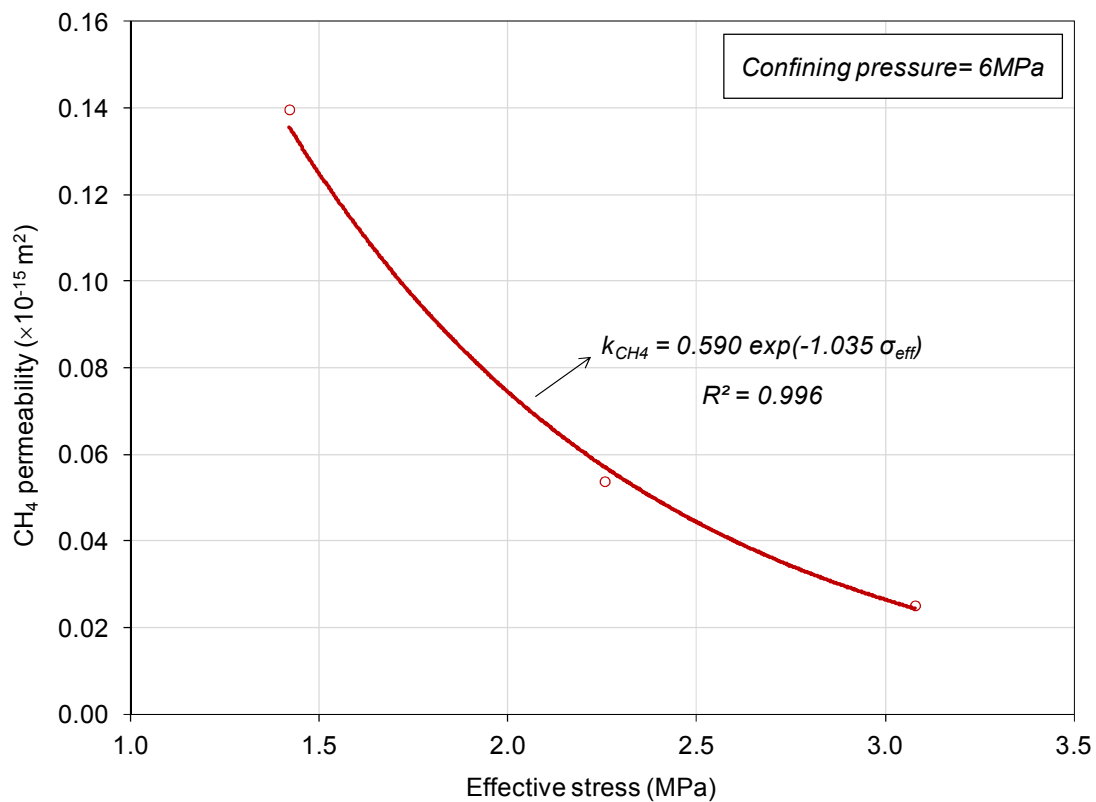


Figure 4b. Variation of coal permeability to helium with effective stress for the sample of this study and a sister sample obtained from same block of coal (Hadi Mosleh, 2014).



31 **Figure 5.** The relationship between permeability of the coal sample to CH₄ and effective stress.

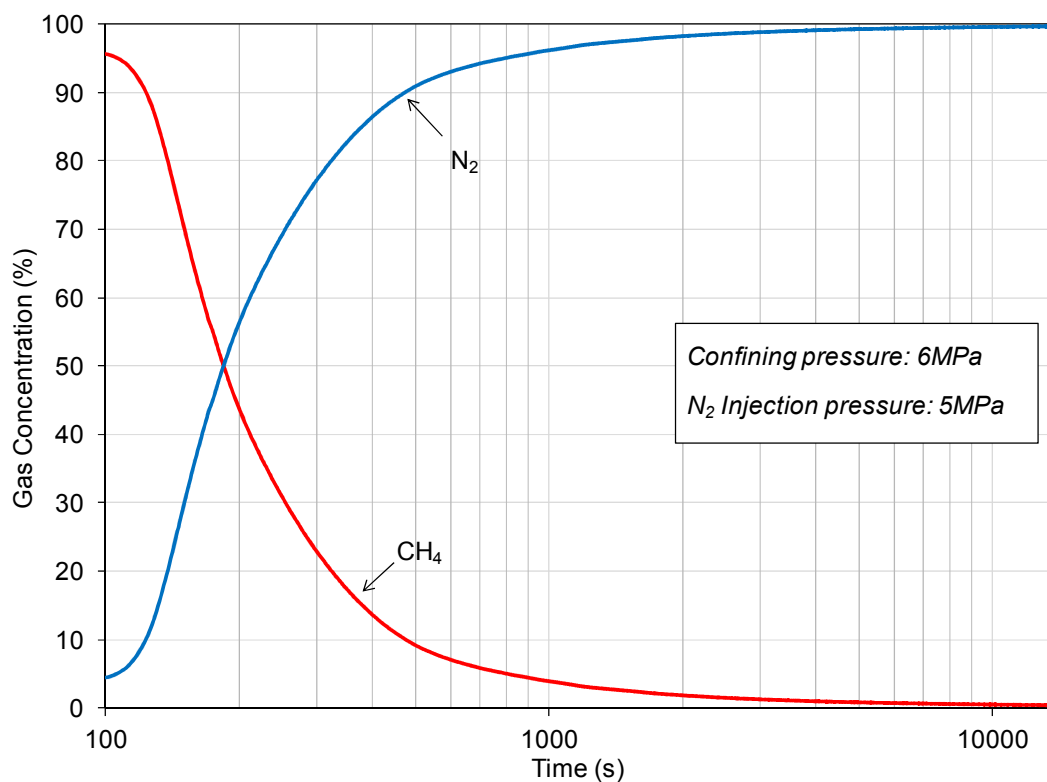


Figure 6. The composition of the production gas with time during the N_2 experiment.

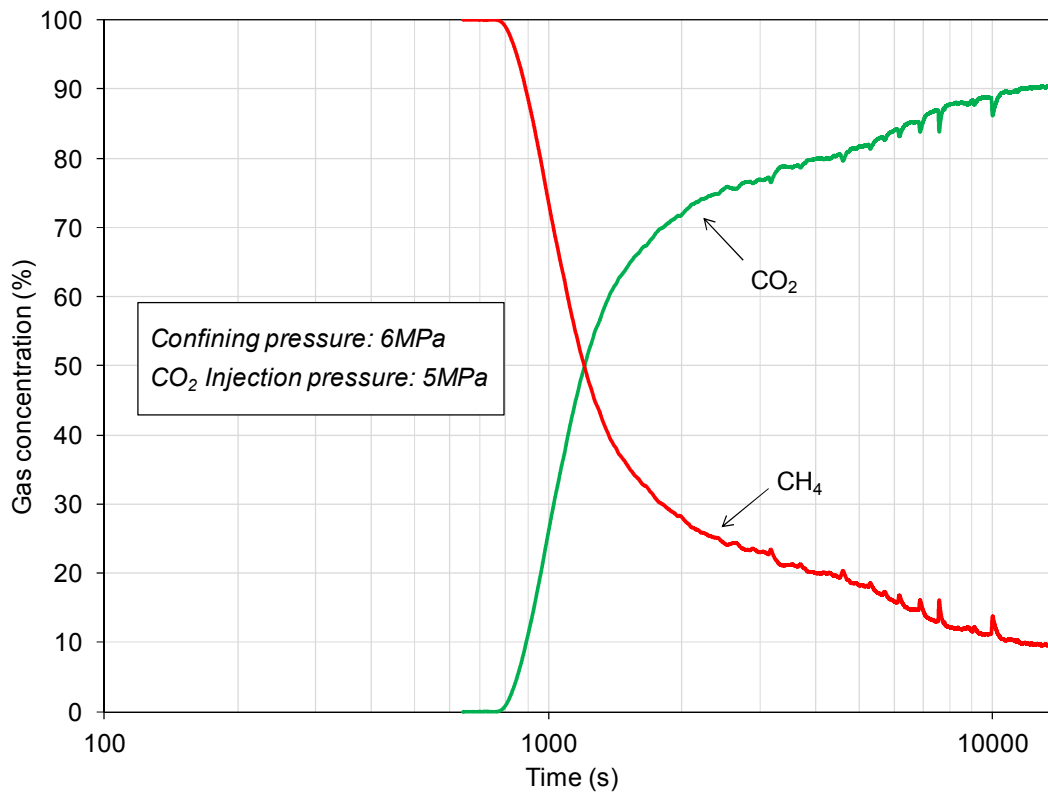


Figure 7. The composition of the production gas with time during the CO₂ experiment.

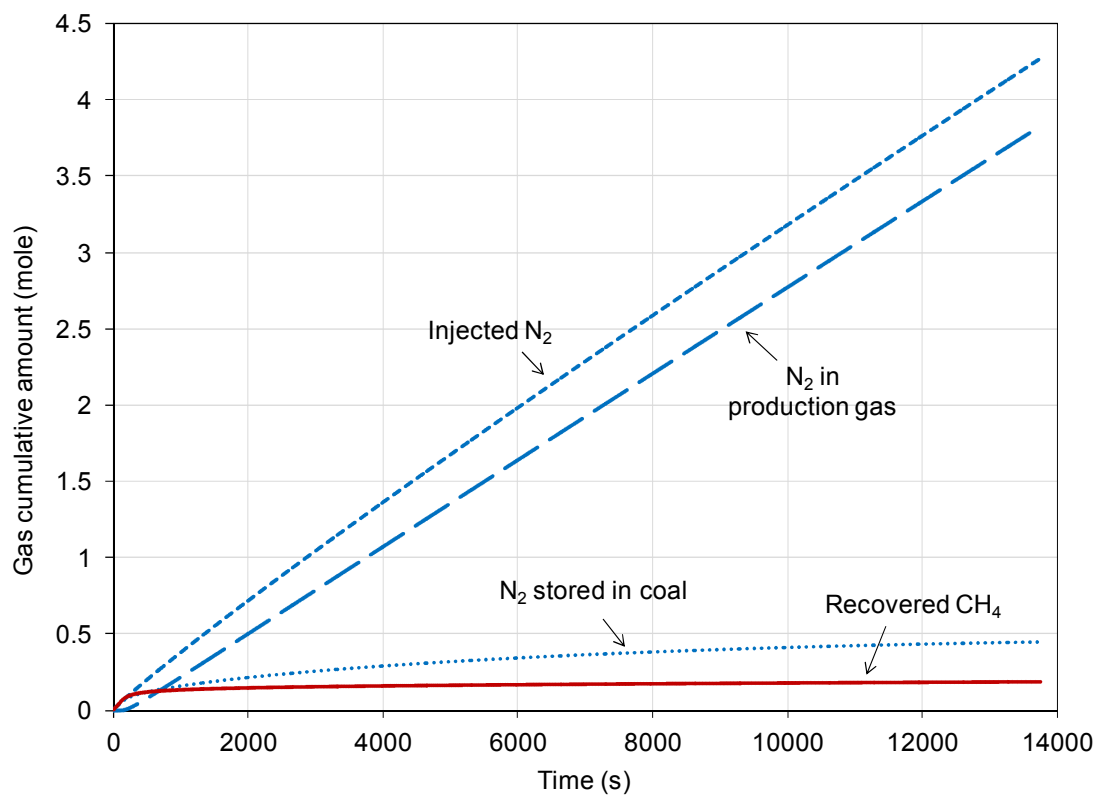


Figure 8. Cumulative amounts of N₂ injected, recovered and stored with time during the N₂-ECBM experiment.

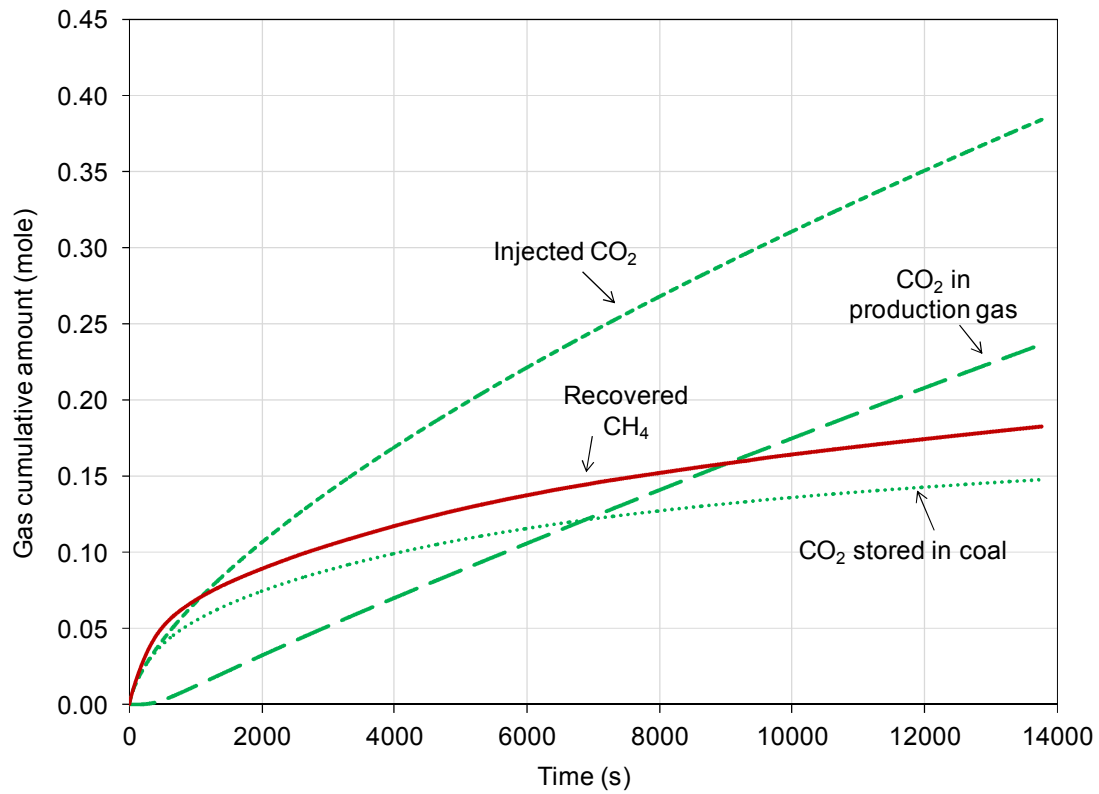


Figure 9. Cumulative amounts of CO₂ injected, recovered and stored with time during the CO₂-ECBM experiments.

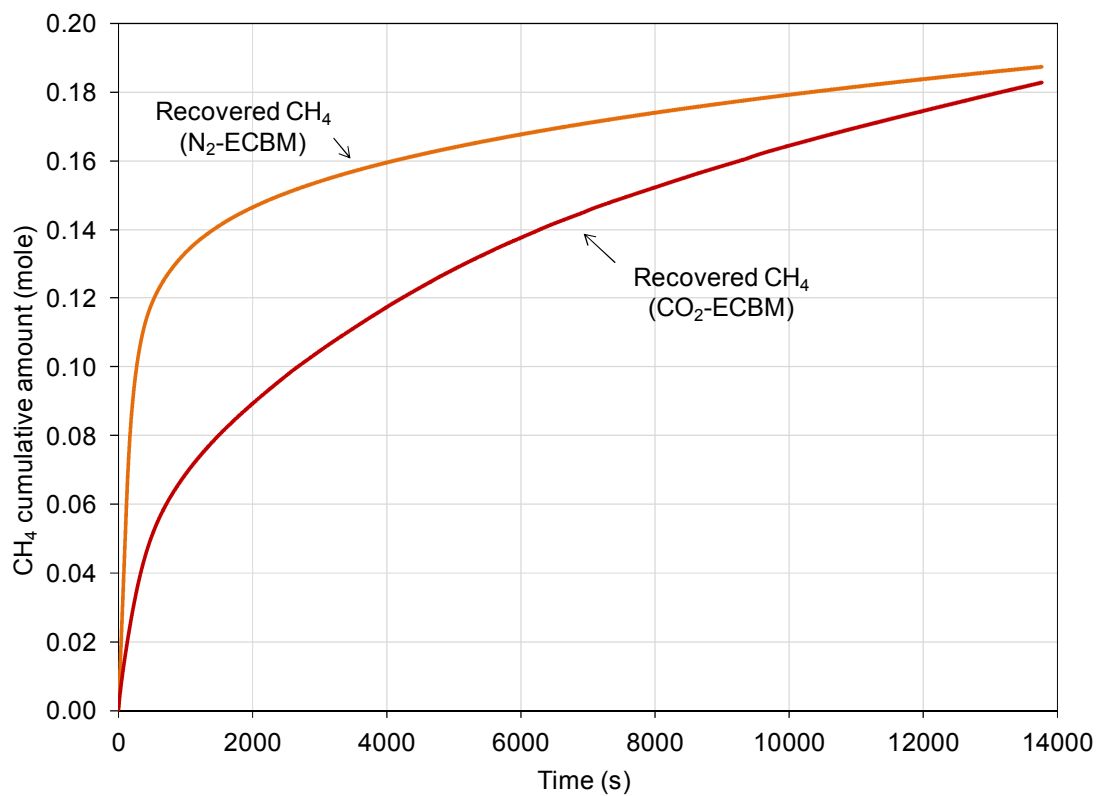


Figure 10. Cumulative amounts of CH₄ recovery during the N₂-ECBM and CO₂-ECBM experiments.

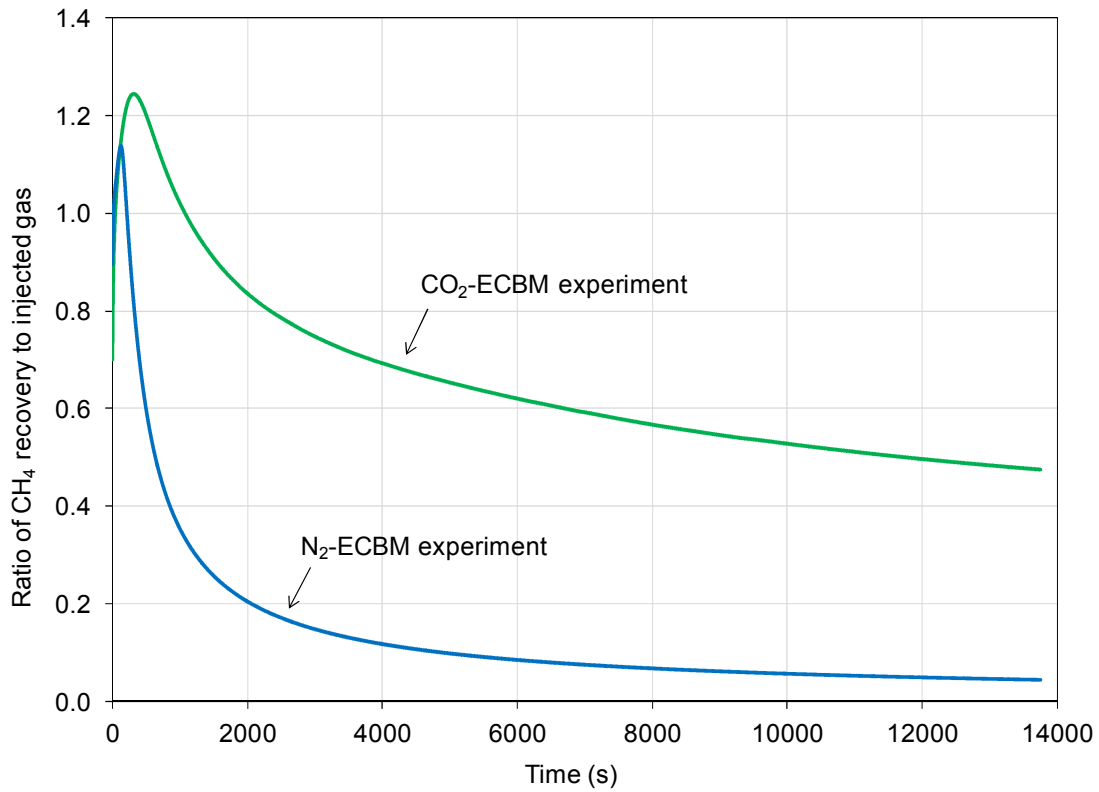


Figure 11. The ratio of CH₄ recovery to injected gas and its variation with time.

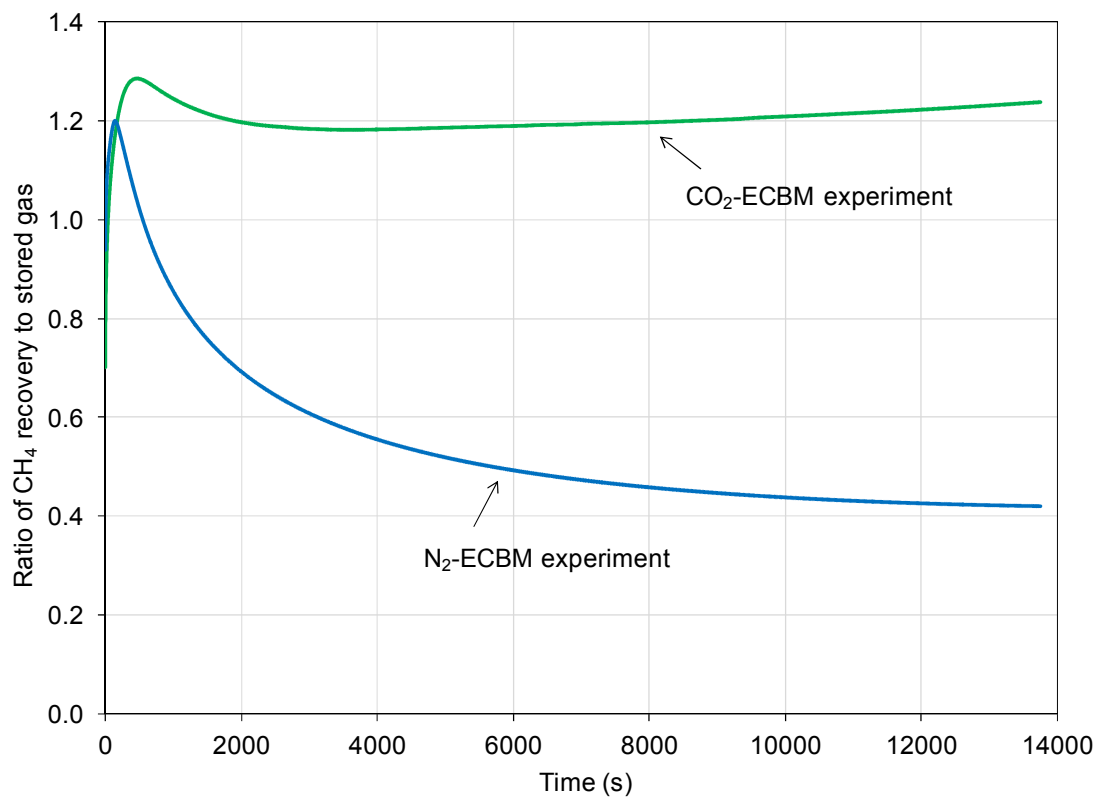


Figure 12. The ratio of CH₄ recovery to stored gas and its variation with time.