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Impact of clays on CO_2 adsorption and enhanced gas recovery in sandstone reservoirs

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ABSTRACT

Carbon dioxide enhanced gas recovery (EGR) is a promising technique to sequester CO_2 and boost natural gas recovery from conventional depleted and unconventional tight gas reservoirs. Clay minerals are usually present in sandstone reservoirs and their influence on the efficiency of CO_2-EGR is yet to be examined. In this study, the impact of clays on CO_2 adsorption was evaluated for different sandstone rocks with various amounts and types of clays in the temperature range from 50–100 °C and pressures up 20 bars. The results showed that the adsorption of CO_2 on sandstone rocks depends on the clay type, amount, and distribution. Clay-rich sandstone rocks, which have swellable clays such as illite, showed the highest CO_2 uptake at a temperature of 50 °C and a pressure of 20 bars with total CO_2 uptake of 4.6 and 2.6 mg/g for Kentucky and Scioto rocks, respectively. In contrast, sandstone samples with low clay content and a considerable percentage of carbonates showed CO_2 uptake just above 1.5 mg/g for Bandera sandstone and 1.1 mg/ gm for Berea sandstone at similar conditions. Moreover, raising the temperature to 75 °C decreased the CO_2 uptake on sandstones. However, the alteration of clays crystallinity at a temperature of 100 °C improves the CO_2 adsorption. Adsorption isotherm analysis revealed that at the CO_2 adsorption is monolayer at low temperature (50 °C) and pressure of 20 bars; whereas multilayer adsorption at 75 and 100 °C is predicted by Freundlich isotherm model. The thermodynamic analysis illustrated that the adsorption of CO_2 on sandstone rocks is physisorption and exothermic on Kentucky, Scioto, and Berea sandstones and endothermic on Bandera sandstone. Core flooding experiments at 100 °C revealed the potential of CO_2-EGR for clay-rich sandstone and highlighted the role of clays distribution.

1. Introduction

Increasing consumption of energy has upraised carbon dioxide (CO_2) emissions worldwide. Consequently, global warming side effects such as high-temperature levels are daily noticed (International Energy Agency (IEA), 2019; Zhang et al., 2020). Therefore, clean energy resources such as natural gas as well as sequestering CO_2 in large capacity sinks are highly demanded to reduce CO_2 levels. Among the available techniques to sequester CO_2, depleted gas reservoirs have the competency of high storage capacity under reliable cap rock sealing (Ajayi et al., 2019; Hamza et al., 2020; Huo et al., 2017; Liu et al., 2013b). Sandstone gas reservoirs are heterogeneous in nature and mainly composed of clay minerals and silica with a small amount of carbonates.

Clays are interlayer aluminosilicates minerals that have different structures. The main types of clay that could be found in typical sandstone rocks are illite, chlorite, smectite, and kaolinite. The chemical structure of illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ shows the existence of water and tetrahedral sheets of aluminum (Al^{3+}) interlayered by potassium (K^+), less commonly divalent ions such as magnesium (Mg^{2+}) and calcium (Ca^{2+}) (Civan, 2016; Hendraningrat et al., 2013). In contrast, kaolinite has a 1:1 structure and contains a Si-O layer and water-Al layer ($Al_2Si_2O_5(OH)_4$), which makes kaolinite a non-swelling and non-expandable clay type. Smectite $(Na,Ca)0.33(Al,Mg)_2(Si_4O_{10})$ has 1:2 of Al^{3+} to silica layers and exhibits a hydrational swelling in contact with water. Chlorite has a crystal structure similar to illite with an additional octahedral layer comprising Mg^{2+} or another cation ($NaClO_2$) or $(Mg(ClO_2)_2$ instead of K^+ layer in illite which

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Nomenclature

q	The estimated gas uptake, mg/g
Q_m	The maximum uptake of the adsorbed gas, mg/g
k_L	The Langmuir constant, l/bar
b	Freundlich constant
K_c	Freundlich constant
p	the pressure, bar
p_s	the saturation pressure of a gas at a given temperature
k_b	BET constant
ΔH^0_{ads}	Change in adsorption heat, kJ/mol
ΔS^0_{ads}	Change in entropy, J/mol.K
ΔG^0_{ads}	Change in Gibbs free energy, kJ/mol
R	The gas universal constant, 8.314 J/mol K
T	he temperature, K
q_e and p_e^b	The amount of gas adsorbed by Freundlich and pressure at equilibrium

provides more expandability to chlorite. The existence of clays enhances the adsorption capacity of sandstone rocks because of their high surface area (Bashir, 2018).

Sandstone rocks such as Berea and Kimachi and minerals of sandstone formations such as albite, quartz, and clays showed an adsorption affinity toward CO_2 (Fujii et al., 2010). Studies on swellable clays such as smectite depicted the intercalation of CO_2 in the layered aluminosilicates structure because of the low charge on the layers (Cygan et al., 2012). Moreover, swelling behavior has been reported for other clay types such as illite and non-swelling kinds such as kaolinite at low and high pressures even in the presence of bound water (Pang et al., 2020). Nano and mesopores surrounded by illite preferentially adsorb CO_2 over CH_4 especially when potassium (K^+) cations are present as exchangeable cations (Loganathan et al., 2020; Zhang et al., 2016). The influence of the cation exchange capacity of clays on CO_2 adsorption is believed to be significant at low pressures (about 10 bars) (Jin and Firoozabadi, 2013). On the other hand, recent studies have confirmed that the variation in adsorption capacity between the swellable and non-swellable clays is related to the cation exchange capacity which is low in non-swelling types such as kaolinite (Hu et al., 2019). The simulation results showed that montmorillonite clay mineral has the highest CO_2 adsorption capacity, followed by illite, and kaolinite. Zhou et al. (2019) found out that CO_2 has a higher adsorption ability on the kaolinite surface compared to methane. The pressure and mineral pore volume have a high impact on the adsorption capacity of both CO_2 and methane.

Many types of clays are found in the matrix structure of the sandstone rocks which prompt competitive adsorption sites toward CO_2 and CH_4. Fujii et al. (2010) revealed that CO_2 adsorption on Berea sandstones was 162 mg/g at 50 °C and 123.2 mg/g at 100 °C at a pressure of 200 bar, respectively. Eliebid et al. (2017) investigated the adsorption of CO_2 and methane (CH_4) in Kentucky sandstone at different temperatures (50–150 °C) and pressure up to 45 bar. The total gas uptake initially decreased from 143.1 mg/g to around 50 mg/g when the temperature was increased from 50–100 °C, then both CO_2 and CH_4 adsorption increased after raising the temperature to 150 °C to about 500 mg/g at 50 bar. This behavior was explained by the alteration in the crystallinity of the clays at 150 °C. Mahmoud et al. (2019) revealed that rocks with high clay content in their surfaces such as sandstone and shale have a higher affinity to adsorb CO_2 compared to CH_4 at high temperatures (> 100 °C). Accordingly, injecting hot CO_2 (at temperatures up to 150 °C) will lead to double the natural gas production gas reservoirs compared to 50 °C and hence simultaneously improve CO_2 sequestering in depleted gas reservoirs. Previous studies have revealed that CO_2-EGR could provide 53 % CH_4 recovery in tight sandstone cores which was about 18 % higher compared to the depletion stage (Wang et al., 2018a). Jia et al. (2019) showed that an average of 10 % EGR was obtained after injecting CO_2. Nevertheless, the impact of clays on the CO_2-EGR was not addressed in these studies.

Clays in sandstone rocks have a significant role in CO_2-EGR and adsorption of CO_2 in depleted gas reservoirs. However, few studies have been reported in the literature to evaluate the impact of mixed clays on CO_2-EGR and CO_2 sequestering in depleted sandstone gas reservoirs. Therefore, this study aims to investigate the effect of clay content and type on the adsorption of CO_2 in Berea, Bandera, Scioto, and Kentucky sandstones. Furthermore, it addresses the impact of temperature on CO_2 adsorption at 50, 75, 100 °C at pressures up to 20 bar. Moreover, the experimental results are used to reveal the nature of CO_2 adsorption and predict the total gas uptake at various conditions. The thermodynamic analysis is conducted to understand the CO_2 adsorption behavior on sandstone rocks. Finally, the efficiency of implementing CO_2-EGR is accomplished using core flooding experiments to simulate the dynamic reservoir conditions.

2. Experimental work

2.1. Materials

Sandstone core samples with various clay contents were obtained from Kocurek Company, USA. The samples were crushed to a small size of about 0.125 mm for characterization experiments. Intact cubes were prepared using a cutting machine in dry conditions for sorption measurements. Pure gases (purity > 99.9 %) helium (He), carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2) were supplied by a local gas supplier.

2.2. Sandstone rock characterization

The mineral composition of the sandstone samples was determined by X-ray diffraction (XRD). Whereas scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) were utilized to investigate the surface morphology of the samples and elemental analysis, respectively. Brunauer-Emmett-Teller (BET) analysis was conducted to estimate the surface area of the sandstone samples as well as pore volume.

2.3. Sorption experiments

Intact sandstone cubic samples with various mineral composition and clays content were used for the sorption experiments. The sorption measurements were conducted on Rubotherm magnetic suspension balance (MSB) set-up (Fig. 1).

Before the adsorption runs, the samples were dried at 80 °C for 24 h to remove the humidity without affecting the clay structure (Eliebid et al., 2017). Then the sandstone samples were loaded on the sample basket. The sorption procedures were as follows: blank test followed by buoyancy were done using Helium at different pressures up to 20 bar (±0.2 bar) (in 6 steps) and pre-specified temperature. The sorption measurements were accomplished at static conditions at temperatures of 50, 75, and 100 °C (±1 °C) by CO_2 which was injected at a rate of 100 mg/minute at each pressure step from atmospheric pressure up to 20 bars. The duration of each step was 30 min which was found to be enough to reach equilibrium.

2.4. Core flooding experiments

The impact of clays on the efficiency of CO_2-EGR was evaluated using a core flooding system (Fig. 2). CO_2 was injected at 1 cm^3/minute into clays-rich sandstone core samples (Kentucky and Scioto) which have a diameter of 1.5 in. and length of 6 inches. Both core samples have low permeability between 0.2 and 0.25 mD and an average porosity of 12.5

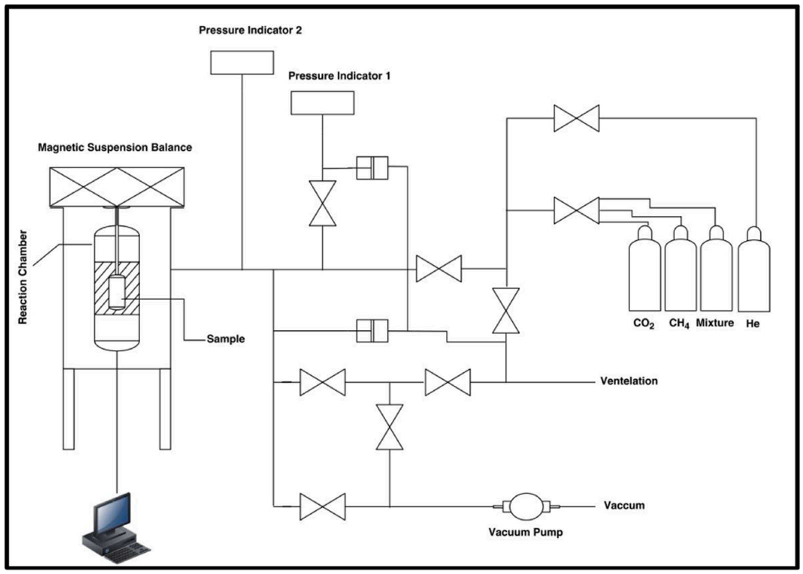

Fig. 1. Rubotherm magnetic suspension balance (MSB).

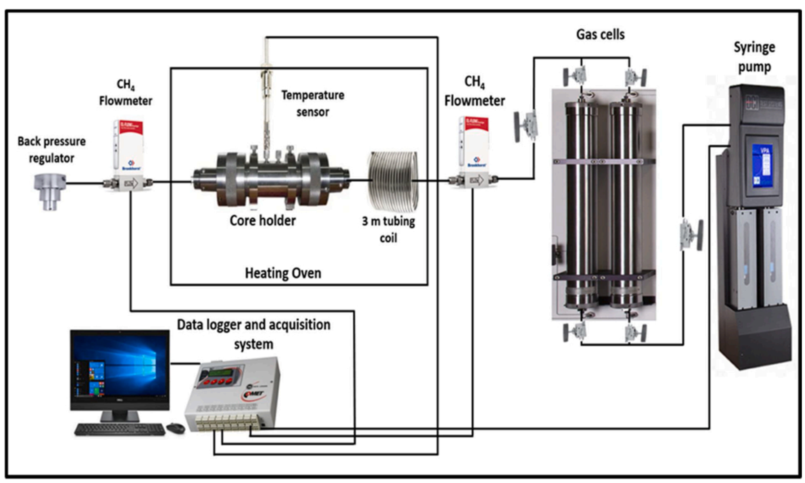

Fig. 2. Core flooding set-up.

%. Scioto sample has 7.6 m^2/mg compared to 5.1 m^2/g for Kentucky sandstone (Table 1). Table 2 describes the properties of CH_4 and CO_2 at a temperature of 100 °C.

Table 1
Properties of sandstone core samples and core flooding conditions.

Property	Kentucky	Scioto
Temperature, °C	100	100
Back pressure, psi	700	700
Flow rate, cm^3/minute	1	1
Core length, in	1.5	1.5
Diameter, in	6	6
Permeability, mD	0.2	0.25
Porosity, %	13	12
Pore volume, cm^3	22.6	20.84
BET surface area, m^2/g	5.1	7.6
Total Clay, %	14	22

Table 2
CH_4 and CO_2 properties at 100 °C.

Property	CH4	CO2
Z-factor	0.89	0.977
Viscosity, cP	0.0114	0.0146
Density, lb/ft^3	1.74	4.3

3. Results and discussion

3.1. Sandstone samples characterization

Berea, Bandera, Kentucky, and Scioto sandstones have different mineral compositions and hence various clay content in terms of quantity and distribution. Table 3 illustrates the mineralogy of the sandstone samples. Kentucky and Scioto sandstones have 14 % and 22 % clay in their composition, respectively. In contrast, Berea and Bandera have lower clay content compared to Kentucky and Scioto. Moreover, the total carbonate percent is about 16 % of the Bandera minerals. Fig. 3 shows SEM images of various clay-rich sandstone samples. Berea sandstone contains kaolinite and a low percentage of illite, chlorite, and

Table 3
Mineralogy of sandstone samples (Mahmoud et al., 2015).

Mineral	Berea	Bandera	Kentucky	Scioto
Quartz	87	57	66	70
Illite	1	10	14	18
Kaolinite	5	3	Trace	Trace
Chlorite	2	1	–	4
Plagioclase	–	12	17	5
Feldspar	3	–	2	2
Calcite	2	–	–	–
Dolomite	1	16	–	–

carbonates. Kaolinite is featured by fleecy and ragged edges in the SEM images (Du et al., 2010). In contrast, Bandera comprises about 10 % illite, about 3 % kaolinite, and a tiny amount (1 %) of chlorite.

The EDX results (Figs. 4–7) confirmed the presence of clays in the sandstone samples by the existence of other cations with Si^{+4} such as K^{+}, $Mg^{+2,}$ and Ca^{+2}. Moreover, the high percentage of K^{+} indicates the high amount of illite clay in the Scioto sandstone sample.

The XRD analysis (Fig. 8) showed the peaks of the minerals in each sandstone sample. Quartz is characterized by the peaks around 27° and 50°. Clays such as kaolinite as well as aluminosilicates such as plagioclase can be identified by the peaks below 25°. Furthermore, plagioclase also appeared at 37, 45, and 47°. Moreover, carbonate peaks appear around 30°. Feldspar peaks are in diffraction angles, 27 and 37°. Illite is overlapping other aluminosilicates peaks at 27, 37, 42, and 45° (Eliebid et al., 2017).

3.2. *Effect of clays on CO_2 adsorption*

Sandstone samples with different clay content have been exposed to CO_2 to evaluate the impact of clay type and amount on CO_2 adsorption. Fig. 9 depicts the adsorption/desorption of CO_2 on the surface of clay-rich sandstones at 50 °C and pressure up to 20 bar. Kentucky sandstone revealed the highest CO_2 uptake (4.6 mg/g ± 300 micrograms) at a temperature of 50 °C and a pressure of 20 bars because of the high percent of illite and other aluminosilicates such as feldspar and plagioclase which have similar mineral composition to clays but with a different structure. The heterogeneity, variety of minerals, and their distribution on the sandstone surface control CO_2 adsorption. Scioto sandstone has more illite compared to Kentucky; however, the total CO_2 uptake in Kentucky was 1.8 times Scioto. This can be attributed to the presence and distribution of non-expandable clays such as chlorite, which has a lower surface area compared to illite, on the surface of Scioto sandstone. Additionally, the quantity of aluminosilicates such as plagioclase is greater in Kentucky compared to the Scioto sample which provides more adsorption sites for CO_2 and hence extra storage capacity.

Fig. 10 shows the schematics of the proposed mechanism of CO_2 adsorption in clays. CO_2 is adsorbed on the surface of the clay as well as in the interlayer space between the layer structure because the size of the CO_2 molecule diameter is less than the interlayer distance (Okolo et al., 2019). Many factors in clay structures such as cation exchange capacity, charge on the clay surface and interlayer distance result in the various capacities of CO_2 adsorption as well as selectivity in the case of mixed clays are found (Jin and Firoozabadi, 2013; Liu et al., 2013a;

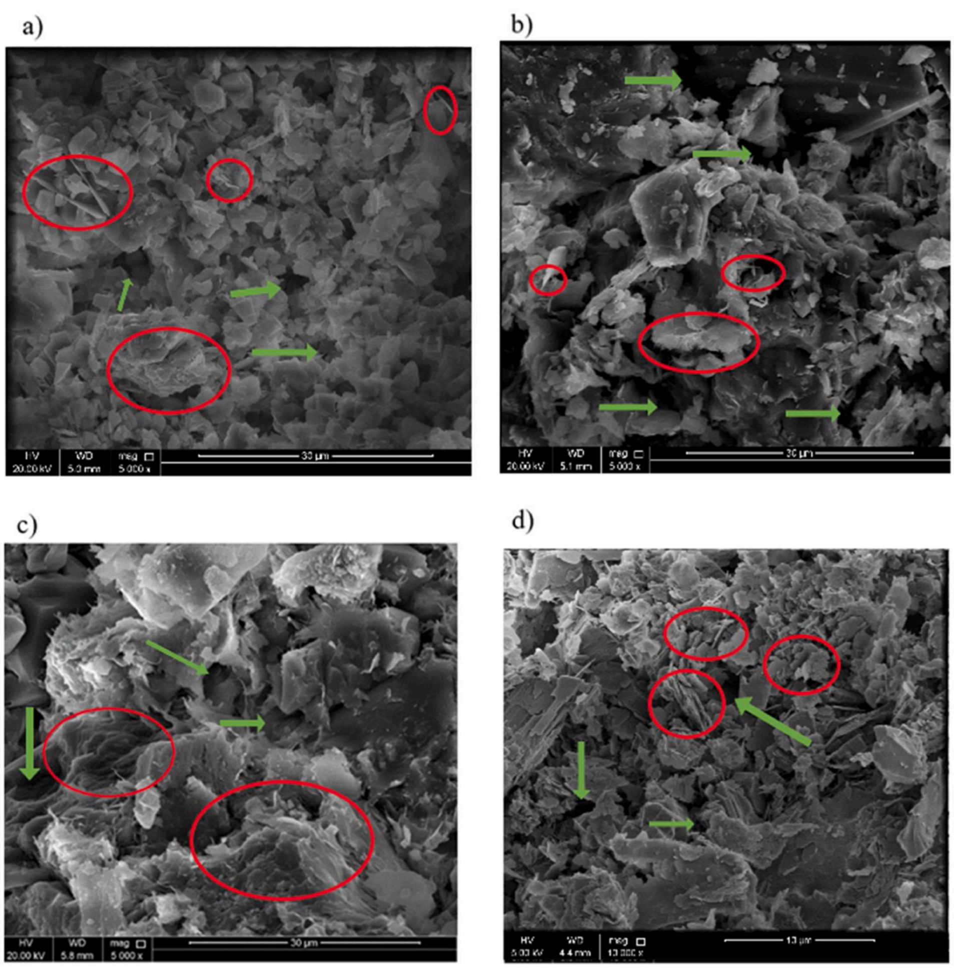

Fig. 3. SEM images indicating clays (red circles) and pores (green arrows) in a) Berea, b) Bandera and c) Kentucky at a resolution of 30 μm and d) Scioto at a resolution of 10 μm.

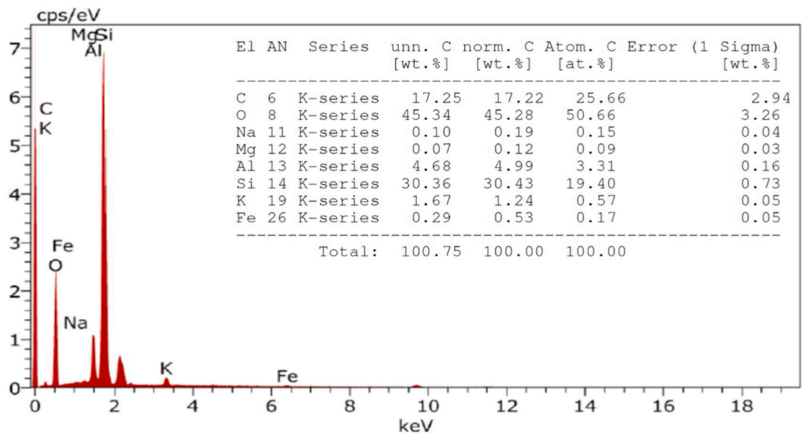

Fig. 4. EDX elemental analysis of Berea sandstone.

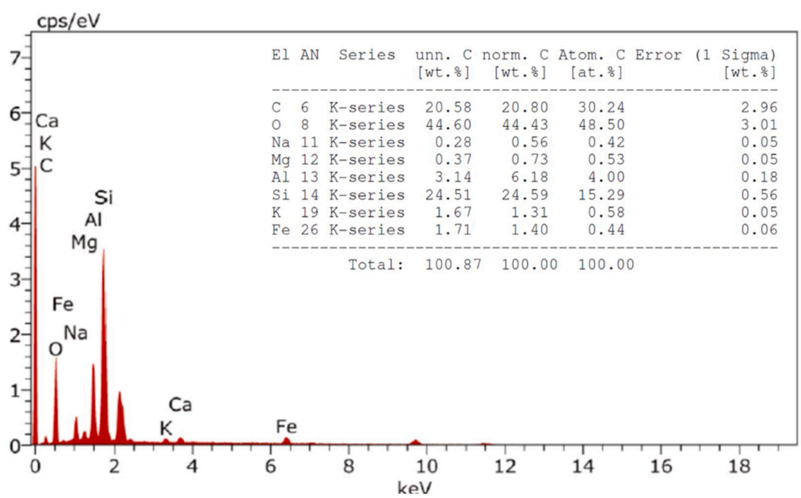

Fig. 5. EDX elemental analysis of Bandera sandstone.

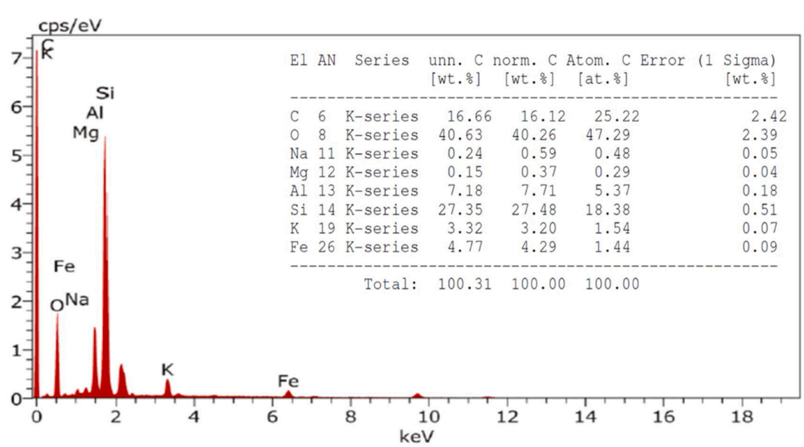

Fig. 6. EDX elemental analysis of Kentucky sandstone.

Zhang et al., 2016).

3.3. Effect of temperature on CO_2 adsorption in sandstone rocks

The impact of reservoir temperature was simulated by increasing the temperature up to 75 and 100 °C, respectively. Increasing the temperature to 75 °C reveals a drop in the adsorbed amount of CO_2 on the surface of sandstone rocks. This reduction is obvious since the temperature decreases the affinity of the CO_2 molecules to the rock surface. Bandera sandstone showed the lowest drop in the CO_2 adsorption because these conditions are within the range of favorable conditions of adsorbing CO_2 on carbonate minerals. Fig. 11 illustrates the results of CO_2 adsorption on sandstone rock samples at a temperature of 75 °C. The drop of CO_2 uptake at pressures above 16 bar could be due to the

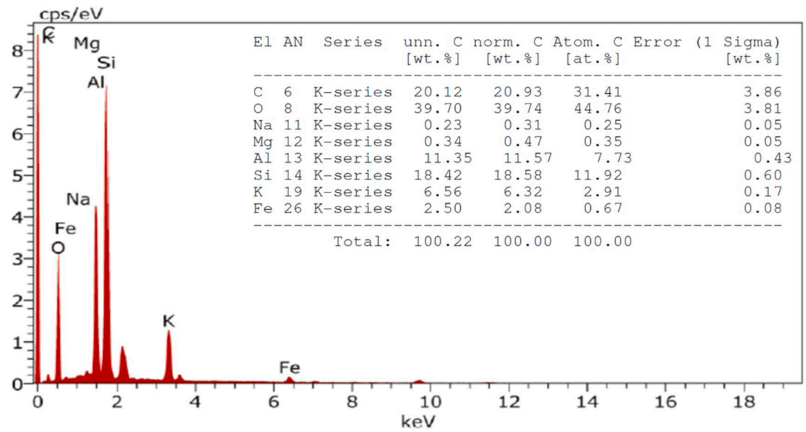

Fig. 7. EDX elemental analysis of Scioto sandstone.

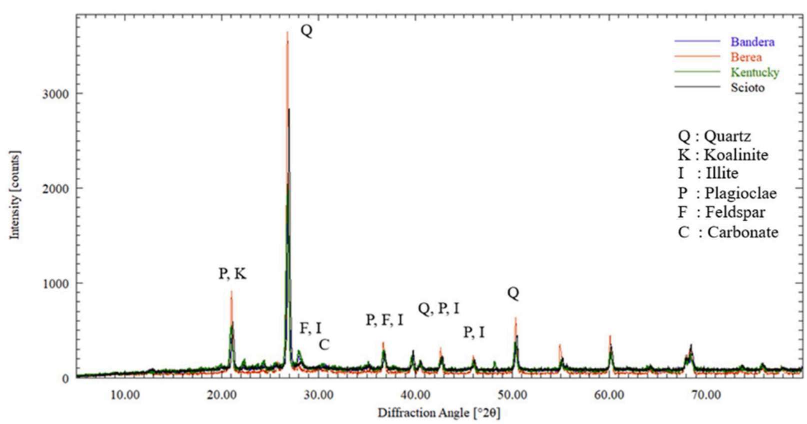

Fig. 8. XRD analysis of sandstone samples.

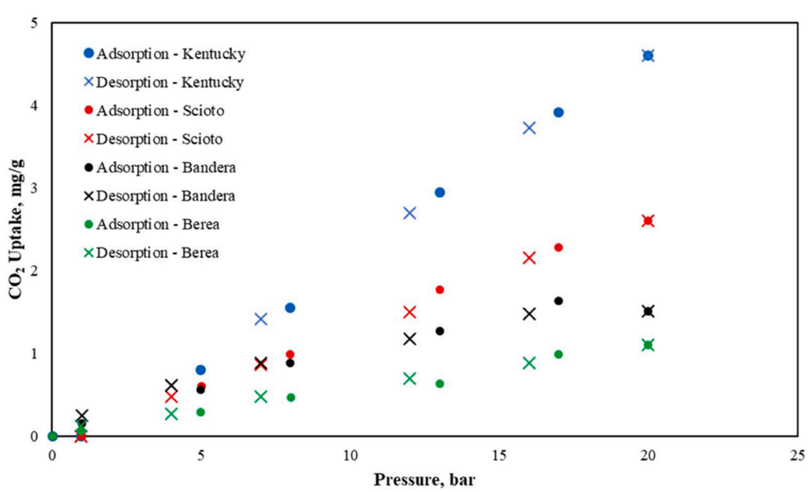

Fig. 9. CO_2 adsorption/desorption in different sandstone rocks at 50 °C.

effect of buoyancy of the adsorbed CO_2 volume and change in CO_2 density. A similar trend even at high pressures has been reported previously for CO_2 adsorption on silicate minerals (Fujii et al., 2010).

Raising the temperature to 100 °C shows an increase in CO_2 adsorption compared to the adsorbed amount of CO_2 at 75 °C for all sandstone samples. This upraises in the CO_2 uptake on the sandstone rocks are attributed to the change in the clays' crystallinity. Fig. 12 reveals CO_2 uptake at a temperature of 100 °C on sandstone rocks.

Fig. 13 shows an example of Kentucky samples that were heated at 50, 75, and 100 °C and analyzed for XRD after cooling down to room temperature to reveal the change in crystallinity. The crystallinity alteration of clays is barely noticed at 100 °C and is expected to be more obvious at temperatures higher than 100 °C as shown in our previous work (Eliebid et al., 2017). It should be noticed that water evaporation from clay is ruled out as a possible reason since water is still in the liquid state at such high pressures for all of the temperature range covered in

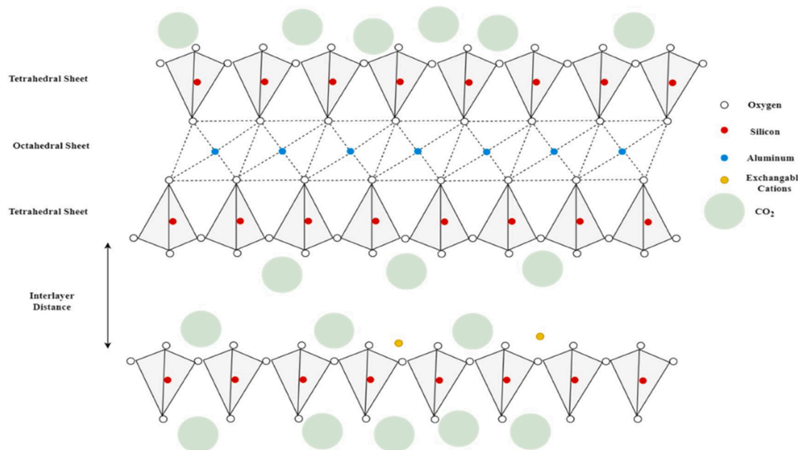

Fig. 10. Adsorption of CO_2 on the clay surface and between the interlayers.

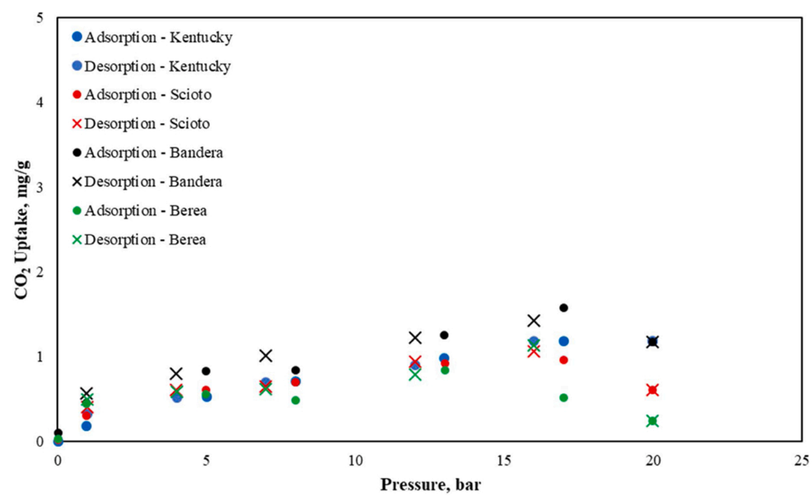

Fig. 11. CO_2 adsorption/desorption in different sandstone rocks at 75 °C.

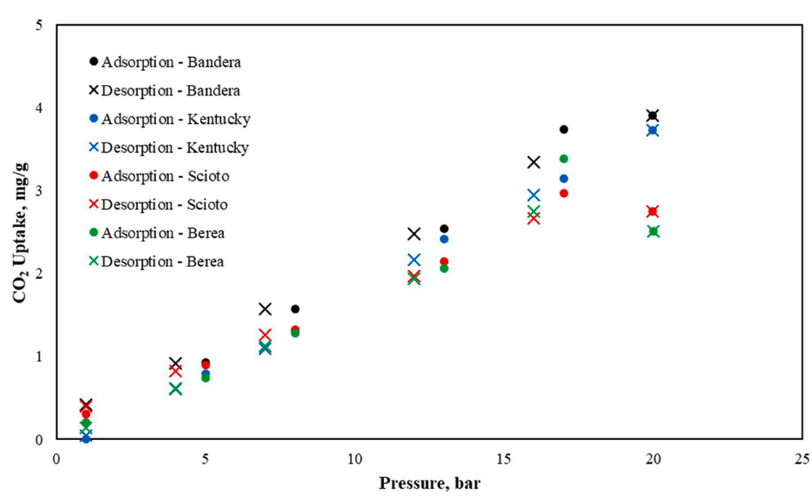

Fig. 12. CO_2 adsorption/desorption in different sandstone rocks at 100 °C.

this study. At pressures up to 20 bars and a temperature of 50 °C, smectite clay has a better affinity toward CO_2 compared to illite and kaolinite. Whereas adsorption of CO_2 on chlorite surface is negligible at similar pressure and temperature (Busch et al., 2016, 2008). Therefore, sandstone samples with high illite and kaolinite content such as Kentucky and Scioto have shown higher CO_2 uptake compared to Berea and Bandera. Nevertheless, competitive adsorption on the minerals of sandstone rocks hinders the high uptake at low pressures in the range of depleted reservoirs.

However, previous work on CO_2 adsorption on Kentucky sandstone

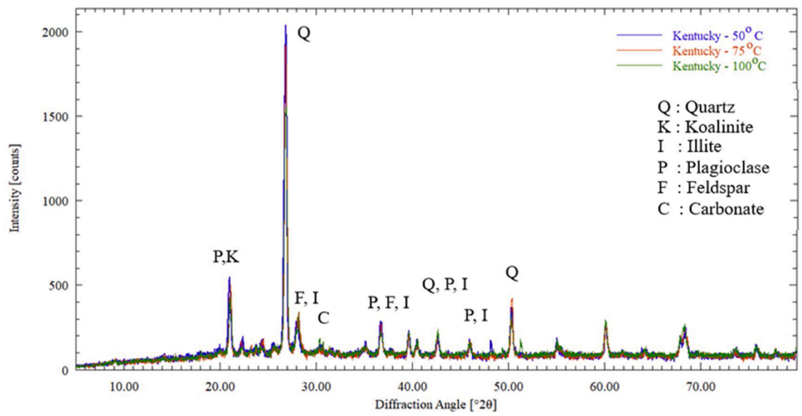

Fig. 13. XRD analysis of Kentucky sandstone sample at various temperatures.

at a higher pressure range (up to 45 bars) has revealed the large adsorption capacity of sandstone reservoirs (Eliebid et al., 2017). Moreover, access to interlayer adsorption sites in clays and aluminosilicate minerals requires high pressures because of the small distance between the aluminum sheets (Liu et al., 2013a). Therefore, the adsorption of CO_2 in clays interlayers contributes to improving CO_2 uptake (Wan et al., 2018). Furthermore, interlayer water in the structure of the clays could be expelled at a temperature higher than 100 °C depending on the pressure. Fig. 14 summarizes the influence of temperature on the CO_2 adsorption in various sandstone rocks at a temperature range between 50–100 °C and pressure of 20 bars.

3.4. Adsorption isotherms

Standard isotherm models such as Brunauer-Emmett-Teller (BET), Freundlich, and Langmuir have been implemented to understand the nature of gas adsorption on adsorbents. Langmuir isotherm model depicts the monolayer cover of gas molecules on a rock surface based on the following formula:

$$q = \frac{Q_m k_L p}{(1 + k_L p)} \tag{1}$$

The Freundlich isotherm model shows adsorption of multilayers' of gas molecules on a rock surface considering the variation of energy on the surface. Freundlich model is expressed by:

$$q = K_c p^b \tag{2}$$

Brunauer, Emmett, and Teller (BET) model considers forming multilayers on the surface of an adsorbent. BET model is described mathematically as follows:

$$q = \frac{Q_m k_b p}{(p_s - p)[1 + (k_b - 1)\frac{p}{p_s}]} \tag{3}$$

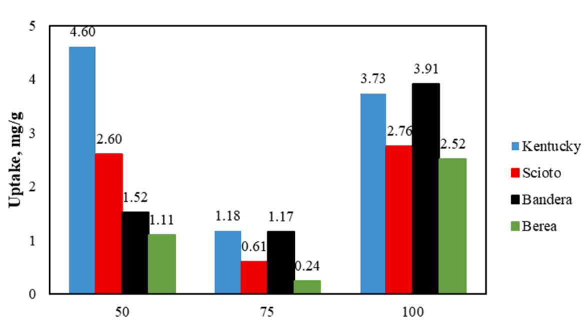

Fig. 14. Effect of temperature on CO_2 adsorption on sandstone rocks.

Single-layer and multilayer isotherm models were applied to fit the adsorption experimental results to determine the type of adsorption on sandstone rock surfaces at various temperatures.

Table 4 reveals the predicted amount of CO_2 to be adsorbed on the sandstone rocks at 5075 and 100 °C. Langmuir isotherm fits the adsorption measurements at 50 °C, while both Freundlich and BET isotherms showed better fit at 75 and 100 °C. This variation in data fitting at elevated temperatures can be explained by the build-up of multilayers of CO_2 molecules on the surface of sandstone rocks because increasing the temperature from 50 °C to 75 °C will increase the distance between the gas molecules which enable more CO_2 molecules to be attached to the rock surface. However, the decrease in the adsorbed amount of CO_2 is because of the repulsion force between the adjacent CO_2 molecules is greater than the attraction force between the molecules and sandstone rock surfaces. Furthermore, the rise of temperature to 100 °C leads to an increase in the CO_2 uptake because of the alteration in clays crystallinity.

3.5. Thermodynamics of CO_2 adsorption on sandstone rocks

Recognizing the drives, potential, and strength of the adsorption of CO_2 molecules on sandstone surfaces can be obtained by understanding the thermodynamics of the process. Gibb's free energy, ΔG^0_{ads}, the standard entropy, ΔS^0_{ads}, and the standard heat of adsorption, ΔH^0_{ads} (equation 4–6) of CO_2 on the rock surface are generally used as indicators of the strength of the gas adsorption on the rock surface:

$$\Delta G^0_{ads} = -RT\ln K_c \tag{4}$$

$$\ln K_c = \frac{\Delta S^0_{ads}}{R} - \frac{\Delta H^0_{ads}}{RT} \tag{5}$$

$$K_c = \frac{q_e}{p_e^b} \tag{6}$$

Freundlich isotherm constants were used to estimate the thermodynamic properties by plotting $\ln K_c$ vs. 1/T in Kelvin. Then, ΔH^0_{ads} is estimated from the slope of the plot while ΔS^0_{ads} is calculated from the intercept. Table 5 shows the estimated values of Gibbs free energy, adsorption heat, and entropy of the sandstone rock samples. The negative values of the heat of adsorption indicate the physisorption nature of CO_2 adsorption on sandstone rocks surfaces.

It can be noticed that the value of the heat of the adsorption increases with the temperature which indicates that the adsorption is favorite at elevated temperatures (>100 °C). The obtained trend matches the findings in the literature (Eliebid et al., 2017; Mahmoud et al., 2019). Nevertheless, no universal models can be generated for the thermodynamic parameters since CO_2 adsorption depends on clays types and distribution in the rock matrix as well as the temperature. Generally, two

Table 4
Model fitting parameters for adsorption of CO_2 on sandstone rocks at different temperatures.

Isotherm Model	Parameter	Kentucky			Scioto			Berea			Bandera		
		50°C	75°C	100°C	50°C	75°C	100°C	50°C	75°C	100°C	50°C	75°C	100°C
Langmuir	Q_m	35,343.5	35,000	35,343.54	35,343.54	35,343.54	35,343.54	35,343.54	35,343.54	35,343.54	35,343.54	35,343.54	35,343.54
	k_L	6.38E-06	1.95E-06	5.20E-06	4.45E-06	1.47E-06	4.45E-06	1.57E-06	9.42E-07	4.45E-06	2.53E-06	2.32E-06	5.75E-06
	R^2	0.989	0.990	0.992	0.997	0.960	0.950	0.999	0.960	0.874	0.986	0.926	0.989
	SSE	0.226	0.079	0.079	0.030	0.324	0.289	0.007	0.324	0.909	0.144	0.422	0.127
Freundlich	K_c	0.133	0.199	0.130	0.133	0.351	0.257	0.056	0.351	0.215	0.197	0.440	0.186
	b	1.190	0.611	1.125	1.190	0.000	0.822	0.994	1.190	0.886	0.712	0.384	1.031
	R^2	0.989	0.999	0.997	0.998	0.960	0.966	0.999	0.991	0.880	0.995	0.990	0.990
	SSE	0.055	0.005	0.028	0.024	0.049	0.196	0.010	0.010	0.869	0.052	0.122	0.122
BET	Q_m	10.587	1.107	7.195	4.252	0.658	3.385	1.671	0.414	3.650	1.631	1.072	6.359
	k_b	1.291	11.520	1.673	2.263	69.141	4.962	2.543	644.537	4.179	7.690	36.590	2.380
	P_s	73.7	73.7	73.7	73.7	73.7	73.7	73.7	73.7	73.7	73.7	73.7	73.7
	R^2	0.995	0.999	0.995	0.997	0.964	0.964	0.999	0.985	0.854	0.995	0.980	0.988
	SSE	0.219	0.006	0.048	0.067	0.051	0.207	0.019	0.136	0.884	0.100	0.137	0.138

ranges exist based on the alteration in clays crystallinity can be identified based on the temperature. Furthermore, CO_2 adsorption on sandstone rocks depends on the temperature at which no further changes occur on the clays minerals which makes the estimation of the total uptake very complicated since the aluminosilicates exhibit morphology alterations at the reservoir conditions of temperature and pressure (Busch et al., 2016).

The estimated values of the heat of adsorption indicate that CO_2 adsorption is exothermic on Kentucky, Scioto, and Berea whereas s the adsorption is endothermic on Bandera sandstone. The endothermic behavior of CO_2 adsorption on Bandera sandstone could be due to the high carbonate content. The negative values of the change of entropy imply that CO_2 adsorption on sandstone rock samples is transforming from a random state to an ordered state (Du et al., 2020).

3.6. *Impact of clays on CO_2-EGR*

Sorption measurements revealed that clay-rich sandstone rocks have a high affinity toward CO_2. Accordingly, the efficiency of displacing CH_4 by injecting CO_2 into clays-rich sandstone (Kentucky and Scioto) was evaluated at a temperature of 100 °C to simulate the real reservoir conditions. Fig. 15 displays the process of CO_2-EGR in sandstone core samples. Initially, the sandstone core samples were flooded with only methane for three pore volumes at an injection rate of 1 cm^3/minute. Then, CO_2 was injected at a similar injection rate to displace CH_4.

The core flooding results show that some methane was retained physically in both cores and this phenomenon is believed to be because of the clays. The methane retention was higher in the low clay content sample (Kentucky) compared to the high clay content sample (Scioto). However, CO_2 performed better in the high clay content and recovered more gas. Previous experiments showed that most of the clays are dispersed in the pores, this was investigated before by injecting acids and fresh water and both confirmed the contact of the clays with the injected fluids. For example, when fresh water was injected, the damage in Scioto was higher compared to Kentucky because of the higher clay content.

The CO_2 breakthrough in the Scioto core was almost four minutes late compared to that in the Kentucky core sample. This delay can be attributed to that Scioto has more clay content compared to Kentucky. More clays in the Scioto core adsorbed more CO_2 and delayed its breakthough and this showed the advantage of EGR in high clay content sandstone compared to low clay sandstones. Scioto reservoirs will retain more CO_2 compared to Kentucky reservoirs, in addition to the high storage capacity, Scioto core sample has yielded more methane recovery compared to Kentucky due to more adsorption of CO_2. The methane recovery from both cores can be determined by the area under the curve. The area under the curve in the case of Scioto core is 19.5 cm^3 and this represents a recovery factor of 93.5 % (area under the curve/pore volume). In the case of Kentucky core, the area under the curve was 18 cm^3 and this represents a recovery factor of 82 %. The methane recovery was higher in addition to the CO_2 storage as well in high clay content sandstones (Scioto).

Sorption measurements have illustrated that not only clay amount has an influence on CO_2 adsorption but also clay type since clays contain different surface areas and hence varying capacity to store CO_2. Moreover, clays have a significant impact on the CO_2 adsorption. Previous studies showed that CH_4 has a low affinity toward clays such as illite in clay-rich rock samples (Cheng and Huang, 2004; Ji et al., 2012; Mahmoud et al., 2020). Furthermore, methane retention was also reported implicitly during the CO_2-EGR core flooding in tight sandstone cores (Wang et al., 2018b).

4. Conclusions

CO_2 adsorption was studied on different sandstone rocks that have various amounts and types of clays at a reservoir temperature range

Table 5
Thermodynamic parameters of CO_2 adsorption on sandstone rocks at different temperatures.

#	Kentucky			Scioto			Berea			Bandera		
Temperature, °C	50	75	100	50	75	100	50	75	100	50	75	100
-ln K	−2.018	−1.615	−2.042	−1.358	−1.047	−2.178	−1.535	−1.027	−2.874	−1.681	−0.820	−1.624
ΔG (kJ/mol)	−5.420	−4.672	−6.332	−3.646	−3.030	−6.754	−4.123	−2.971	−8.912	−4.514	−2.373	−5.035
AVG ΔG (kJ/mol)	−5.475			−4.477			−5.335			−3.974		
ΔH (kJ/mol)	−0.072			−15.764			−25.715			1.949		
ΔS (J/mol.K)	−1.917			−6.978			−10.703			−0.701		

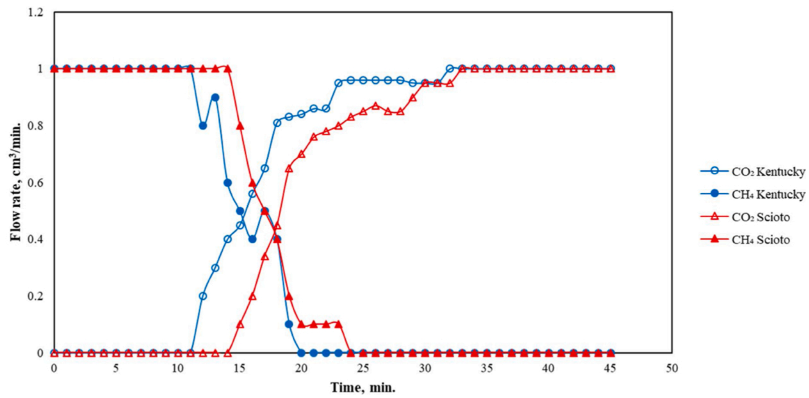

Fig. 15. CH_4 displacement by injecting CO_2 in core flooding set-up at 100 °C.

from 50–100 °C and pressure up to 20 bars. Based on the obtained results, the following conclusions can be drawn:

- Sandstone rocks contain high swellable clay content such as illite showed the highest CO_2 uptake at a temperature of 50 °C and pressure of 20 bars.
- Raising the temperature to 75 °C decreased the CO_2 uptake on sandstones. However, the alteration of clays crystallinity at a temperature of 100 °C improves the CO_2 adsorption.
- At low temperature (50 °C) and pressure of 20 bars, the CO_2 adsorption is believed to be monolayer while multilayer behavior is dominant at 75 and 100 °C.
- The thermodynamic analysis illustrated that the adsorption of CO_2 on sandstone rocks is physisorption and exothermic on Kentucky, Scioto, and Berea samples whereas endothermic behavior was found on Bandera.
- Core flooding experiments at 100 °C revealed the potential of CO_2-EGR in clay-rich sandstone where the higher the clay content provided the highest methane recovery.

CRediT authorship contribution statement

Ahmed Hamza: Conceptualization, Methodology, Writing - original draft, Writing - review & editing. **Ibnelwaleed A. Hussein:** Conceptualization, Data curation, Writing - original draft. **Mohammed J. Al-Marri:** Methodology, Writing - original draft, Writing - review & editing. **Mohamed Mahmoud:** Conceptualization, Methodology, Writing - original draft. **Reyad Shawabkeh:** Conceptualization, Methodology, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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