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Review of experimental sorption studies of CO_2 and CH_4 in shales

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ABSTRACT

In recent years CO_2 injection in shale has been investigated with aim to enhance shale gas recovery (ESGR) and permanently sequester CO_2. This paper reviews the state of research on CH_4 and CO_2 sorption in shale. We present the interaction of CO_2 and CH_4 with shale rocks and discuss the dependence of gas sorption on shale properties including organic matter content, kerogen type, mineralogy, moisture and temperature as well as shale selectivity for either species. Dynamic CO_2-CH_4 exchange studies are also summarized together with the geochemical and mechanical impact of gas sorption in shales. We note that most experimental work is still performed on crushed samples rather than whole cores. Also, CO_2 is preferentially adsorbed over CH_4 when both species co-exist in shale. Both gases are in supercritical state at typical reservoir conditions. Especially CO_2 adsorption is not well described by standard isotherm models in this state.

1. Introduction

Natural gas production from shales has become exceedingly important in satisfying the ever-growing global energy demands. This unconventional hydrocarbon system is globally abundant, with large technically recoverable resources reported in China (1115 tcf), Argentina (802 tcf), US (665 tcf) and Canada (573 tcf) (EIA, 2013). Commercial exploitation of shale resources has led to a shale energy revolution in the last decade. Successful implementation of large-scale horizontal drilling and hydraulic fracturing techniques (Wang and Krupnick, 2015) made this possible and is attributed to collaborative efforts by the natural gas industry (notably Mitchell Energy) and the U.S. Department of Energy (DOE) from the 1980s.

A typical gas shale system is a blend of organic-rich deposition and complex mineralogy that forms a fine-grained clastic sedimentary rock with a unique geological framework where the shale independently exists as source, trap and reservoir. Common types are black shale (rich in organic matter), carbonaceous shale (rich in organic matter that has been carbonized), siliceous shale (high amount of quartz), iron shale (having some fractions of iron oxides, hydroxides, etc.) and oil shale (containing a certain amount of bitumen/asphalt) (Curtis, 2002; Wang et al., 2012). Shale rocks have grains with sizes often less than 62.5 μm with pore body and throat sizes ranging from micropores (<0.1 μm) to nanopores (nm) (Sondergeld et al., 2010; Chen et al., 2019). The pores in shale are associated with both organic and mineral matter (Tang et al., 2016). Loucks et al. (2012) presented a descriptive classification of shale matrix-related pore types, differentiating between interparticle (located between particles and crystals) and intraparticle (existing within particles) pores affiliated with the mineral matrix and intraparticle organic matter pores. The hydrocarbons are generated in-situ through biogenic and thermogenic processes (Krooss et al., 1995) and are stored in three different states; as free compressed gas in the open pores and microcracks; as adsorbed gas on the nanopore/micropore inner surfaces of shale organic and inorganic components; or as solution gas absorbed within the solid organic matter and connate water (Bustin et al., 2008). Natural gas in shale is predominantly methane (>94%) with minor fractions of ethane, propane and butane plus traces of CO_2 and N_2 (Kalkreuth et al., 2013).

Low intrinsic matrix permeability (e.g. 0.1 μD for Huron shales (Soeder, 1988)) coupled with structural heterogeneity and complex pore networks complicates fluid transport and storage within the formation and poses tremendous challenges to technical evaluation and effective development. Although current technological advancements in horizontal drilling and fluid fracturing have contributed to primary production, only 5–10% of the original gas in place (OGIP) is estimated to be recovered economically (Rassenfoss, 2017) leaving a high potential

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for enhanced recovery methods. The gas stored by sorption in the shale matrix is estimated to account for 20–80% of the total gas fraction (Lane et al., 1989; Bruner and Smosna, 2011; Edwards et al., 2015). Desorption is triggered by pressure reduction and/or presence of a favourably adsorbing gas.

Experimental results have shown that shales have greater adsorption affinity for CO_2 than CH_4 (Weniger et al., 2010; Heller and Zoback, 2014). CO_2 is also favourably adsorbed over CH_4 when both gas species co-exist within the shale (Pino et al., 2014; Cancino et al., 2017; Ma et al., 2018). A huge potential for enhanced shale gas recovery (ESGR) is therefore feasible through injection of CO_2 (Blok et al., 1997; Oldenburg et al., 2001) which can stimulate the desorption of pre-adsorbed methane through an in-situ molecular swapping mechanism at the sorption sites, releasing the otherwise trapped methane into the porous system to increase the rate and volume of CH_4 recovered (Regan, 2007). This technique is referred to as CO_2 enhanced shale gas recovery, CO_2-ESGR and is considered a viable means for simultaneous CO_2 storage in the shale formations with recent reviews provided by Liu et al. (2019) and Rani et al. (2019). This concept of CO_2 utilization in shales is illustrated in Fig. 1. Godec et al. (2013) demonstrated through simulation that at optimal operational conditions, 7% incremental CH_4 production could be obtained through CO_2 injection in the Marcellus Shale in Eastern United States. They estimated 12 trillion cubic meters of methane to be technically recoverable with an associated storage of 55 billion tonnes of CO_2. Khosrokhavar (2015) demonstrated that for an approximate storage of 12 kg of CO_2 in a characteristic gas shale system, 1 kg of CH_4 can be produced and yield 55 MJ energy while spending 12 MJ energy for compression. They noted that the energy gain was still substantial when accounting for CO_2 capture and storage (CCS) as quantified by IIijima et al. (2011). Logistically, in most cases, a surface gas pipeline distribution network could easily be modified to transport CO_2 to the wellhead whereas the cost of CO_2 injection into the subsurface formation is drastically minimized by repurposing the available well infrastructure to accommodate CO_2 injection (Tao et al., 2014).

2. Objectives and scope

The mechanisms in the CO_2-ESGR system are complex, many and coupled. Key parameters include storage capacity and form of CH_4 and CO_2, CO_2-CH_4 competitive sorption, isotherms and diffusion; chemical and geomechanical impact of gas sorption and desorption (shrinkage and swelling); CO_2 injectivity and trapping integrity. Many of these parameters are interrelated, further coupled to the intricate petrographic nature of shales, inherent structural heterogeneities and variation of pressure and temperature. To limit our scope, our objectives are:

- Evaluate the state of experimental findings regarding gas sorption in shales
- Determine gaps in experimental research that should be addressed

Detailed theories of adsorption phenomena, experimental tools and associated uncertainties are not specifically addressed. For such aspects we refer to Polanyi (1932); Steele (1974); Sing et al. (1985); Sircar (1985); Malbrunot et al. (1997); Neimark and Ravikovitch (1997); Cavenati et al. (2004); Ross and Bustin (2007b); Busch and Gensterblum (2011); Rudzinski and Everett (2012).

The paper is organized as follows:

- Mechanisms for gas sorption on shale and relevant isotherm models (3.1), definition of useful thermodynamical parameters (3.2) and adsorption behavior of individual gas species (3.3).
- Dependence of CO_2 and CH_4 sorption capacity on shale physico-chemical parameters such as organic matter (4.1), thermal maturity (4.2), kerogen type (4.3), inorganic content (4.4), moisture content (4.5) and temperature (4.6).
- CO_2 versus CH_4 comparative adsorption capacity on shale (5.0).
- Recent advances in experimental work related to dynamic CO_2-CH_4 exchange and transport in gas shales (5.1).
- Experimental work on geomechanical (5.2) and geochemical (5.3) impact of gas adsorption-desorption on shale.
- Brief discussion of presented findings
- Conclusions and recommendations

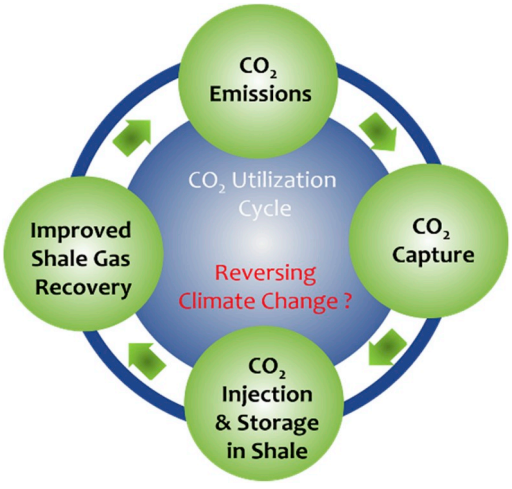

Fig. 1. Concept of CO_2 capture and utilization for enhanced shale gas recovery and carbon sequestration.

3. Gas sorption on shale

Gas sorption in shales is a comprehensive term for surface accumulation onto organic and mineral surfaces (adsorption), absorption (soaking or imbibition) into organic molecular (kerogen) openings and capillary condensation within the pores. Gas adsorption on shale matrix surfaces is governed by physisorption (Brunauer et al., 1940). This is a result of weak van der Waals and electrostatic interaction forces between the gas molecules (adsorbates) and the shale surface (the adsorbent). This is enhanced by the abundant nano-microscale pores (Nelson, 2009) that provide a large internal surface area and restrictions that force the fluid-solid phases closely enough for weak dipole-dipole interaction to occur and bind the gas species to the shale surfaces. Physisorption is deemed reversible, due to the absence of adsorbate-adsorbent covalent bonds.

Sorption of CO_2 or CH_4 onto shale matrix is frequently examined in the laboratory by construction of sorption isotherms, which involves measuring the uptake or release of either gas species on a shale sample at controlled temperature and pressure conditions. The measured sorption is a combination of adsorption, absorption or capillary condensation which individually are difficult to distinguish. Although these mechanisms are characteristically different, the net result is a storage of gas molecules in a denser phase relative to the bulk (free gas) phase in the open pores (Ross and Bustin, 2009). The experimental procedures to measure sorption vary but can be categorized into mass-based or volumetric-based. In the mass-based method the change in sample mass associated with adsorption at each fixed pressure and temperature condition is measured with a microbalance of high accuracy. The volumetric technique is based on Boyle's law, where the adsorption isotherms are constructed by computing the amount of adsorbed gas using the real gas equation, which accounts for the gas compressibility factor at each equilibrium pressure (Heller and Zoback, 2014). The former approach is limited to the use of very small sample sizes whereas the latter can satisfactorily accommodate different sample sizes.

The reviewed literature depicts tremendous challenge with performing experimental flow-through tests due to the characteristically

ultra-low permeability of shale rocks. Hence most experimental evaluations of gas sorption have been conducted with crushed samples as opposed to whole cores. Likely sources of experimental errors and uncertainties in these tests are discussed by Fraissard and Conner (1997); Busch and Gensterblum (2011). In general, high-pressure isotherm experiments determine sorption capacity, whereas structural properties (e.g. specific surface area, pore size distribution, nano-, micro- or mesopore volumes) are evaluated via low-pressure (<1 MPa) sorption tests.

3.1. Gas sorption isotherm models

The quantity obtained in laboratory measurements is excess sorption (also called Gibbs sorption) (Burwell, 1977). It is the amount sorbed in excess of the molecular gas volume that would be present in the sample if the sorbed-phase volume were filled with bulk gas (Heller and Zoback, 2014). The total or absolute amount sorbed is computed by mathematical modelling, before fitting the data to one of many available mathematical isotherm models (e.g. Henry, Langmuir, BET, DR, Pore-filling). It is suspected that adsorption occurs as a monolayer at low pressures and as multilayers at higher pressures. The Langmuir model, which assumes monolayer adsorption, is widely reported as the most suitable fit for gas adsorption on shales (Lu et al., 1995; Nuttal et al., 2005; Chalmers and Bustin, 2008; Ji et al., 2012; Yuan et al., 2014; Hong et al., 2016).

This isotherm is reasonably simple and can be fit to data with a two-parameter equation (Langmuir, 1916, 1918) given as:

$$V_p = \frac{V_L P}{P_L + P} \tag{1}$$

where V_p is the adsorbed volume at pressure P, V_L is the Langmuir volume (total adsorption volume at infinite pressure), and P_L is the Langmuir pressure (the pressure at which half the Langmuir volume is adsorbed). Some authors (e.g. Duan et al., 2016) have also found the BET model (which accounts for multilayer adsorption) as a satisfactory choice. Indeed, the acceptance of a single model for universal description of sorption in shales is still contended amongst researchers. A review by Tang et al. (2017) presents some widely used adsorption models with comparisons and distinctive applications. Besides revealing the adsorptive potential for a material, the magnitude and shape of the sorption isotherm suggests the relation between pore accessibility and pressure, information regarding adsorption/desorption, sorption capacity, rates, pore structure, as well as surface properties of the shale matrix. This is primarily because the physical sorption process is inextricably linked to the effects that the confined pore space exerts on the state and thermodynamic stability of the gas species held onto the nano-pores (Thommes, 2010).

3.2. Adsorption thermodynamics

Sorption isotherms are frequently employed as basis for applying thermodynamical principles to interpretation of adsorption phenomena. This often implies the computation of parameters such as adsorption energy, binding energy, activation energy or heat of adsorption. The latter has especially been applied in the evaluation of CH_4 and CO_2 adsorption on shales (Chikatamarla and Crosdale, 2001; Rexer et al., 2014; Xiong et al., 2017; Chen et al., 2019). The isosteric heat of adsorption indicates the strength of interaction between the adsorbent and adsorbate (in this case the shale surfaces and the gas species; greater values indicative of stronger adsorbate-adsorbent bonding). By classical definition, it reflects the energy evolved when one molecule of adsorbate is added to an adsorption system. It depends on the gas type, surface chemistry and pore structure. It is a strong function of adsorbate density and surface coverage. The heat of adsorption for CO_2 is reportedly greater than for CH_4 in gas shales; indicative of greater affinity of shale for CO_2 over methane (Luo et al., 2015; Duan et al., 2016). In adsorption, activation energy is the minimum energy needed (to overcome the adsorbate-adsorbent repulsion) for the gas molecules to react/interact with adsorption sites in the shale rock formation. Also, when adsorbate (gas) molecules interact with surfaces of an adsorbent (i.e. shale, in this case), the adsorption energy (E_{ads}) is defined as:

$$E_{ads} = E_{sys} - \left(E_{mol} + E_{surf}\right) \tag{2}$$

where E_{sys}, E_{mol} and E_{surf} represents the energy of the total adsorbate-adsorbent system, the gas phase molecules and the shale surface respectively. E_{ads} also equals sum of the binding energy (E_b, characterizing the interaction between a single isolated gas molecule with the shale surface) and adsorbate stabilization energy ($E_{inter\text{-}ad}$) which accounts for intermolecular interactions between the gas molecules (Bocquet et al., 2005)

$$E_{ads} = E_b + E_{inter-ad} \tag{3}$$

CO_2, CH_4 adsorption is an exothermic process, making E_{ads} a negative variable. On the other hand, a negative (or positive) binding energy implies that the adsorption is favorable (or unfavorable) (Scaranto et al., 2011). The nature of these parameters, interrelationship and theoretical variance has been discussed by Saha and Chowdhury (2011) and Inglezakis and Zorpas (2012).

3.3. Single component sorption of CO_2 or CH_4 at reservoir conditions

The majority of shale formations have temperatures ranging from 96 to 122 °C, with pore pressures in the range of 15–25 MPa (Lu et al., 2016). The subsurface sorption phenomenon will most likely proceed as a supercritical adsorption-desorption process (Menon, 1968) since both CH_4 and CO_2 will typically exist in the supercritical state (CH_4: $T_{cr} = -82$ °C and $P_{cr} = 4.64$ MPa; CO_2: $T_{cr} = 31$ °C and $P_{cr} = 7.38$ MPa). A peculiar feature in adsorption isotherms of supercritical fluids is the possible occurrence of a peak in adsorption with pressure (Aranovich and Donohue, 1995, 1996). Its occurrence will depend on the gas type, the proximity of pressure and temperature conditions to the supercritical ('sc') state of the gas, the void volume determination technique, and the sample properties (e.g, pore size distribution) (Murata et al., 2001; Gumma and Talu, 2003; Herrera et al., 2011; Gasparik et al., 2012). Laboratory experiments thus should be performed at relevant subsurface pressure and temperature conditions, but often the experimental literature is restricted to lower pressures due to available equipment and experimental constraints.

In that context, CH_4-CO_2-shale adsorption processes are conveniently divided into three stages owing to the pressure range and adsorption rate: low pressure (<3 MPa; below supercritical conditions), intermediate pressure (3–10 MPa; transition into supercritical conditions) and high-pressure (>10 MPa; supercritical state) adsorption stages that vary depending on the gas species and sample properties. The low-pressure stage is characterized by sorption on the sites with highest adsorption energy (i.e. the smallest pores) first, and progression towards larger pores (as pressure increases) which causes gradual reduction in the isosteric heat of adsorption (Stoeckli, 1990). This is indicative of physisorption by pore-filling as originally suggested by Dubinin (1975) for gas sorption in microporous materials. Further increase in pressure will eventually cause only small changes in the adsorption content. The isosteric heat of adsorption reduces with pressure until equilibrium is established, and no more gas can adsorb.

In the reviewed literature, CH_4 excess adsorption on gas shales is reported to increase monotonously with pressure (in both gaseous and supercritical states) and gradually reach a constant value at high pressures (Bi et al., 2016; Wang et al., 2016; Li et al., 2017). Gas-phase CO_2 adsorption also increases monotonously with pressure to the supercritical transition point, however adsorption of CO_2 in supercritical state causes the adsorption profile to reach a maximum, after which further increase in pressure will cause CO_2 to desorb monotonically. Typical

sorption behavior for both CH_4 and CO_2 is depicted in Fig. 2 for sorption experiments on crushed Devonian shale samples at a fixed temperature of 45 °C and pressures ranging up to 25 MPa. The characteristic difference in the adsorption of either gas is clearly revealed, with maxima observed only for CO_2. The same trend in experimental profiles of CO_2-CH_4 sorption is reported by Strubinger et al. (1991); Sudibandriyo et al. (2003); Busch et al. (2008); Weniger et al. (2010); Schaef et al. (2013); Gasparik et al. (2014); Schaef et al. (2014); Lu et al. (2016); Merey and Sinayuc (2016) on either gas shale samples of original composition or pure inorganic minerals.

In shales, the gradual increase in CO_2 adsorption near supercritical conditions has been attributed to the sharp change (i.e. increase) in fluid density when gaseous CO_2 is converted to supercritical fluid. This favors overall CO_2-shale interaction by increased (binding) energy and more molecular layers are attached onto the surfaces. For CO_2, Schaef et al. (2013) observed that with continued adsorption, the cross-over point (Fig. 2b) is reached because the stabilization energy ($E_{inter\text{-}ad}$) of the supercritical CO_2 molecules increases as the pressurized system brings the gas molecules closely together. Meanwhile, the adsorbate-adsorbent adsorption energy (E_{ads}) decreases (becomes less negative). This could drive the adsorbent-adsorbent binding energy (E_b) to negative ranges (see equation (3)) and thereafter desorption dominates as the principal mechanism and a decline is observed in the isotherm curve. Recently, Jia et al. (2018) reported a similar trend of CO_2 adsorption behavior, where a crossover region was observed before and after the critical pressure point, through sorption measurements from low-to high-pressure conditions (temperature was kept constant at 30 °C) in a shale core from the Green River Formation in Colorado. The discontinuity of CO_2 adsorption at pressures above CO_2-P_{cr} may have crucial implications on CO_2-ESGR and CO_2 storage. It must be noted that the occurrence of an adsorption peak has also been reported in some cases for CH_4, although mostly for dried overmatured gas shales (Moffat and Weale, 1955; Gasparik et al., 2012; Merkel et al., 2015; Zhou et al., 2018) and pure carbon adsorbents (Xiong et al., 2017). Most single- and multi-component adsorption isotherms are monotonous; showing no distinct peaks even at relatively high pressures (e.g. the Langmuir type). Capturing physical behavior at reservoir conditions may require more general isotherm approaches, especially when significant peaks and declines are demonstrated in lab measurements.

4. Dependence of gas sorption on shale properties

Most sorption studies are available on gas shale samples of original composition or pure individual shale components. The literature indicates that shale adsorption capacity correlates directly to factors that can generate more micropores, but inversely to factors that reduce or plug micropores. This is because small pores generate larger surface area and stronger adsorbate-adsorbent interaction energy which results in greater adsorption. Sorption experiments on samples from across the world (see Fig. 3) have been reviewed in this section to gain insight into the relationship between sorption, rock compositional and geological features to outline the major factors that controls gas sorption capacity of shales.

4.1. Influence of organic matter (richness) on gas sorption

The shale organic matter (OM), also known as kerogen, is associated with the in-situ generation of hydrocarbons. The organic richness is frequently expressed by the Total Organic Carbon (TOC). It is primarily responsible for the microporous nature of shale and is the main contributor to the surface area and total pore volume (Cao et al., 2015; Zhou et al., 2018). The TOC wt% of the shale varies substantially among shale reservoirs and within a formation itself. Table 1 shows the TOC content reported for some shale gas plays. Although these values may not exactly be large, the microporosity associated with the organic fraction is the principal control on CH_4 and CO_2 sorption; there the trapping forces are enhanced due to coalescing of molecules and overlap of interaction energies between the sorbed gas molecules (Thommes, 2010). In stark contrast, immature gas shales with appreciable matrix bituminite can store gas by dissolution and may demonstrate large sorbed gas capacities that are unrelated to micropore volume (Ross and Bustin, 2009). Bituminite, originally described by Teichmüller (1971), could be considered as a semi-solid portion of degrading organic matter that lacks definite shape or form (Kus et al., 2017). It is often present in immature source rocks and may have a dominantly fluidal or granular internal structure within which gases could be stored by dissolution.

The reviewed literature confirms that CH_4 and CO_2 sorption capacities on shale is strongly correlated with TOC. A strong positive linearity is observed for CH_4 and CO_2 sorption datasets (Ross and Bustin, 2007a, 2008; 2009; Zhang et al., 2012; Wang et al., 2013; Heller and Zoback, 2014; Hong et al., 2016; Cancino et al., 2017; Zhou et al., 2018) sourced from experimental measurements on a wide range of shale samples (Fig. 4). The regression factors for both CH_4 and CO_2 are relatively high under both dry and moist conditions and demonstrate the shale TOC to have primary control on adsorption of either gas species. It is interesting to note that the regression constants for both species is higher for moisture-equilibrated samples relative to dry samples. This implies a much stronger correlation of gas adsorption to TOC in the presence of water and could infer that water adsorbs primarily to water-wet inorganic (i.e. clay) mineral phases within the shale formation.

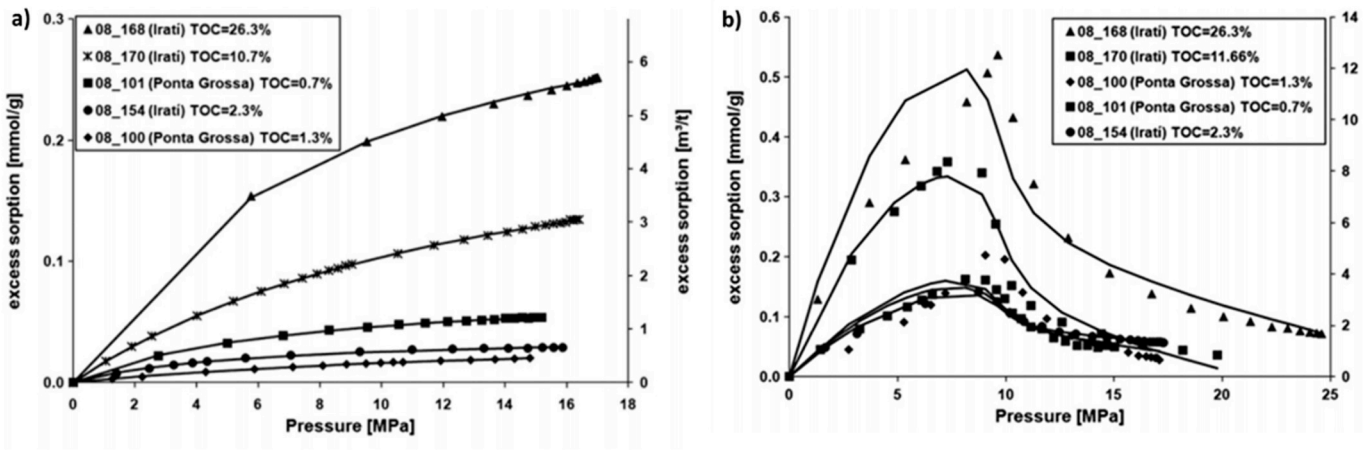

Fig. 2. Comparison of adsorption isotherm (excess sorption vs pressure) for CH_4 (a) and CO_2 (b) on gas shale samples of the Paraná Basin in Brazil (Weniger et al., 2010). Experiment was conducted on crushed dry samples at a fixed temperature of 45 °C.

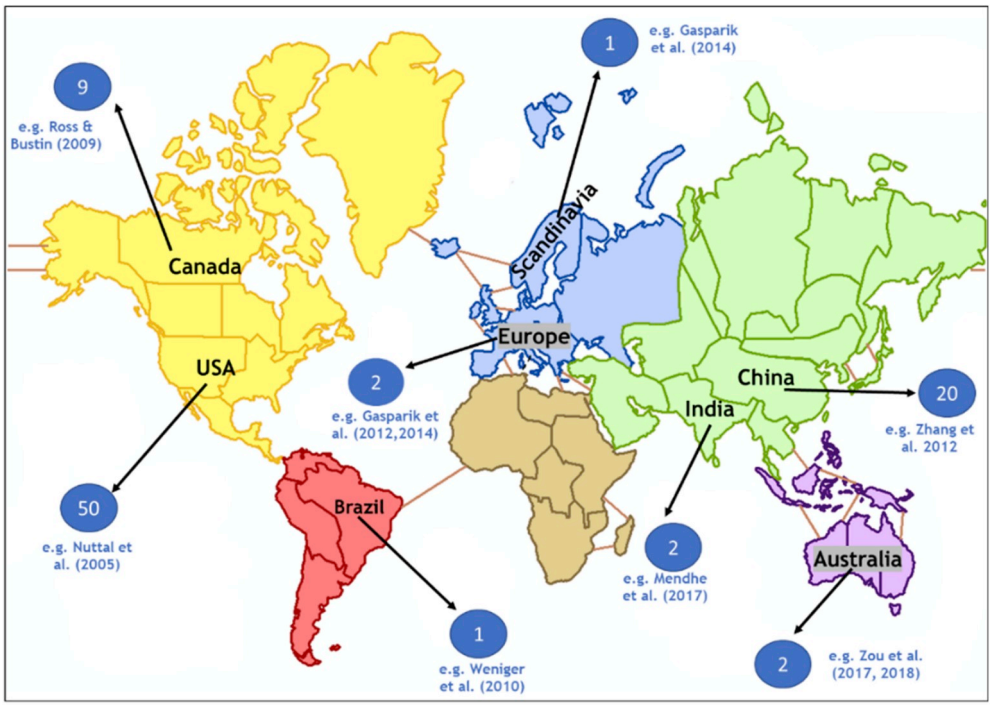

Fig. 3. Worldwide illustration of shale formations actively investigated by researchers. The numbers are purely based on the literature reviewed in this study with focus particularly on CH_4 and CO_2, sorption tests and auxiliary evaluations relevant to CO_2-ESGR.

Table 1
Typical TOC of some shale plays and formations (fm.) adapted from Chalmers and Bustin (2007); Ross and Bustin (2007a, 2008); Ambrose et al. (2010); Zhang et al. (2012); Wang et al. (2013).

Region	Shale/Play	TOC (wt %)
North – American Shale systems, U.S	Barnett	2.5–7.9
	Marcellus	1–10
	Haynesville	0–8
	Horn River	3
	Woodford	5
Northeastern British Columbia region, Canada	Lower Jurassic fm.	0.8–11.8
	Lower cretaceous fm.	0.53–17
	Poker Chip fm.	0.8–2.2
Western Canada Basin	Besa River fm.	0.9–5.7
	Horn River fm.	2.5–3.5
	Muskwa fm.	0.4–3.6
	Fort Simpson fm.	<1
	Mattson	<1.2
Sichuan Basin, China	Qiong-zhu-si fm.	0.5–4
	Long-ma-xi fm.	0.5–2.3
	Da-long and Long-tan fm.	1.0–10

It is noted that extrapolating the regression lines to TOC concentrations of zero reveals the influence of other non-organic adsorption sites, hence significant deviations from this trend could be observed for individual samples depending on the compositional makeup. High-pressure gas sorption isotherms reported by Tan et al. (2014) showed sorption capacities of samples with similar clay content, thermal maturity and moisture content to exhibit even stronger positive linear correlations with TOC. The dependence of gas adsorption on TOC content has been reported by many other researchers (Manger et al., 1991; Schettler and Parmely, 1991; Lancaster and Hill, 1993; Lu et al., 1995; Zuber et al., 2002; Chalmers & Bustin, 2007, 2008; Ross and Bustin, 2007a; Ruppel and Loucks, 2008; Beaton et al., 2010; Strapoc et al., 2010; Weniger et al., 2010; Chareonsuppanimit et al., 2012; Wei et al., 2012; Gasparik et al., 2014; Rexer et al., 2014; Bi et al., 2016; Wang et al., 2016; Yang et al., 2016; Chang et al., 2017; Mendhe et al., 2017; Xia et al., 2017; Sharma and Galvis-Portilla, 2018). There are however existing studies that have reported little to no correlation between TOC and adsorption capacity (Gasparik et al., 2012; Zou et al., 2017). This trend is particularly notable in shales with low organic matter content and high clay content.

4.2. Influence of thermal maturity

Thermal maturity describes the heat-driven diagenetic changes of organic matter in sedimentary source rocks to generate hydrocarbons. Vitrinite reflectance, V_r, is widely used as indication of thermal maturity in shale analysis. It is measured by optical microscopy and reported by % R_o (where high %R_o indicates high maturity), the percentage of incident light reflected from the surface of vitrinite particles in the shale rock. In shales, thermal maturity of organic matter can generate additional micropores (Bae and Bhatia, 2006; Jarvie et al., 2007; Chalmers and Bustin, 2008; Loucks et al., 2009; Ambrose et al., 2010; Sondergeld et al., 2010; Curtis et al., 2011; Bernard et al., 2012; Ma et al., 2015; Wu et al., 2017; Delle Piane et al., 2018; Zheng et al., 2018). This is due to the structural transformation of organic matter during maturation that generates smaller (nano-micro scale) pores as kerogen is thermally converted. The generation of more micropores with organic matter maturity increases the adsorption capacity.

It was previously suggested (Ramos, 2004) that the strong correlation between sorption and TOC masks the relationship between adsorption capacity and thermal maturation. However, Ross and Bustin (2009) found the sorption capacities of low TOC (0.2–4.9 wt%) overmature D-M shale samples ($1.6\% < R_o < 2.5\%$) to be higher than for high TOC (1.4–11.8) immature Jurassic shales ($R_o < 1.2\%$). This was qualitatively attributed to creation of sorption sites, and/or opening up microporosity onto which gas could sorb from structural transformations of the organic matter during thermal maturation. Nonetheless, other researchers have found concomitant decrease in CH_4 sorption capacity with increasing maturity (Chalmers and Bustin, 2007, 2008). This suggests, as previously pointed out by Schieber (2010) that

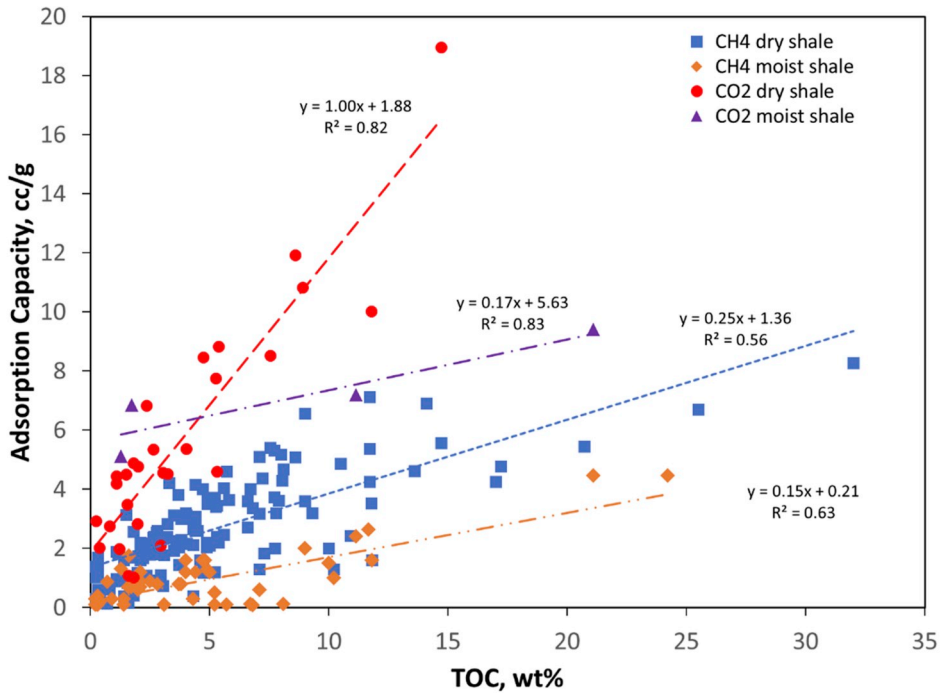

Fig. 4. Correlation between TOC and CH_4, CO_2 sorption capacity of dry and moisture equilibrated shales. Data points are representative of langmuir volume reported in the evaluations of (Nuttal et al., 2005; Ross and Bustin, 2009; Weniger et al., 2010; Zhang et al., 2012; Wang et al., 2013; Gasparik et al., 2014; Heller and Zoback, 2014; Luo et al., 2015; Hong et al., 2016; Cancino et al., 2017; Pozo et al., 2017; Zhou et al., 2018). The regression constants of both species are relatively high and extrapolation to zero TOC content shows impact of auxillary sorption sites.

intraparticle OM pore generation in thermally matured rocks may depend on the OM type. Loucks et al. (2012) also reported absence of OM pores in a matured (R_o of 0.89%) shale sample from the Atoka formation in the Midland Basin. The relationships established for any specific shale system, therefore, may not be directly applied elsewhere. But in general, the reviewed literature indicates that overmature and high TOC samples will show higher sorption capacity for both CH4 and CO_2 than the low mature and low TOC shales.

Some literature also reports thermal maturity to have noticeable effect on the shape of excess isotherms. Zhang et al. (2012) reported the methane Langmuir pressure, P_L of three Barnett shale samples (% $R_o = 0.58, 0.81, 2.01$) to distinctly shift towards lower pressures from the immature to overmature gas shale samples under the same temperature conditions. Similar trends have been reported by Gasparik et al. (2014) and Tan et al. (2014). In a related study, Gasparik et al. (2012) also found positive correlation between TOC-normalized sorption capacities and maturity for black shales, but the trend became negative for over matured samples with R_o in a range of 2.8–3.3%.

4.3. Influence of kerogen type

Although TOC content has a superior control on gas sorption in shales, another key factor is kerogen type. Kerogen is the fraction of organic matter in sedimentary rocks (in this case, shale rocks) that is insoluble in organic solvents. It is formed from the decomposition of organic matter and is the precursor of hydrocarbon generation in source rocks. Kerogen is categorized as either Type I, which consists mainly of algal and amorphous kerogen and is highly likely to generate oil; Type II, which is formed from mixed terrestrial and marine source materials and can generate both oil and gas (but mostly waxy oil); and Type III, which is formed from terrestrial plant debris and typically generates gas upon maturation. In essence, the kerogen type depends on the source rock material and the deposition environment (Seewald, 2003; Boyer et al., 2006; Vandenbroucke and Largeau, 2007; Glorioso and Rattia, 2012).

Chalmers and Bustin (2008) investigated CH_4 sorption capacity for the Lower Cretaceous Buckinghorse Formation in Canada and found that per unit TOC volume basis, the capacity trend was Type II/III mixtures > Type III > Type II > Type I. They attributed this to Type III kerogen being more mature and generating more hydrocarbons and micropores at a given temperature compared to the other kerogen types. Zhang et al. (2012) conducted high pressure (0–16 MPa) methane sorption tests on organic-rich bulk shale samples and their isolated kerogens, with thermal maturity and kerogen type being the main variation in the samples. At all temperature conditions (35, 50, 65 °C), the CH_4 sorption capacity was in the order of Type III > Type II > Type I (Fig. 5). The trend was attributed to extensive aromatization from immature (Type I) to overmature (Type III) organic matter. They indicated that the progression from kerogen Type I to Type III, represents an increase in the relative fraction of aromatic hydrocarbons compared to the aliphatic and naphthenic hydrocarbons, as reported by other researchers (Tissot and Welte, 1984; Helgeson et al., 2009). The findings of Zhang et al. (2012) depict methane adsorption to be influenced by the chemical structure of the organic matter. The details and concept of the effects exerted by organic functional groups on gas adsorption, particularly CO_2 is not well addressed in the literature and deserves further investigation. We also note, as indicated by Loucks et al. (2012) that different kerogen types exhibit differing propensities to the development of intraparticle OM pores. The storage capacity trend reported for a shale Basin system based on kerogen types may therefore not be applicable to shales from different Basins. This complicates the generalization of the effects that kerogen type exerts on adsorption capacity. We recommend further studies on the association of OM pores and kerogen type to elucidate this phenomenon.

4.4. Influence of inorganic components

Shale usually contains clay, quartz or carbonate mineral phases with trace amounts of albite and pyrite. These inorganic constituents contribute enormously to the surface area and influence pore size, cumulative porosity and sorption properties. Particularly, the clay minerals are reported (Slatt and O'Brien, 2011; Milliken et al., 2013) to contribute to the shale micropore volume. In contrast to coals, where mineral matter seems to have little influence on CH_4 sorption capacity (e.g. Faiz et al., 1992; Rice et al., 1993; Bustin and Clarkson, 1998) but significantly affects CO_2 sorption (e.g. Karacan and Mitchell, 2003; Weniger et al., 2010), mineral components in gas shale systems have

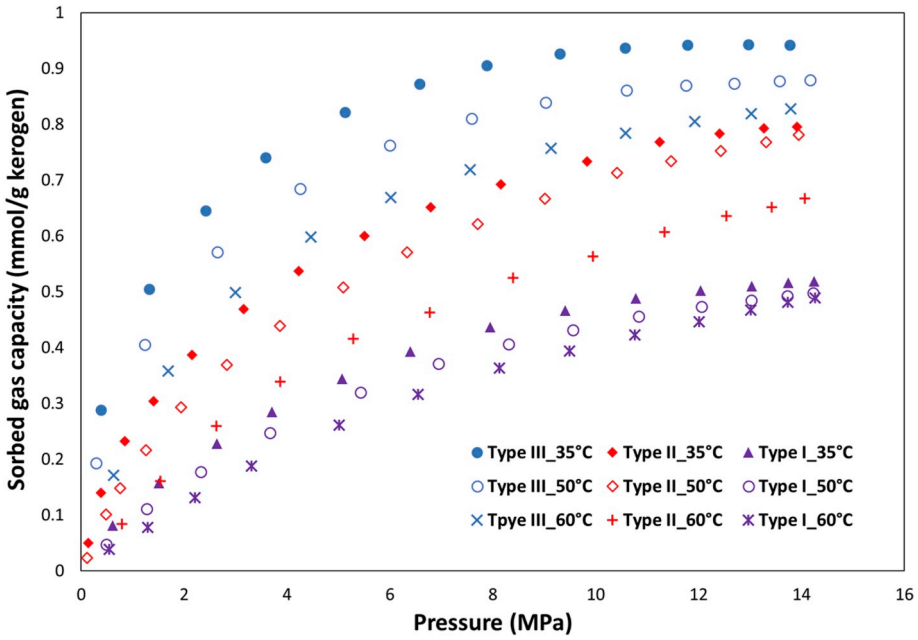

Fig. 5. Effect of kerogen type on methane sorption capacity at different temperatures (Zhang et al., 2012).

been proven to have appreciable sorption capacity for both gases (Aylmore, 1974; Heller and Zoback, 2014).

Preliminary adsorption studies on Devonian gas shale samples by Schettler and Parmely (1991); Lu et al. (1995) exclusively highlighted the inorganic clay minerals to contribute as sorption sites in shale systems due to their microporous nature. Schettler and Parmely (1990) originally postulated TOC to be of secondary importance in shale systems with low organic content. This conclusion was later reiterated by Busch et al. (2008) who attributed the high CO_2 sorption capacity of Muderong shales (TOC < 0.5%) entirely to its clay mineral constituents. The strong positive correlation of shale clay content to sorption capacity is emphasized in other reports (Chalmers and Bustin, 2008; Gasparik et al., 2012; Luo et al., 2015; Wang and Yu, 2016; Lutyński et al., 2017) where low TOC shale samples demonstrated high sorption due to their high clay contents. The specific influence of clay on shale sorption, however, is less evident in shales with high TOC content (Wang et al., 2013; Gasparik et al., 2014; Tan et al., 2014; Bi et al., 2016).

The microporous crystal layers of clay serve as ideal adsorption sites due to the large surface area (Aringhieri, 2004; Cheng and Huang, 2004; Venaruzzo et al., 2002). The contributions differ with clay type. Ross and Bustin (2009) reported clay-rich (low Si/Al ratio) shales to have superior gas storage capacities over their silica-rich (high Si/Al ratio) counterparts. Ji et al. (2012) conducted sorption experiments (up to 15 MPa) on dried clay-rich rocks at varying temperatures (35–65 °C) to shed light on the relative influence of clay type on methane adsorption. They established physisorption as the dominant mechanism for CH_4 adsorption on clay and noted sorption capacity to proceed in the order of montmorillonite > illite/smectite mixed layers > kaolinite > chlorite > illite. High-pressure CO_2 sorption experiments on pure clay minerals showed Ca-rich montmorillonite to have greater storage capacity than Na-rich montmorillonite (Busch et al., 2008). Gas shale reservoirs are dominated by illite (Jarvie et al., 2001; Gasparik et al., 2012), possibly due to the illitization of kaolinite and smectite which occurs at temperatures between 80 and 120 °C (Pytte and Reynolds, 1989). The temperatures of high organic content shale systems is in the range 96–277 °C (Lu et al., 2016). It is likely that at adequate conditions (especially in tropical zones) a blend of chemical and temperature gradient change could trigger a transition from illite to smectite (Eberl, 1984). This may occur particularly for uplifted shales exposed to weathering (e.g. shallow reservoir sections and outcrops). Since smectite has larger surface area (Šucha et al., 2001) and thus greater sorption, this could lead to potential overestimation of gas storage capacity during shale gas exploration. Additional study is recommended to understand the possibility of illite-smectite reversal transformation in clays found in shale formations.

It must be pointed out that clays are naturally hydrophilic and may present experimental challenges when correlating shale sorption capacity to clay content. For example, Chalmers and Bustin (2008) observed that the TOC-normalized CH_4 sorption capacity in dry samples from the Bucking horse formation in Canada positively correlated with clay content whereas no correlation existed for moisture equilibrated samples. Data obtained from as received or moisture equilibrated, and dried samples should therefore be evaluated carefully to accommodate this fundamental clay-water affiliation.

4.5. *Influence of moisture*

Moisture is reported to correlate positively with organic matter and clay content in shale formations (Chalmers and Bustin, 2007; Passey et al., 2010) which makes it a crucial subsurface component to be analyzed in sorption experimental procedures. Many authors have addressed the effect of moisture on gas adsorption by comparing the adsorption capacity of dry samples and moisture equilibrated samples (Lu et al., 1995; Ross & Bustin, 2007a, 2009; Busch et al., 2008; Gasparik et al., 2012, 2014; Aljamaan, 2013; Tan et al., 2014; Yuan et al., 2014; Yang et al., 2016; Zou et al., 2018) The result indicates that sorption capacity decreases with increasing moisture content until a certain equilibrium (critical) moisture content is attained for the sample. This equilibrium moisture content is representative of the maximum moisture saturation that can adsorb on the shale surfaces.

When present, water sorbs strongly on organic functional groups containing oxygen via hydrogen bonding (Dubinin, 1980) and has secondary tendencies to interact with pre-adsorbed water and charged surfaces of mineral matter (especially chemisorptive clay). Thus, besides attaching to primary (water-wet) sorption sites in the clay matrix, molecular water also competes with CO_2 and CH_4 for adsorption sites and causes a reduction in the gas sorption capacity. In shales, besides attaching onto surfaces, water molecules can condense in inorganic pores, occupying the smaller capillaries first before filling the larger pores as relative humidity increases (Zolfaghari et al., 2017a, 2017b).

The water molecules can also aggregate as clusters at high pressure (Aljamaan, 2013; Yang et al., 2016; Huang et al., 2018) to block gas-enterable pores and serves as an added negative effect on gas sorption capacity.

The equilibrium moisture content depends on the shale maturity, organic richness and organic type (Chalmers and Bustin, 2008). The value for selected European gas shale samples was estimated (Gasparik et al., 2014) to be at or below 75% relative humidity (RH). Merkel et al. (2015) reported similar values for the moisture saturation threshold (50–75% RH) of Bossier and Haynesville shales from the U.S. A recent report by Fan et al. (2018) indicated that the methane sorption capacity versus moisture content exhibited three distinct decreasing stages separated by two threshold moisture contents (Fig. 6). They performed CH_4 sorption experiments on gas shale samples from the Sichuan Basin in China at 35, 45 and 55 °C and pressures up to 10 MPa. They attributed the initial reduction (stage I) to competitive adsorption between water and methane until an extended stagnant period (stage II) where all possible hydrophilic sites are filled. They postulated that water condensation in the clay pores and some organic hydrophobic pores was responsible for the late convex-like decrease (stage III) in the adsorption capacity. The moisture effect is however reported to be masked in high TOC and over mature gas shales (Ross and Bustin, 2007a; Wang and Yu, 2016).

4.6. Influence of temperature

Thermodynamically, adsorption is an exothermic process and the effect of changing the equilibrium temperature is hinged to the Le Châtelier principle. Therefore, less adsorption is expected with increasing temperature. This relation was first reported for shales by Lu et al. (1995) who investigated sorption as a function of both pressure and temperature on Devonian shales and showed the sorption capacity to decrease with temperature. Recently, Merey and Sinayuc (2018) confirmed through adsorption measurements at 25, 50 and 75 °C that adsorption capacity increases for both CH_4 and CO_2 when temperature is decreased. This concurs with other experimental evaluations (Guo, 2013; Guo et al., 2013; Hao et al., 2013; Fan et al., 2014; Duan et al., 2016; Chang et al., 2017; Pozo et al., 2017; Zou et al., 2017; Liu et al., 2018).

Zhang et al. (2012) reported that the decrease in sorptive capacity with temperature occurred on both bulk gas shale samples (of original composition) and their isolated kerogens. Gasparik et al. (2014) constructed methane isotherms at experimental temperatures ranging up to 100 °C for immature ($V_r = 0.5$) and mature ($V_r = 0.9$) shale samples and up to 150 °C for over-mature ($V_r = 1.5$) samples and reported that besides reduction in sorptive capacity, this sorption capacity was reached at a higher pressure when the temperature was increased. This implies that for the same sample, adsorption capacity decreases with temperature and that less gas can adsorb at lower pressures. The interrelation of adsorbed gas amount with temperature and pressure is depicted in Fig. 7.

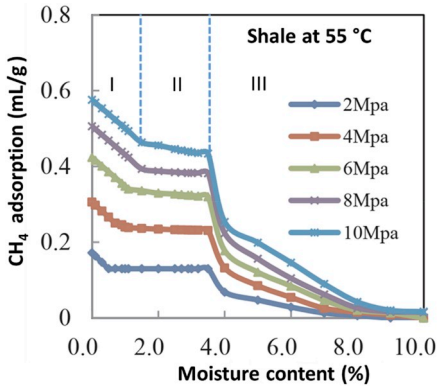

Fig. 6. Effects of moisture content on methane maximum sorption capacity at 55 °C (Fan et al., 2018).

5. CO_2 versus CH_4 sorption on shale

The first investigation of CO_2 and CH_4 sorption on the same shale material was conducted by Nuttal et al. (2005). They measured isothermal CH_4 and CO_2 adsorption on several Devonian black shales from Kentucky and found CO_2 absolute mass adsorption to be approximately 5 times greater than that of CH_4 at the same pressure. Following their report, several authors (Weniger et al., 2010; Kang et al., 2011; Chareonsuppanimit et al., 2012; Aljamaan, 2013; Heller and Zoback, 2014; Luo et al., 2015; Charoensuppanimit et al., 2016; Hong et al., 2016; Cancino et al., 2017; Pozo et al., 2017) have performed CO_2 and CH_4 gas sorption measurements on the same gas shale sample under controlled experimental conditions and reported consistently higher CO_2 sorption relative to CH_4. The reported CO_2/CH_4 absolute mass sorption ratio ranges between 1.3 and 10 for dry shale samples (Fig. 8). The ratio is expected to be relatively lower at moist conditions for the same shale sample since sorption capacity in general is lower for moist shales (see Fig. 4). There is limited data in the literature that compares the CO_2/CH_4 sorption ratio for the same sample at dry and moist conditions. Such an experimental study would be relevant to confirm this trend.

The relative sorption capacity of gas shale materials for either CO_2 or CH_4 is controlled by the respective interaction energy (thermodynamic forces), molecular size and accessibility of each gas type to the microporous network of the shale matrix system (steric forces). The tetrahedral molecular geometry of CH_4 is somewhat rounded, compared to CO_2 which has a linear molecular geometry. The dynamic diameter of CO_2 is about 0.33 nm as compared to 0.38 for CH_4 (Duan et al., 2016). The effective size of CO_2 is therefore smaller and can access narrower pores in the shale matrix and contacts a greater volume of the shale system (Kang et al., 2011). The reviewed experimental results depict that the steric and thermodynamic controlling parameters favor adsorption of CO_2 over CH_4 in gas shales. The mechanism of CO_2 accessibility is reportedly enhanced at supercritical conditions where gaseous CO_2 transitions to supercritical CO_2 (Sc-CO_2). Sc-CO_2 is completely wetting to the shale rock, with liquid-like density, but with viscosity and diffusive properties close to gas behavior (Wang et al., 2012). This unique physicochemical feature can improve the volumetric sweep during CO_2 injection and potentially increase the CO_2 subsurface storage amount by allowing Sc-CO_2 to contact more available sorption sites deeper within the formation.

Binary CO_2-CH_4 and mixed-gas sorption experiments evaluating the selectivity of gas shales for either gas species under the same pressure and temperature conditions have also been recently reported on the same shale sample in the literature. In these tests, a gas detection device (e.g. gas chromatograph) supplements the conventional sorption experimental setup that allows the determination of the gas mole fraction of each species in the mixture. During the tests, the shale samples are initially saturated with varied molar ratios of CO_2 and CH_4 at the desired experimental conditions. The majority of these authors (Pusch et al., 2012; Luo et al., 2015; Duan et al., 2016; Cancino et al., 2017; Huang et al., 2018; Ma et al., 2018) observed preferential adsorption of CO_2 over CH_4. It is reported that the selectivity of CO_2 in a gas mixture experiment evolves with pressure and is significantly higher at low pressures (Cancino et al., 2017) most likely due to the dominance of micropore filling associated with low temperatures. The adsorption selectivity parameter (represented as α) is frequently used to evaluate the competitive adsorption between CO_2 and CH_4 and given as (Duan et al., 2016):

$$\propto_{CO_2/CH_4} = \frac{x_{CO_2}\, y_{CH_4}}{x_{CH_4} y_{CO_2}} = \frac{V_{LCO_2}/P_{LCO_2}}{V_{LCH_4}/P_{LCH_4}} \quad (4)$$

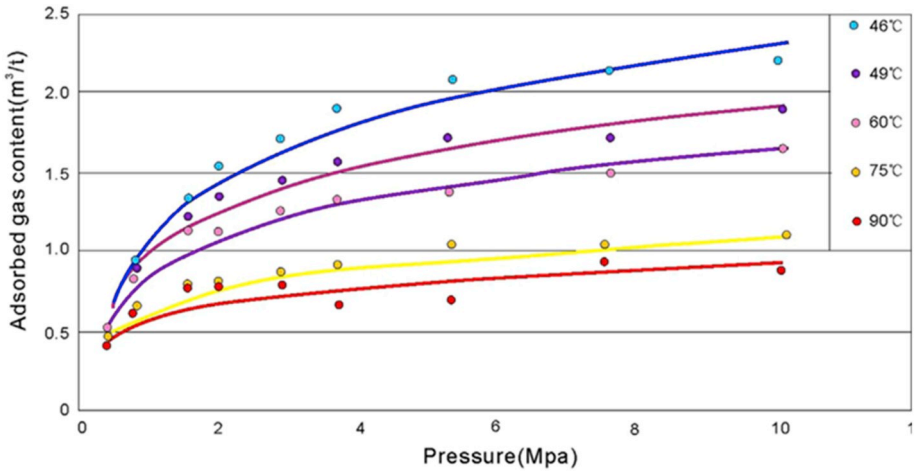

Fig. 7. Variation of adsorbed CH_4 amount with temperature performed on gas shale samples of the Ordos Basin in China (Guo, 2013).

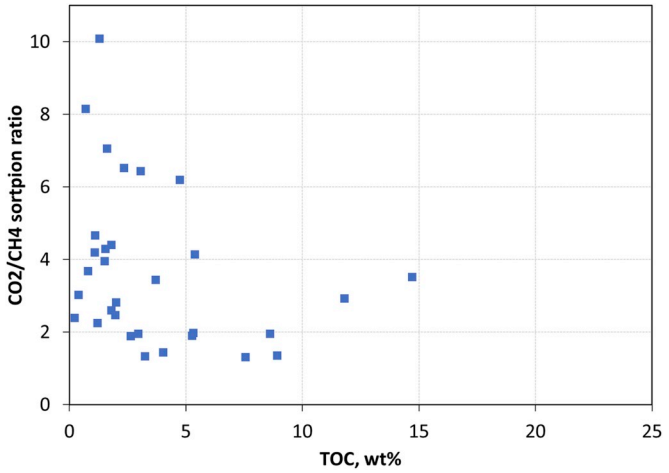

Fig. 8. CO_2/CH_4 sorption ratio for different dry shale samples as a function of total organic carbon content. Data sets are taken from Langmuir volumes reported in the evaluations of Nuttal et al. (2005); Heller and Zoback (2014); Luo et al. (2015); Hong et al. (2016); Cancino et al. (2017); Pozo et al. (2017).

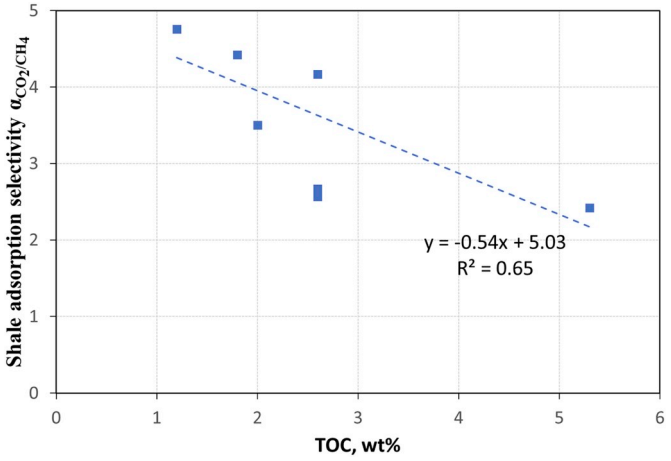

Fig. 9. Variation of shale adsorption selectivity $\propto_{CO_2/CH_4}$ different dry shale samples from China and the U.S. as a function of total organic carbon content (Heller and Zoback, 2014; Pei et al., 2015; Duan et al., 2016; Cancino et al., 2017).

where x and y variables are the molar fractions of the gas species in the adsorbed phase and free gas phase respectively for gas mixture evaluations and V_L, P_L are the Langmuir parameters. A value of $\propto_{CO_2/CH_4} > 1$ suggests that adsorbed CH_4 can be displaced by CO_2. Larger values represent stronger displacement capacity of CO_2 over CH_4. The CO_2 selectivity over CH_4 depends on shale matrix composition and pore structure. For iso-TOC samples, high clay content and micropores favours higher $\propto_{CO_2/CH_4}$ (Duan et al., 2016). The variation of $\propto_{CO_2/CH_4}$ for some selected shales in China and the U.S are shown in Fig. 9 where the selectivity is seen to decrease with increasing TOC.

In coals, preferential adsorption of CH_4 over CO_2 in mixed-gas sorption experiments has been reported, particularly at low pressures (Crosdale, 1999; Busch et al., 2003, 2006; Majewska et al., 2009). In shale samples, however, consistent CO_2 preferential adsorption in the entire pressure range has been experimentally proven and verified by simulation studies (e.g Merey and Sinayuc, 2016). These experiments are however limited, and further studies of multi-component sorption in gas shales is recommended to validate the trend.

6. Current practice of dynamic CO_2-CH_4 exchange

In gas shales, the experimental approaches to evaluate CO_2-CH_4 exchange and gas recovery have been conducted implicitly by measuring how effectively CO_2 can replace already adsorbed CH4 in a closed system. The procedures differentiate between the CO_2 and CH_4 molecules existing as adsorbed or free phase throughout the dynamic CO_2-CH_4 exchange within the shale sample at specific time steps. During these tests, usually shale material (which is often crushed) is initially saturated with CH_4 at desired experimental conditions and allowed to equilibrate before CO_2 is injected at specified criteria. The CH_4 recovery yield is quantified by the resulting amount of originally adsorbed CH_4 released from the adsorbed state.

Some authors have employed the usual Gibbsian surface excess (GSE) variable for computations through the application of conventional sorption techniques (see Section 3), whereas others have used fluid detection techniques, like Nuclear Magnetic Resonance (NMR), for evaluation. NMR characterizes the existing states of hydrogen (^1H) proton-containing fluids existing within a porous media (Coates et al., 1999). NMR-based techniques have been used successfully for petrophysical characterization of nano-porous structures in coal and gas shale (Mullen, 2010; Jin et al., 2017; Yin et al., 2017b; Zhou et al., 2018), monitoring flow and dispersion in porous media (Manz et al., 1999), evaluating CO_2 and CH_4 self-diffusion (Pusch et al., 2012) and CO_2 sorption on rock surfaces (Bernin and Hedin, 2018). A summary of the various findings from CO_2-CH_4 exchange tests are presented in Table 2.

7. Discussion and key research issues

A vast amount of investigations have been carried out to study the effectiveness and feasibility of CO_2- ESGR. However, some key research issues should be looked into:

- The majority of experimental work reported in the literature is conducted on crushed samples. To our knowledge, only Nuttal et al. (2003) reported adsorption data acquisition using an intact core. Their report highlighted the experimental difficulty involved since they only managed to capture CO_2 adsorption isotherm data for a single whole core out of twenty-six Devonian black shale samples. Using crushed samples is a quick and convenient means to perform measurements on shales, but an obvious trade-off is uncertainty in whether the data would be representative of actual reservoir conditions since it alters the structure of the porous medium (e.g. micro-fractures) and could lead to misrepresentative estimates of formation characteristics.
- The impact on gas sorption (i.e. isotherm shape) from organic matter content (TOC) and maturity, temperature and pressure and clay and moisture content are all relations that deserve attention. Particularly, lowered P_L values (associated with decreasing temperature or higher maturity) indicate that CH_4 will desorb more readily at lower pressures on higher maturity shales. Such affinity to remain sorbed in matured shales indicates that a greater reduction in CH_4 partial pressure will be required to desorb CH_4 during production. The selectivity of the surface towards CO_2 can be the solution to release the strongly sorbed CH_4 and is in such cases even more important to measure. The question of how significant adsorbed gas will be to overall production is a key concept and further investigation is required to properly correlate the P_L reduction to these parameters. Furthermore, measuring the density of the adsorbed gas phases is a key parameter in the commonly used modelling approaches that has not received much attention in experimental assessments.
- A notable concern for CO_2-ESGR is the impact of moisture which preferentially binds to hydrophilic clay surfaces and reduces sorption (and hence CO_2 sequestration) potential. Dried samples may overestimate the adsorption capacity. Although water in principle like CO_2 can substitute CH_4 by adsorbing to hydrophilic surfaces and give EGR, water will usually exist also in aqueous phase and cause mobility issues related to presence of multiple phases and water blocking effects near the wellbore or macro-fractures. Pressurized fracking fluids are essential for creating flow paths in the reservoir. The standard is use of water, but there is potential in using water-free fracking methods (e.g. propane-gel, supercritical CO_2). Gas soluble fracking fluids should be positive for recovery as well as the environment (reduction of produced water).
- Reports (Heller and Zoback, 2014; Lu et al., 2016; Yin et al., 2016) indicate crushed shale to swell (especially for high clay-content shales) during gas adsorption which changes both the pore structure and roughness. The degree of adsorption-induced swelling is shown to vary depending on the shale composition and pore characteristics and achieves a stable state when adsorption equilibrium is attained. The extent to which swelling during CO_2 injection impacts sorption isotherms, rock mechanical and hydrological (permeability, porosity) properties is crucial. In particular, Guo et al. (2017) observed through series of experiments that adsorption effects had substantial impact on shale permeability both at low and high pressures.
- Mechanical weakening of organic-rich gas shales by CO_2 saturation has been reported, especially for supercritical CO_2 (Lyu et al., 2016a, 2016b, 2018a, 2018b; Yin et al., 2017a) This is attributed to the modification of in-situ acid-base equilibria that triggers precipitation and dissolution of minerals (Liu et al., 2012; Carroll et al., 2013) and the ability of supercritical CO_2 to act as an organic solvent to extract non-polar aliphatic and polycyclic aromatic hydrocarbons from shale (Jiang et al., 2016; Yin et al., 2016). This could expand originally present gas seepage channels or generate flow channels with influence on the safety of sequestered CO_2. Most of the experimental results are reported for gas saturated shale samples monitored over a couple of days.
- Geochemical alterations of Australian Muderong shales were suggested to explain differences in specific surface areas before and after CO_2 sorption experiments conducted at reservoir conditions ($T = 45–50\,^{\circ}C$; $P < 20$ MPa) (Busch et al., 2008). The inferred geochemical changes however could not be quantified and seemed to occur only at high pressures. In a subsequent study, Busch et al. (2009) assessed the interrelation of CO_2-mediated reactions and transport properties in the Muderong shale by exposing crushed samples to CO_2 in the presence of water at 15 MPa and 50 °C for different equilibration time periods. They reported significant changes (equilibration times < 1 month) in mineralogical composition, particularly with the increase of smectite and K-feldspar contents and reduction in illite content. Mineral changes in shale sample

Table 2
Experimental studies of CO_2-CH_4 dynamic exchange conducted on shales.

Author (s)	Location	Procedure	Operating Conditions	Findings	Cons
Huo et al. (2017)	Longmaxi shales, China	Volumetric-based method applied to dried crushed samples	Fixed temperature of 45 °C. Constant initial equilibrium pressure of CH4 of 4.5 MPa CO_2 injection at varied pressures of 5.2, 6.3, 7.3, 8.4, and 9.3 MPa. Final system equilibrium pressures ranged were 4.7, 5.6, 6.5, 7.5 and 8.4 MPa respectively	The amounts of recovered CH_4 and stored CO_2 increase with CO_2 injection pressure. CH_4 recovery yield was higher for shales with smaller micropores (i.e. having lower CH_4 adsorption performance)	Inherent uncertainties of evaluating excess sorption measurements. Final system equilibrium pressure not allowed to reach injection value. It is unclear what determined when to stop the test for each injection pressure step
Liu et al. (2017)	Longmaxi shales, China	Nuclear Magnetic Resonance (NMR) based method on dried crushed samples	Fixed temperature of 35 °C. Varied initial equilibrium pressure of CH_4-saturated sample of 0.1 MPa and 1.5 MPa CO_2 injected at constant pressure of 4.5 MPa	CO_2 injection improved recovery yield of CH_4 in the adsorbed phase by an additional ~25%.	Rather simplified laboratory conditions devoid of relevant in situ reservoir complexities (e.g High temperature, high pressure, presence of water). Uncertainties in NMR detection capabilities, particularly in the presence of e.g. moisture, pyrite
Zhao and Wang (2018)	Longmaxi shales, China	NMR-based technology on dried crushed samples	Fixed temperature of 25 °C. Initial equilibrium pressures of the CH_4-saturated sample was ~10 MPa CO_2 injection pressure not specified. Final equilibrium system pressures varied between 11.8 and 12.5 MPa.	Decreased adsorbed molar amounts of CH_4 due to CO_2 injection. They suggested the inclusion of secondary stimulating (e.g. hydraulic fracturing) methods in the design of shale CO_2 injection since the CH_4 was predominantly restricted to the pore centre after desorption by CO_2 exchange.	

plugs have also been reported in the literature (Wollenweber et al., 2009; Battistutta et al., 2010). The extent to which these changes could influence storage integrity needs further investigation. Available data (Angeli et al., 2009; Busch et al., 2010; Wollenweber et al., 2010; Edlmann et al., 2013) indicates shale cap rocks to be adequately resilient towards CO_2 leakage and demonstrates an encouraging note for the sequestration of CO_2 in gas shale systems.

As seen, production and enhanced recovery of gas from shales is a complex process. Sorption is a central mechanism in this interplay. Despite this complexity, promising results have been achieved at lab and field scales (Louk et al., 2017) and CO_2 injection for ESGR is becoming a better understood process.

8. Conclusions

- Both CH_4 and CO_2 exist in critical thermodynamical state for most relevant reservoir conditions. CH_4 sorption increases monotonously with pressure from pressures near ambient to reservoir and can in most cases be described by a Langmuir isotherm. CO_2 however changes sorption behavior at the critical pressure. At lower pressures, the sorption increases monotonously, while near the critical pressure a peak in adsorption is reached and desorption occurs with increased pressure. This is not captured in low pressure experiments and standard isotherm models, e.g. multicomponent Langmuir models, are not sufficient. Extended isotherms or PVT-relations that treat both the gas and sorbed phases accurately should be applied.
- CH_4 and CO_2 adsorption storage capacity have a strong positive correlation with Total Organic Carbon, where a greater capacity is measured for CO_2.
- More mature shales tend to have higher storage capacity, but also lower Langmuir pressure indicating that the gas desorbs less easily on pressure reduction.
- Kerogen type also influences storage capacity of CH_4 with capacity trend as Type III > Type II > Type I. More experimental data is suggested to fully support this trend. Especially, there seems to be little or no data on the correlation between CO_2 storage capacity and kerogen type.
- Clays can increase the storage capacity for gas adsorption, but they strongly associate with water. Measurements on dry samples are therefore likely to yield higher capacity than original state or moisture equilibrated samples.
- Adsorption is an exothermic process and the heat of adsorption for CO_2 is greater than for CH_4 in shales. CO_2 is therefore more favourably adsorbed. Increased temperature opposes the adsorption reaction and explains observed trends; both gases adsorb less at higher temperature.
- Recent advances have allowed NMR studies to track and distinguish gaseous and sorbed CH_4 and CO_2 in shale.

Acknowledgments

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