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REVIEW ARTICLE

Low-field NMR application in the characterization of CO_2 geological storage and utilization related to shale gas reservoirs: a brief review

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Abstract CO_2 geological storage and utilization (CGSU) is considered a far-reaching technique to meet the demand of increasing energy supply and decreasing CO_2 emissions. For CGSUs related to shale gas reservoirs, experimental investigations have attracted variable methodologies, among which low-field NMR (LF-NMR) is a promising method and is playing an increasingly key role in reservoir characterization. Herein, the application of this nondestructive, sensitive, and quick LF-NMR technique in characterizing CGSU behavior in shale gas reservoirs is reviewed. First, the basic principle of LF-NMR for ^{1}H-fluid detection is introduced, which is the theoretical foundation of the reviewed achievements in this paper. Then, the reviewed works are related to the LF-NMR-based measurements of CH_4 adsorption capacity and the CO_2-CH_4 interaction in shale, as well as the performance on CO_2 sequestration and simultaneous enhanced gas recovery from shale. Basically, the reviewed achievements have exhibited a large potential for LF-NMR application in CGSUs related to shale gas reservoirs, although some limitations and deficiencies still need to be improved. Accordingly, some suggestions are proposed for a more responsible development of the LF-NMR technique. Hopefully, this review is helpful in promoting the expanding application of the LF-NMR technique in CGSU implementation in shale gas reservoirs.

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1 Introduction

Worldwide climate change poses a major challenge to the current situation of energy consumption, and accordingly much attention has been drawn to the development of comprehensive technology as a way of enhancing energy supply and simultaneously reducing carbon emissions (Abdussalam et al., 2021; Qiu et al., 2021). In this context, a technique called CO_2 geological storage and utilization (CGSU) has raised increasing concerns in recent years because it is a win–win strategy and typically promotes synthetic rewards, namely, acquiring energy from geological formations, that is, the economic perspective, and trapping CO_2 in underground strata, namely, the environmental demand (Kirli and Fahrioglu, 2019; Wang et al., 2020; Duguid et al., 2021; Fan et al., 2021; Hu et al., 2021; Pereira et al., 2021). Basically, shale gas reservoirs have been widely accepted and recognized as a suitable geological target to deploy the CGSU technique; however, this method is not mature enough to experience large-scale field promotion and implementation (Streich et al., 2010; Liu et al., 2013; Zhao et al., 2020; Cheng et al., 2021; Liu et al., 2021a; Liu et al., 2021b; Zhao et al., 2021). As a result, the shale-based CGSU is receiving considerable scientific investigation (Xie et al., 2014; Middleton et al., 2015;

Sun et al., 2017; Shi et al., 2018; Xie et al., 2021), of which low-field NMR (LF-NMR) plays an increasingly important role among a number of methodologies during related experimental works (Liu et al., 2017, 2019a, 2019 b; Tian et al., 2020).

In the shale-based CGSU process, CO_2 is first captured and purified from exhaust gases of fossil fuel combustion or other industrial production, after which it is injected into underground shale formations, aiming at 1) enhancing gas recovery by CH_4 displacement during CO_2/CH_4 adsorption in shale and, 2) reducing CO_2 emissions by CO_2 sequestration during CO_2/CH_4 interactions in shale (Fig. 1) (Godec et al., 2014; Liu et al., 2017; Liu et al., 2019a; Keles et al., 2020; Rani et al., 2020). Essentially, CGSU behavior in shale reservoirs is a result of complicated multiffluid coaction under a thermohydromechano-chemical (THMC) multifield coupling environment (Fatah et al., 2020; Iddphonce et al., 2020; Zhou et al., 2020), where fluids are the conative detection targets for LF-NMR measurements. Regarding CGSU operation in shale gas reservoirs, fluids mainly include H_2O, CH_4, and CO_2 after external CO_2 is injected into shale reservoirs underground (Liu et al., 2016; Luo et al., 2019; Zhou et al., 2020). In other words, the critical point to decode CGSU behavior is to describe the multicomponent and multiphase fluids in shale gas reservoirs. For CH_4 and CO_2, adsorbed and free phases exist, supplemented with few dissolved phases in H_2O, while H_2O is usually distributed as adsorbed and free phases in shale reservoirs (Gensterblum et al., 2014; Li et al., 2019). Moreover, the interaction of multicomponent and multiphase fluids therein is generally a dynamic process, with continuous CO_2 injection into shale gas reservoirs during a CGSU operation (Liu et al., 2019a, 2021b; Fatah et al., 2020). Under these circumstances, LF-NMR is expected to work in such complicated environments, providing new perspectives regarding CGSU studies in shale gas reservoirs.

Meanwhile, to the best of our knowledge, the application of LF-NMR in the CGSU field depending on shale gas reservoirs has not yet been systematically reviewed. Therefore, considering that LF-NMR is an emerging technique for studying the CGSU process in shale gas reservoirs, this brief review mainly concentrates on its current application status and possible future development trends regarding LF-NMR applications in studying CGSU behavior in shale gas reservoirs, mainly for experimental works. Herein, this review first provides an overview and discusses LF-NMR theory and then summarizes the already developed function of LF-NMR in recognizing and monitoring the coupling interaction of multicomponent and multiphase fluids related to CGSU behavior in shale gas reservoirs and accordingly proposes an outlook about this CGSU-related LF-NMR technique. Hopefully, this brief review is helpful in deepening the knowledge on LF-NMR applications for studying CGSU behavior in shale gas formations and has referential significance to other CGSU investigations with other geological strata, such as coal, sandstone and salt rock.

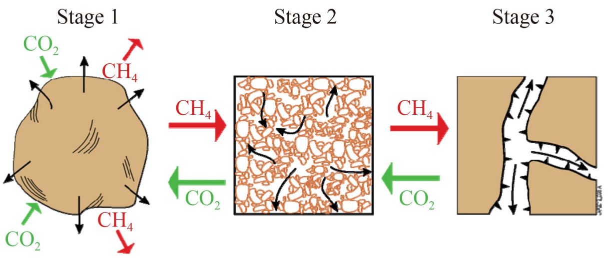


Fig. 1 Schematic of the flow dynamics of CO_2 and CH_4 in shale gas reservoirs (Godec et al., 2014).

2 Basic principle of LF-NMR

Basically, NMR behavior is induced by NMR-active nuclei (i.e., ^1H and ^{13}C) in a magnetic field or exposed to pulsed radiofrequency (RF) irradiation (Hatzakis, 2019; van Beek, 2021). Therein, relaxation comes into being and is characterized as a complicated process whereby nuclei transition from an excited state to equilibrium, owing to the splitting of the nuclear spin levels (Zeeman effect) of an applied magnetic field (Cornillon and Salim, 2000). In general, NMR technology is regularly classified into three types, that is, high-field NMR ($\geqslant$ 1.0 T), middle-field NMR (0.5–1 T) and LF-NMR ($\leqslant$ 0.5 T), according to the magnetic field strength (Wang et al., 2021). Therein, compared to high-field NMR and middle-field NMR, the LF-NMR instrument not only requires low costs but also contains shields inside and does not need extra refrigeration; for example, the cost of high-field NMR is ~10 times that of LF-NMR (Wang et al., 2021). Moreover, in geology-related areas, LF-NMR is known for its nondestructive, sensitive, and quick properties in measuring targeted parameters of a certain rock, such as porosity, permeability and wettability (Yao and Liu, 2012; Yao et al., 2015; Yin et al., 2017; Sun et al., 2018; Guo et al., 2020; Liu et al., 2020a). Accordingly, a brief introduction regarding the basis of LF-NMR measurement and analysis is summarized to enhance the understanding of LF-NMR applications in CGSU investigations related to shale gas reservoirs and to promote this LF-NMR technique.

2.1 ^1H-fluid identification using LF-NMR

On the basis of precious achievements (Martin, 1995; Dunn et al., 2002; Levitt, 2015; McPhee et al., 2015), Liu et al. (2020b) summarized the processes of LF-NMR measurement-proton alignment, precession and dephasing, raw data and processed data, during the ^1H-fluid identification in porous media (Fig. 2). First, the alignment of ^{1}H-fluid protons is stimulated by immersion into a constant magnetic field (B_0) (Fig. 2(a)), followed by an incline of the aligned protons under an RF pulse and this phenomenon enables an oscillating magnetic field (B_1) orthogonal to the B_0 direction (Fig. 2(b)). Basically, LF-NMR belongs to the submicroscopic field (between molecules) via spin-lattice relaxation (i.e., longitudinal relaxation time, T_1) and spin–spin relaxation (i.e., transverse relaxation time, T_2), in which T_2 is capable of identifying the number of ^{1}H atoms present in the ^{1}H-fluid (Seevers, 1966) and thus is widely adopted in LF-NMR investigations in geological fields, as well as the object of this review.

Afterward, the RF is stopped and the magnitude of the signal at each echo time (TE) is used to calculate the spin-spin relaxation time constant T_2, where the spins are dispersed in the transverse plane and processed at different rates. During this process, a Carr-Purcell-Meiboom-Gill (CPMG) spin-echo sequence is regarded as the gold standard for T_2 mapping (Carr and Purcell, 1954; Meiboom and Gill, 1958), where the relaxation curve is sampled at several TE points and then fitted to a single exponential with a relaxation time T_2, as exhibited in Fig. 3. This represents all dynamic processes that are not completely reversed by the 180° pulses where the spin-echo is formed and B_0 inhomogeneities are removed. Therein, the CPMG sequence involves taking measurements at different echo times (i.e., TE = 2τ) in an echo train to sample the T_2 decay curve, that is, the raw data (Fig. 2(c)). Based on the raw data, inversions are needed to extract relaxation time distributions and reflect the ^{1}H-fluid information (Fig. 2(d)). Accordingly, to seek the best possible solutions, several approaches were proposed, such as the L-curve method (Lawson and Hanson, 1974), generalized cross-validation (GCV) method (Golub et al., 1979), Butler-Reed-Dawson (BRD) method (Butler et al., 1981) and a uniform penalty (UPEN) function (Borgia et al., 1998). By comparison, Testamanti

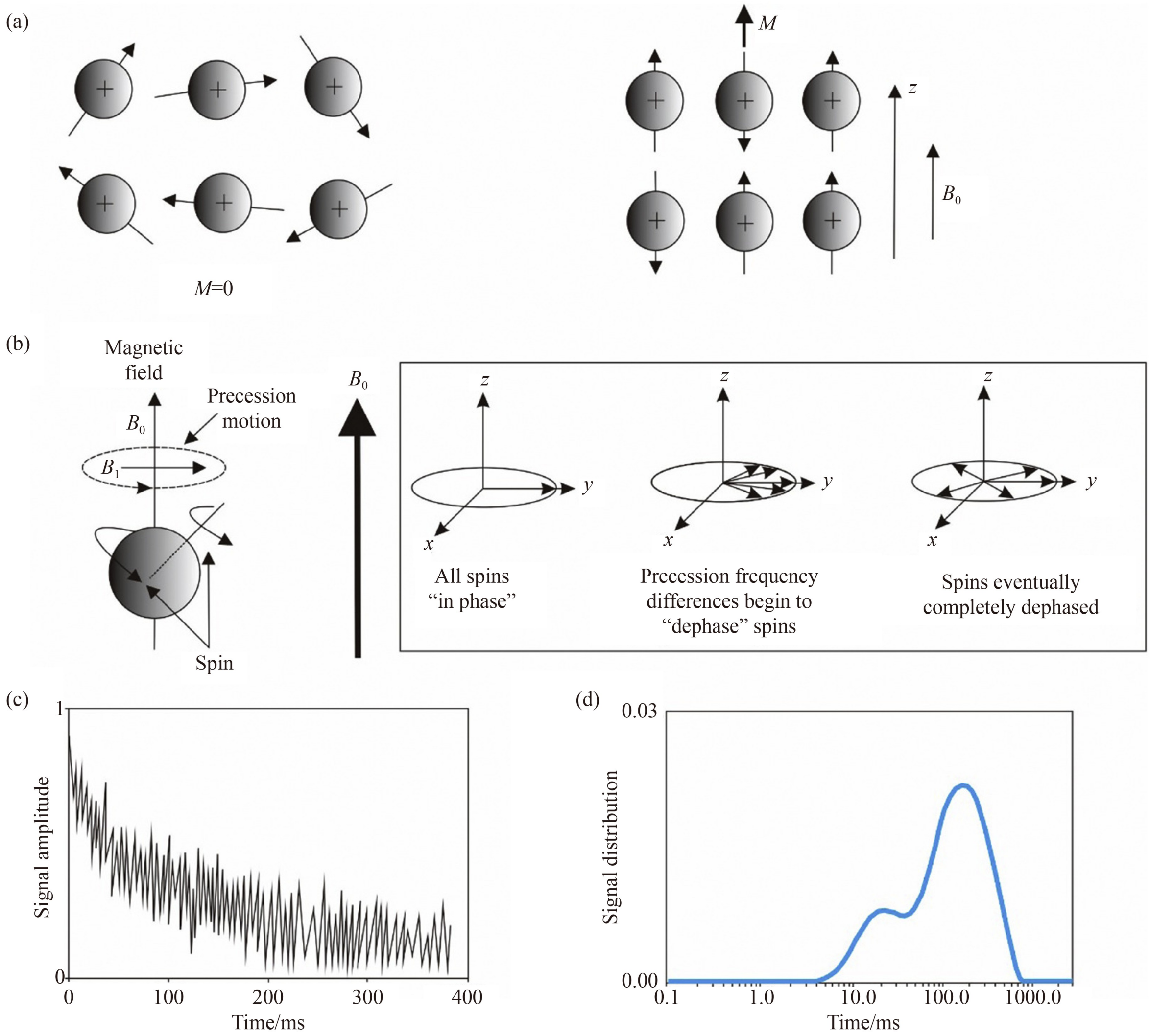


Fig. 2 Four processes of ^{1}H NMR measurement: (a) protons alignment, (b) precession and dephasing, (c) raw data and (d) processed data (Liu et al., 2020b).

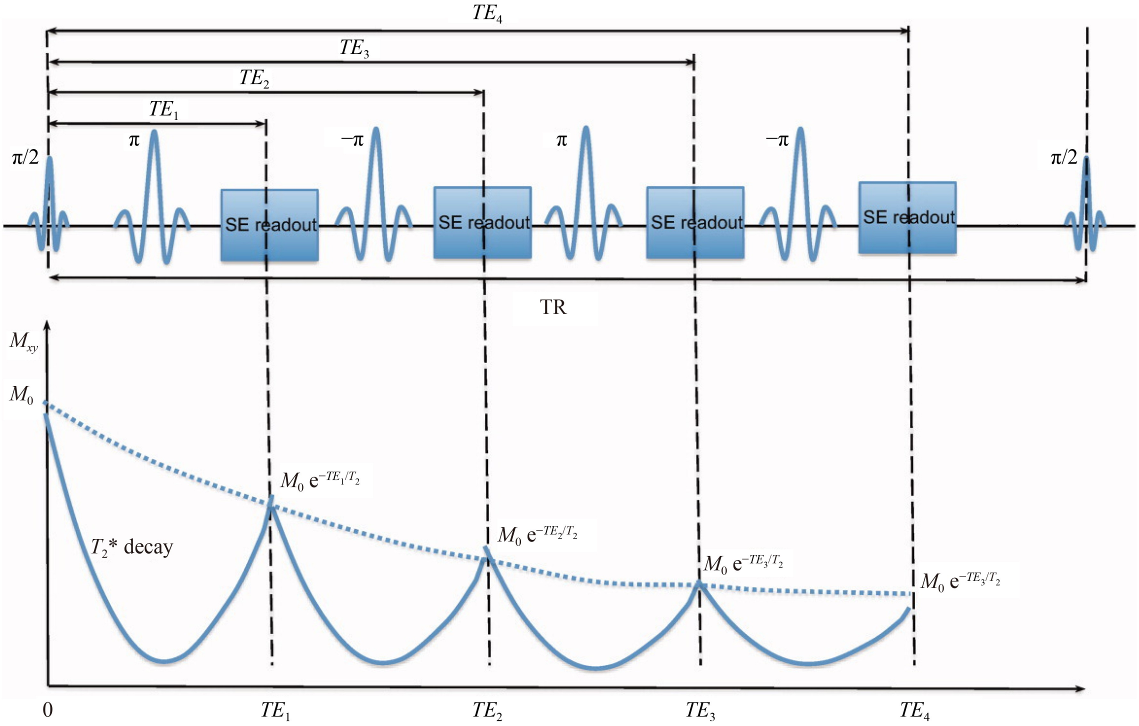


Fig. 3 Schematic representation of a CPMG pulse sequence with a multiecho spin echo sequence (top) and the T_2 relaxation curve (bottom). TE, echo time; TR, repetition time (Cheng et al., 2012).

and Rezaee (2019) concluded that the BRD algorithm has good performance and is reliable for shale-based NMR investigation, among the four mentioned methodologies.

2.2 Relaxation phenomena and mechanisms of LF-NMR

In a typical T_2 measurement of ^{1}H-fluid in shale, the T_2 is codetermined by the bulk, surface and diffusion relaxations (Straley et al., 1994; Brown et al., 2001; Hirasaki et al., 2003; Washburn, 2014):

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}, \tag{1}$$

where the subscripts B, S, and D represent bulk, surface and diffusion relaxation, respectively. Therein, the bulk relaxation (T_{2B}) is regarded as an intrinsic property of the ^{1}H-fluid and is affected by the physical properties (e.g., viscosity), temperature and pressure. Surface relaxation (T_{2S}) occurs at the fluid-solid interface, which is related to the surface area to volume ratio (S/V) of the pores containing ^{1}H-fluid (Coates et al., 1999; Zhao et al., 2022):

$$\frac{1}{T_{2S}} = \rho\left(\frac{S}{V}\right), \tag{2}$$

where ρ is the T_2 surface relaxivity (that is, the T_2 relaxing strength of the grain surfaces, unit: m/s).

In addition, the diffusion relaxation (T_{2D}) is the pore fluid relaxation induced by the proton spins diffusion across a magnetic field gradient (Coates et al., 1999), and it yields:

$$\frac{1}{T_{2D}} = \frac{D(\gamma G T_E)^2}{12}, \tag{3}$$

where D is the molecular diffusion coefficient (m^2/s), γ is the gyromagnetic ratio of a proton (MHz/T), and G is the field-strength gradient (Gs/cm). This also indicates that the influence of T_{2D} on T_2 could be small enough to be ignored if the involved internal field gradient is homogeneous ($G = 0$ Gs/cm) because the $1/T_{2D}$ tends to be 0 in this situation.

Basically, regarding the CGSU investigations related to shale gas reservoirs, the LF-NMR was introduced to obtain the relaxation phenomena of ^{1}H fluid in shale reservoirs and thus to acquire the desired information for the CGSU behavior. Accordingly, this review mainly involves the LF-NMR function in the characterization of CH_4 adsorption, CO_2-CH_4 interactions, and the CO_2 storage ability as well as the recovery enhancement of shale gas during the CGSU operation.

3 LF-NMR measuring CH_4 adsorption capacity of shale

Basically, the identification ability of CH_4 adsorption capacity is the precondition that LF-NMR can be used in the CGSU-related investigations regarding shale gas reservoirs, since CO_2/CH_4 competitive adsorption acts as the driving force during this CGSU behavior (Godec et al., 2014; Liu et al., 2019a). The application of LF-NMR in measuring CH_4 adsorption behavior in shale is an emergent reality in recent years as an extension and supplement in addition to conventional approaches, such as the volumetric method and gravimetric method. To some extent, the LF-NMR measurement of CH_4 adsorption in shale is based on the characterization of CH_4 adsorption on coal using the LF-NMR technique (Yao et al., 2014). During the investigation on the CH_4 desorption process of coal measure shale, it is found that the relationship between gas pressure and the integrated T_2 amplitude for the adsorbed CH_4 demonstrates a Langmuir-like property and thus meets a Langmuir-like function exhibited in Fig. 4, characterized by the LF-NMR technique (Tang et al., 2017). Afterward, depending on the LF-NMR measurement, Li et al. (2018) distinguished adsorption CH_4 and free CH_4 according to the T_2 spectra and built the ratio of adsorption CH_4 relative to free CH_4, which was verified by the isothermal adsorption experiment using volumetric method. Therein, a shorter T_2 spectra of 0.1–1 ms (peaked at 0.2 ms) was treated as the adsorption CH_4 in micropores, while the longer ones of 1–10 ms (peaked at 3 ms) was regarded as the free CH_4 in macropores (Li et al., 2018). Besides, Liu and Wang (2018) conducted the LF-NMR experiments to explore the absolute CH_4 adsorption of shale, which recognized three types of T_2 relaxation of CH_4 in the shale-filled system, i.e., 0.1–13 ms, 13–280 ms, and 280–2500 ms (Fig. 5(a)) and accordingly calculated the integrated amplitudes of the adsorbed CH_4 on the pore surface, the free-state CH_4 in pores, and the bulk CH_4 at different pressures (Fig. 5(b)). The comparison between the achievements made by Li et al. (2018) and Liu and Wang (2018) shows that the adsorbed CH_4 and free CH_4 correspond to variable T_2 spectra for different shale samples during the LF-NMR measurement.

In general, the emerging application of LF-NMR in measuring the CH_4 adsorption in shale is admissive and is regarded as reliable, which is guaranteed by the LF-NMR theory and is confirmed by the practical attempts. A systematic LF-NMR-based work organized by Yao et al. (2019) introduced the implementation strategy about the LF-NMR technique in identifying the multiphase CH_4 in shale, where the dynamic variation in adsorbed CH_4 and free CH_4 was performed with respect to different gas pressures. Therein, the accuracy of the LF-NMR-based CH_4 adsorption capacity is approved by the conventional gravimetric method, displayed in Fig. 6(a) for Sample SZX and Fig. 6(b) for Sample XWX (Yao et al., 2019). In addition, the LF-NMR was also introduced to clarify the dynamic adsorption-desorption process of CH_4 in shale, in which a hysteresis occurred between the adsorption and desorption curves (Fig. 7), similar to the low-temperature N_2 adsorption-desorption phenomenon (Zhou et al., 2021). This CH_4 adsorption-desorption hysteresis is due to the surface layer being affected during the CH_4

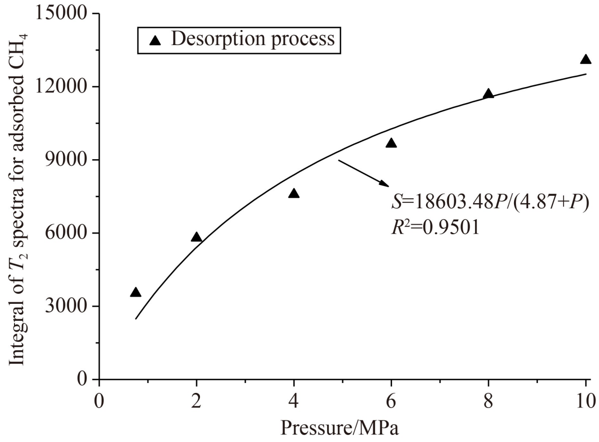
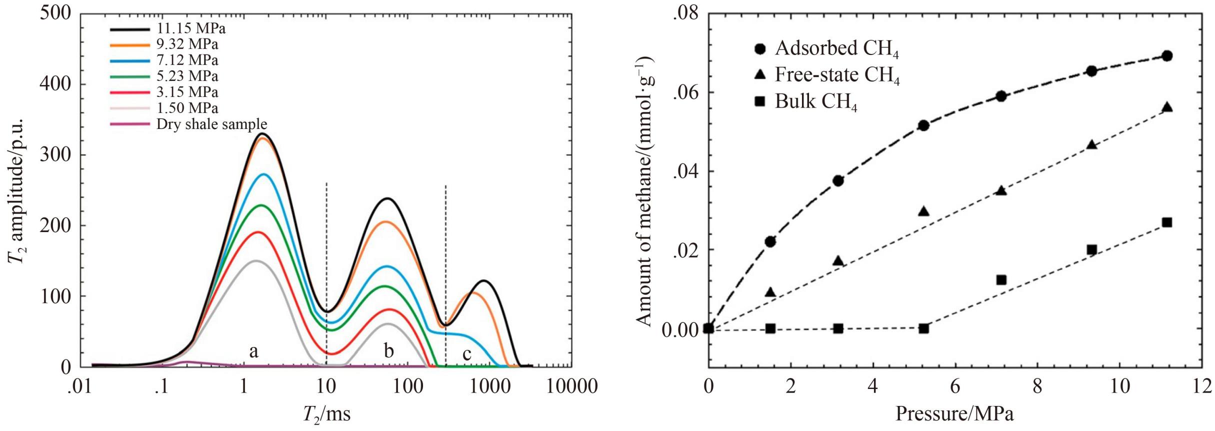


Fig. 4 Relationship between gas pressure and integrated amplitude (S) of shale-adsorbed gas during the desorption process from 10 MPa to 0.75 MPa (Tang et al., 2017).



(a)

(b)

Fig. 5 LF-NMR measurement of CH_4 in shale sample. (a) T_2 spectrum of CH_4 and (b) the specific amounts of "adsorbed CH_4", "free-state CH_4", and "bulk CH_4" (Liu and Wang, 2018).

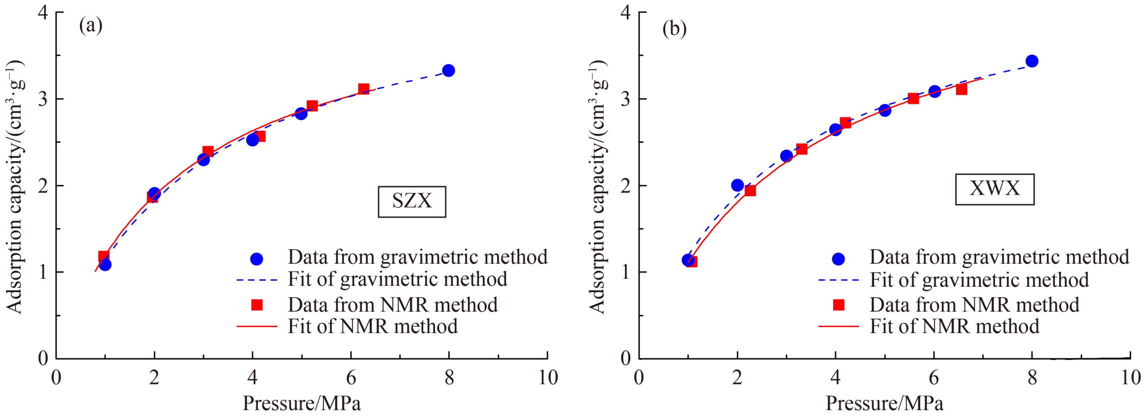


Fig. 6 Isothermal adsorption curves obtained from the LF-NMR technique and gravimetric measurement (Yao et al., 2019).

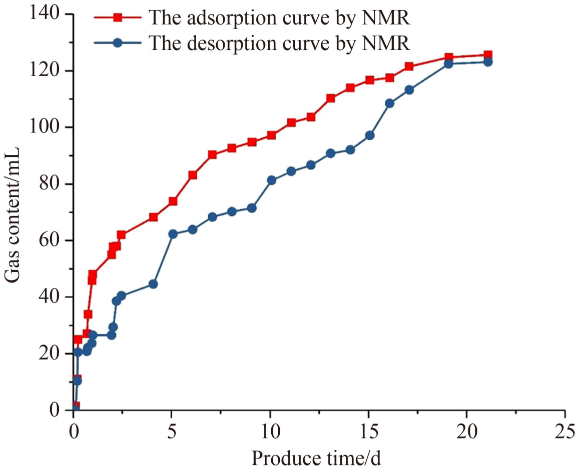


Fig. 7 Comparison of CH_4 adsorption curve and CH_4 desorption curve based on the LF-NMR measurements (Zhou et al., 2021).

desorption process, thus inducing the capillary condensation in the micropores; that is, the molecular adsorption path is singular when the pore structure changes (Zhang et al., 2012).

As a whole, the unremitting efforts from precious works enable the LF-NMR application in measuring the CH_4 adsorption capacity in shale to be more reliable and accredited. Simply, the LF-NMR measurement regarding the CH_4 adsorption is dealing with a single component (i.e., CH_4) in shale sample and thus is somehow the low-hanging fruit of promoting LF-NMR methodology. Therefore, it is bound to need a more profound development for the LF-NMR technique for its application in the CGSU process, since this CGSU behavior is a result of the interaction of multicomponent fluids.

4 LF-NMR characterizing CO_2-CH_4 interactions in shale

The CGSU outcome is enabled by the CO_2-CH_4 interplay after the external CO_2 is injected into the shale gas reservoir and destroys the original fluid phase in shale. Therefore, the characterization of CO_2-CH_4 interactions is of significance for CGSU investigations of shale gas reservoirs. By comparison, CH_4 is a ^{1}H-fluid, while CO_2 is a ^{1}H-free fluid, which means that the relaxation behavior occurs for CH_4 but not CO_2 when the mixed CO_2-CH_4 is immersed in an LF-NMR field. Accordingly, Liu et al. (2017) self-designed an LF-NMR-based setup and conducted a series of experiments, aiming to explain the CH_4 performance after CO_2 injection into shale reservoirs. In the work made by Liu et al. (2017), the dynamic variation in adsorbed CH_4 and free CH_4 content in shale was monitored after CO_2 was injected into shale samples, where CO_2 injection accelerated the desorption rate of the original adsorbed CH_4 (Fig. 8). Therein, compared with the situation without CO_2 involvement, CO_2 injection enables an additional ~25% of residual gas in the adsorbed phase to be recovered at ambient pressure or abandonment pressure, indicating a great potential for CO_2 enhanced shale gas recovery (Liu et al., 2017). Afterward, similar investigations explored the influence of CO_2 on the adsorption of CH_4 on shale (Zhao and Wang, 2019; Huang et al., 2020), where the T_2 measurements on two shale samples indicate that the presence of CO_2 makes the CH_4 in shale samples transform from the adsorbed state to the free-gas state, based on the analysis for the “a”, “b” and “c” regions in Fig. 9. The concept of “a”, “b” and “c” regions is also found in the achievements made by Huang et al. (2019), similarly indicating the ability for injected CO_2 displace the adsorbed CH_4 in shale, depending on the LF-NMR T_2 measurements. Moreover, the LF-NMR was also adopted to investigate the CH_4 adsorption behavior on dry and moisture-equilibrated shale under CO_2 “huff-n-puff” (Tian et al., 2020). Therein, for the adsorbed CH_4, its recovery rate increases continuously first and then tends to level off in both the dry and the moisture-equilibrated shale samples, along with the increasing huffing time, and the recovery rate under the moisture-equilibrated condition is slightly smaller than that under dry conditions (Fig. 10).

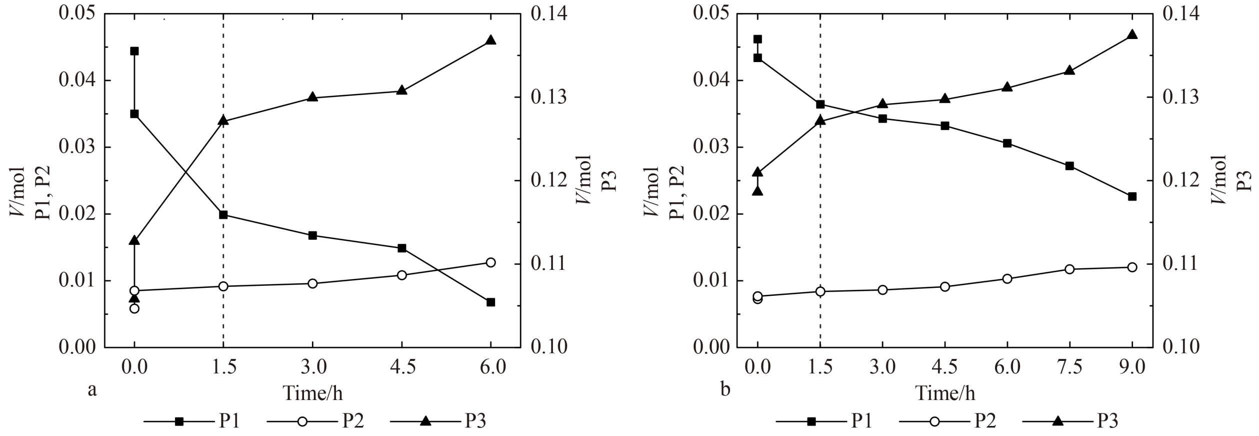


Fig. 8 Content variation of adsorbed CH_4 (P1), free CH_4 (P2) and bulk CH_4 (P3) after CO_2 injection into shale. (a) The ambient pressure and (b) the abandonment pressure condition (Liu et al., 2017).

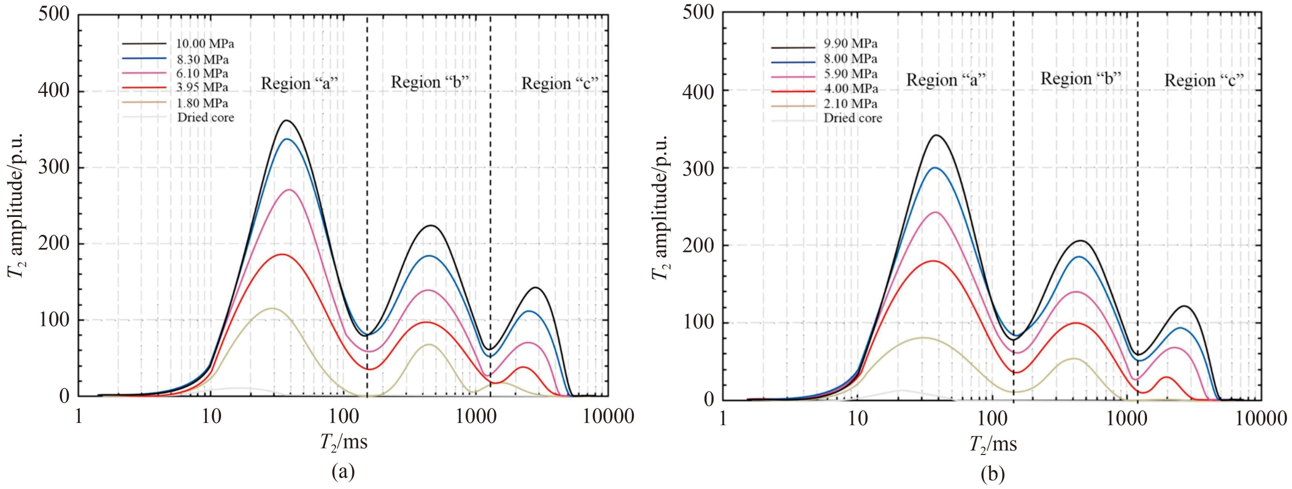


Fig. 9 Measured T_2 spectrum for the "CH_4-saturated" shale samples (a) #1, and (b) #2. Region a (i.e., 0.01–11 ms) represents the adsorbed CH_4 on the pore surface, region b (i.e., 11–300 ms) refers to the free-state CH_4 existing in the pore center, and region c (i.e., 300–2000 ms) represents the free-state CH_4 among shale particles (Zhao and Wang, 2019).

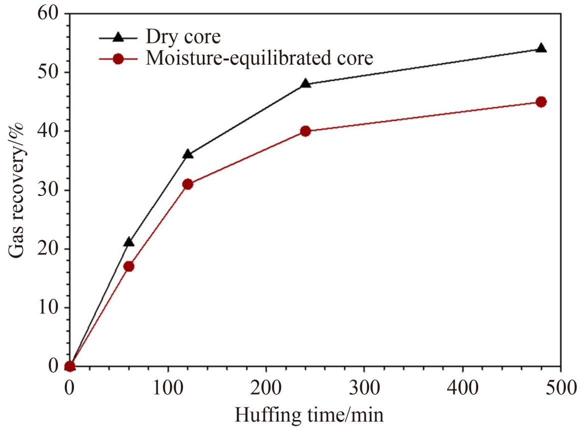


Fig. 10 Recovery of the adsorbed CH_4 from the dry and moisture-equilibrated shale during the CO_2 huff process (Tian et al., 2020).

As mentioned above, the ^1H-containing and ^1H-free characteristics ensure that the LF-NMR relaxation can recognize CH_4 from the mixed CO_2-CH_4 environment and thus observe the CH_4 adsorption/desorption behavior with or without CO_2 involvement. These LF-NMR-based achievements confirm the potential and the actionability of CO_2 enhanced shale gas recovery, resulting from the CO_2-CH_4 displacement. However, the CO_2 performance during the CO_2-CH_4 interaction is usually lacking from the LF-NMR measurements because it is apathetic in the magnetic field (CO_2 is ^1H-free). To make up for this deficiency, Liu et al. (2019a) proposed a novel incorporation of LF-NMR approach and volumetric method, simultaneously monitoring CO_2 and CH_4 in the mixed CO_2-CH_4 environment in a dynamic and quantitative manner. By performing this novel methodology on two shale samples, it is observed that an increasing CO_2/CH_4 pressure ratio makes the adsorbed CH_4 content decline, suggesting that CO_2 can reduce the CH_4 adsorption capacity, probably by competing for a finite number of sorption sites in shale (Fig. 11). In addition, the combination of LF-NMR approach and volumetric method built

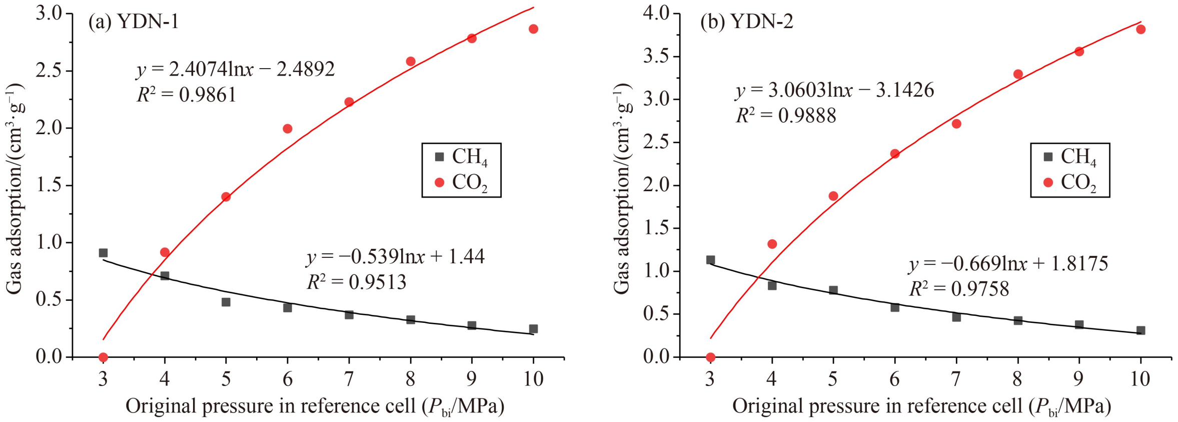


Fig. 11 Adsorption capacity of CO_2 and CH_4 in the environment of fixed CH_4 mass and variable CO_2/CH_4 ratio. Herein the CO_2/CH_4 pressure ratio is approximately (P_{bi} −3)/3 with the partial pressure for CH_4 stabilized at 3 MPa in the reference cell. (a) Sample YDN-1; (b) Sample YDN-2. (Liu et al., 2019a).

the CO_2/CH_4 competitive adsorption ratio, which is defined as the ratio of adsorbed CO_2 content relative to adsorbed CH_4 content under identical conditions in shale (Liu et al., 2019a). Accordingly, the increasing pressures of CO_2 and CH_4 decrease the CO_2/CH_4 competitive adsorption ratio, in spite that the CO_2/CH_4 pressure ratio keeps constant (~1:1) (Fig. 12), corresponding with previous molecular simulations of the CO_2/CH_4 competitive adsorption behavior in shale (Wang et al., 2016; Zhou et al., 2019). This phenomenon is due to the increase in adsorbed CO_2 content being larger than that of CH_4 content at low pressure, and this gap diminishes at high pressure and also indicates the differential sensitivity of content variation for adsorbed CO_2 and adsorbed CH_4 under a certain pressure (Liu et al., 2019a).

Herein, the identification proficiency of the LF-NMR technique in detecting CH_4 from the CO_2-CH_4 mixture has been supported, and all related achievements suggest a great potential for enhanced gas recovery from shale by CO_2-CH_4 displacement. Furthermore, a combined approach, based on LF-NMR and the volumetric method, exhibits a novel capacity in recognizing CH_4 and CO_2 simultaneously in a timely, dynamic, and quantitative way. Basically, the LF-NMR performance is able to characterize the CO_2-CH_4 interaction and thus reveals a sanguine expansion in dealing with the CGSU behavior in shale gas reservoirs.

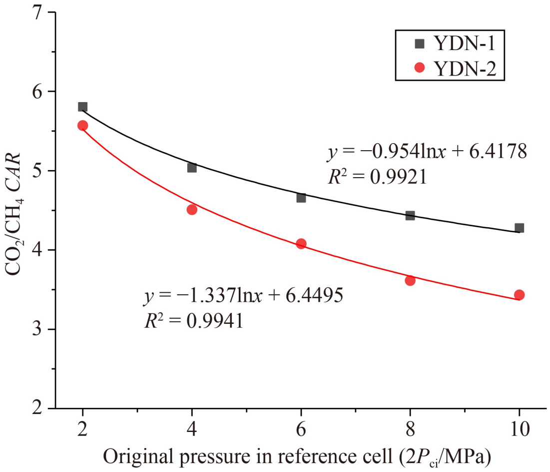


Fig. 12 CO_2/CH_4 *CAR* in shale under a fixed CO_2/CH_4 pressure ratio. *CAR*, competitive adsorption ratio (Liu et al., 2019a).

5 LF-NMR investigating CO_2 sequestration and simultaneous shale gas recovery

In general, the purpose of a CGSU project related to a shale gas reservoir includes 1) retrieving shale gas recovered from the reservoir and 2) simultaneously sequestering injected CO_2 in the shale gas reservoir as much as possible. Therefore, from the perspective of energy and the environment, whether a CGSU project is successful mainly depends on the improved shale gas recovery and the CO_2 storage content after CO_2 is involved (Godec et al., 2014; Iddphonce et al., 2020; Zhao et al., 2020). As for the enhanced shale gas recovery, the variable efficiencies like 5%, 25% and 30% exist in previous achievements (Godec et al., 2013; Fathi and Akkutlu, 2014; Liu et al., 2017), indicating that CO_2-CH_4 displacement promotes variable production enhancement levels for different shale gas reservoirs. Aiming to explore the factors affecting the production enhancement caused by CO_2-CH_4 interactions in shale, Liu et al. (2019b) organized a sequence of experiments using LF-NMR setup, where a methodology for measuring the efficiency of CO_2 enhanced shale gas recovery was proposed and demonstrated. Therein, the CO_2 involvement significantly forced more CH_4 to be recovered from shale, as revealed by the comparison of recovery efficiencies with and without CO_2 injection (Fig. 13(a)), and an efficiency range from 16.22% to 34.34% of CO_2 enhanced shale gas recovery was obtained, with a mean of 23.54% (Fig. 13(b)). Thereafter, with the aid of 1stOpt

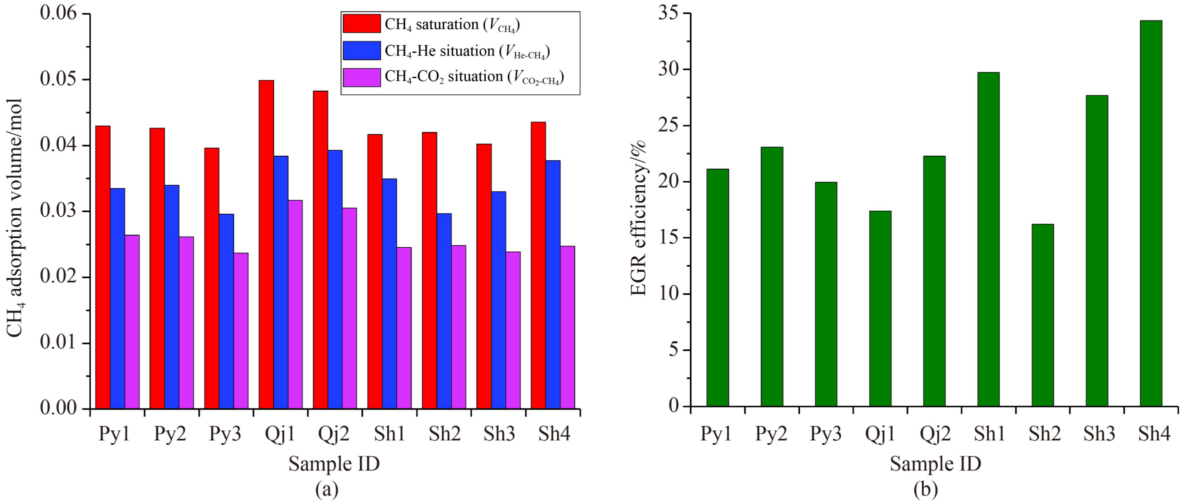


Fig. 13 LF-NMR outcomes for the collected samples. (a) CH_4-adsorption volume under the different experimental conditions and (b) efficiency of CO_2 enhanced shale gas recovery (Liu et al., 2019b).

statistical analysis software with the algorithm of Universal Global Optimization, Liu et al. (2019b) built a model to estimate the CO_2 enhanced shale gas recovery efficiency using the reservoir parameter using LF-NMR measurements, which had also been verified therein. That is

$$y = [0.3986x_1 + 0.1213x_2 + 0.002908\ln(x_3) - 0.1693x_4] \times 100\%, \quad (4)$$

where y is the CO_2-based EGR efficiency (%) and x_1, x_2, x_3, and x_4 represent the numeric values of the TOC content (%), Langmuir volume (m^3/t), permeability (mD) and clay mineral content (%), respectively.

Regarding the CGSU research, as exhibited by the abovementioned achievements, the LF-NMR measurements display a good performance in determining the CO_2 enhanced shale gas recovery efficiency. Unlike the straightforward extraction of diverse desired data from the numerical simulations (Sun et al., 2013; Liu et al., 2016; Cheng et al., 2021), a single experimental work typically offers limited information. Therefore, as far as we are aware, sparing LF-NMR-based work reported the CO_2 sequestration capacity of shale during the CGSU process. By extensive search, we found that Liu et al. (2019a) represented a relationship between the CO_2 adsorption and CH_4 adsorption during the CO_2-CH_4 displacement in shale, relying on the combination of LF-NMR technique and volumetric method (Fig. 14). This LF-NMR-related work indicates that the theoretical capacity for CO_2 sequestration (adsorbed phase) is up to ~3.87 cm^3/g (Fig. 14(a)) for sample YDN-1 and ~5.13 cm^3/g (Fig. 14(b)) for sample YDN-2, when the adsorbed CH4 tends to be entirely desorbed (namely, CH_4 adsorption content approaches 0 cm^3/g), during the CO_2-CH_4 interaction in shale. This work (Liu et al., 2019a) can be considered a useful attempt to measure the CO_2 storage capacity of shale with the participation of the LF-NMR technique, and it is worth popularizing.

Basically, the LF-NMR technique has the capacity of measuring the CO_2 enhanced shale gas recovery with high facility, accomplished by the comparison of CH_4 content with or without CO_2 involvement. That is, the

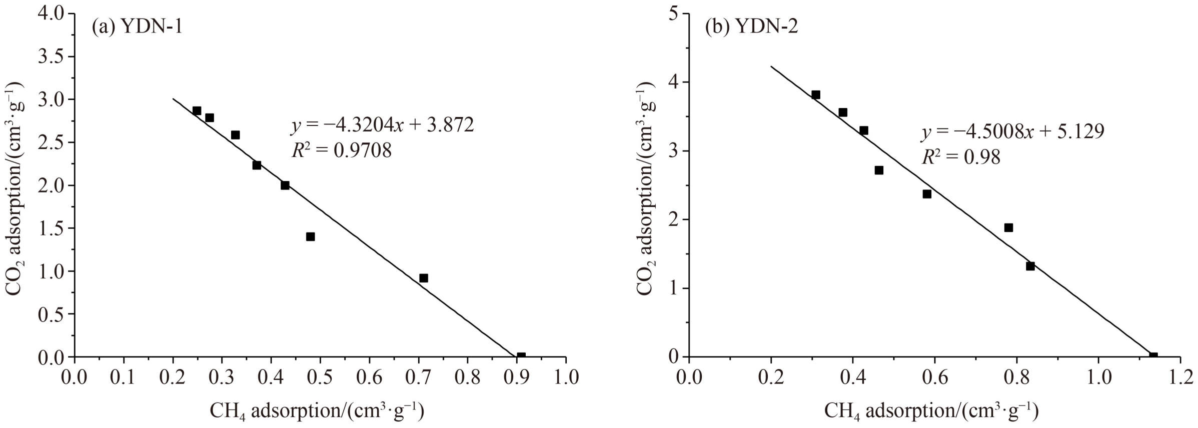


Fig. 14 Relationship between adsorbed content of CO_2 and CH_4 during CO_2-CH_4 displacement (Liu et al., 2019a).

CO_2 appearance or not scarcely affects the detection of CH_4 using LF-NMR theory. Nevertheless, the LF-NME itself feels stuck in measuring the CO_2 (^{1}H-free) in shale reservoirs, resulting in limited LF-NMR-based works that have acquired CO_2 sequestration information. Accordingly, on the basic function of the LF-NMR technique, composite methodologies are expected and are required for the comprehensive expression of CSGU behavior in shale gas reservoirs, for example, the combinatorial method proposed by Liu et al. (2019a).

6 Perspective and outlook

The LF-NMR application in the petroleum industry dates back to 1956 (Brown and Fatt, 1956), and its function in characterizing the petrophysical properties of oil/gas reservoirs, such as porosity, permeability, and wettability, has relatively matured after years of development (Guo et al., 2020; Liu et al., 2020b; Lin et al., 2021); however, its application in determining CGSU behavior has only emerged in recent years, and is regarded as still in its infancy. For the review of the existing achievements, considered as rapid and non-destructive approach, the LF-NMR technique is gratifyingly developing, in an attractive and irresistible manner, in measuring the CH_4 adsorption capacity of shale and in identifying the CH_4 molecule from CO_2-CH_4 mixture, as well as is budding in investigating the CO_2 sequestration capacity, regarding the experimental works studying CGSU behavior in shale gas reservoir. Herein, the continuously expanding application and the contributed degree of LF-NMR in the CGSU related to shale gas reservoir are guaranteed by the resulting relaxion phenomenon of ^{1}H-fluid in a magnetic field; however, in this research area, the objective deficiency and ambiguity remain in the current LF-NMR implementation, by taking a panoramic view of the situation. First, the involved LF-NMR parameters were set without a uniform standard recognized by different researchers. For example, the magnetic field strength values of 0.3±0.05 T, 0.5 T and 0.54 T were adopted, while TE values of 0.15 ms and 0.3 ms were applied by different achievements (Liu et al., 2017; Tang et al., 2017; Liu and Wang, 2018; Yao et al., 2019). As another example, for the waiting time, 1.5 s, 3.0 s, 4.0 s, 6.0 s, 8.0 s, and 10.0 s were used under different pressures for CH_4 adsorption measurement using LF-NMR test, where the rules for these settings were insufficiently clear (Liu and Wang, 2018). According to the basic principle of LF-NMR, these parameter settings influence the accuracy of LF-NMR measurements, e.g., TE affects the resolution ratio of LF-NMR. Second, almost all the LF-NMR achievements regarding CO_2-CH_4 in shale gas reservoirs run in the absence of water, which somehow fails to accord to the real situation that moisture content is generally contained in a natural shale gas reservoir (Huang et al., 2018; Wang, 2019; Yang and Liu, 2020). Nevertheless, a few mentioned works involved moisture-equilibrated shale like the one made by Tian et al. (2020) but gave sparing information on the role of moisture in the CGSU behavior in shale gas reservoirs. This deficiency is probably caused by the limitation in detecting and differentiating CH_4 and moisture where ^{1}H simultaneously exists.

In fact, the rapid development of LF-NMR applications in oil and gas fields meets some other questioned views on the reliability of measurements. For example, with regard to the shale porosity obtained from helium pycnometry and that measured by the LF-NMR method, it is debatable in discussing which porosity is greater (Xu et al., 2015; Adeyilola et al., 2020). Therefore, a responsible application of LF-NMR in investigating CGSU behavior in shale gas reservoirs certainly depends on a constant evolution and improvement in LF-NMR theory and related setups. Herein, we suggest that it is necessary to ferment a widely recognized standard for LF-NMR-based experiments related to the CO_2-CH_4 interplay in shale gas reservoirs, where the key parameter settings, such as the magnetic field strength, waiting time and TE, could be standardized and institutionalized. In addition, the LF-NMR-based experimental design and methodology need to consciously expand the function to differentiate the ^{1}H-containing multiple fluids, such as CH_4 and water, which is the precondition to conduct a more responsible physical simulation of the CGSU process in shale gas reservoirs (usually containing moisture). That is, LF-NMR will play a more important role in this CGSU study field if the CO_2, CH_4 and water in shale gas reservoirs can be identified in a dynamic, quantitative, and timely manner. In view of this, herein, we suggest that D_2O (deuterium oxide) might be a choice to simulate H_2O during the LF-NMR measurement, since D_2O is insensitive to the magnetic field; however, the specific and detailed operation requires close scrutiny and inspection. In summary, LF-NMR is performing increasingly significantly in CGSU-related studies regarding shale gas reservoirs but also needs to be developed in both theory and experimental setup to acquire more responsible and reliable outcomes.

7 Concluding remarks

Regarded as a rapid and nondestructive method, LF-NMR is developing along an irresistible trend in the application of CGSU areas related to shale gas reservoirs. All the achieved advances are based on the basic theory of LF-NMR, that is, the relaxation phenomena of ^{1}H-fluid in a magnetic field, which means that LF-NMR is adept at recognizing CH_4 and/or distinguishing CH_4 from the CO_2-CH_4 mixture in shale. Accordingly, examples of higher-level applications indicate that LF-NMR performs well and holds high potential in measuring the CH_4 adsorption capacity of shale, in characterizing CO_2-CH_4 interactions in shale, and in investigating CO_2 sequestration and simultaneous enhanced shale gas recovery. These gratifying achievements also suggest that LF-NMR is capable of detecting the desired information (e.g., CO_2-CH_4 displacement) in a dynamic, quantitative and timely manner and further demonstrate that LF-NMR can substitute, or at least work as a supplement, for conventional approaches in studying CGSU behavior in shale gas reservoirs, such as volumetric and gravimetric methods for isothermal adsorption. Although previous works have increased the ability of LF-NMR to characterize CGSU behavior in shale gas reservoirs, some limitations remain and need to be investigated further. One issue is how to build a widely approved standard or regulation of the settings parameters (e.g., TE and waiting time) for the LF-NMR measurement. Another urgent issue is the requirement for establishing a valid LF-NMR methodology for simultaneously detecting CO_2, CH_4, and water in shale gas reservoirs in a quantitative manner. These two issues are of significance in promoting the development of this LF-NMR technique in experimentally investigating the CGSU behavior related to real natural shale gas reservoirs. In addition, it would be better if the LF-NMR theory goes a step further, enabling more relaxation (especially fast relaxation) to be detected and thus the adsorbed CH_4 behavior in shale to be quantitated more accurately.

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