Influencing Factors and Mathematical Prediction of Shale Adsorbed Gas Content in the Upper Triassic Yanchang Formation in the Ordos Basin, China

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Abstract: Evaluating absorbed gas content (AGC) in shales is crucial for accurately characterizing shale gas reservoirs and calculating resource potential. To investigate geological factors influencing AGC, 15 shale samples collected from the Yanchang Formation underwent related experiments. Then geochemistry features, mineral compositions, pore structure parameters and external factors were analyzed. The actual AGC was calculated using the Langmuir equation. Single geological factors acting on the AGC were discussed by the single-factor correlation analysis. Finally, four main influence factors (total organic carbon, S1, quartz content and formation temperature) were selected out from the 12 influence factors to establish the mathematical prediction model through the multi-factor regression statistical analysis method using SPSS software. The model was verified as being reliable with $R^2$ as high as 0.8046 and relative error less than ±20%. Comparisons show that both the CH4 isothermal adsorption experimental method and the multi-factor regression analysis method have their own applicability and disadvantages, and they can complement each other in evaluating AGC in shales. Synthetic evaluation of AGC indicates that the Yanchang shale has an overall moderate AGC occupying about 58% of the total, which is helpful to extend shale gas production time of the Yanchang reservoir. Though under the present conditions, economic benefits of the continental shale gas are not obvious, the shale resource potential of Yanchang formation can’t be ignored.

Keywords: influence factor; mathematical prediction; absorbed gas content; Yanchang shale; Ordos Basin

1. Introduction

Unconventional oil and gas development from shales has revolutionized the world energy landscape, especially shale gas [1,2]. Marine shale gas in China, represented by Longmaxi formation shale in the Sichuan Basin, has achieved considerable production, showing great shale gas potential [3]. In contrast, most of the continental shale gas in China is still in the resource evaluation stage due to its low maturity and lower gas show in exploration wells [3–5]. Accurate acquisition of shale gas content is of great significance for analyzing gas accumulation and assessing gas resources [6–11].
Based on occurrence forms, shale gas can be classified into free gas, adsorbed gas and dissolved gas, whose occurrence sits and content in the pore space are quite different [1,10,12]. The adsorbed gas is mainly absorbed on the surface of organic matter (OM) and clay mineral particles [13], free gas is generally stored in organic pores, matrix pores and fractures, while dissolved gas is slightly dissolved in kerogen, bitumen and residual oil [1,14–18]. The relative proportions of shale gas in different occurrence forms varies for different reservoirs, and is restricted by many geological factors, which therefore affect shale gas reservoir assessment and production characteristics greatly [5,19–21]. Since the absorbed gas content (AGC) in shales has been the focus of intense interest, its calculation method has become one of the biggest concerns [1,7,16,22,23].

Generally, there are two primary methods to obtain AGC, namely, the direct laboratorial experimental method and the indirect equation method [24,25]. The direct method refers to calculating AGC through the methane isothermal adsorption experiment and the Langmuir adsorption model [7,9,26]. Using the adsorption model to study the adsorption performance is mainly based on non-linear fitting of the methane adsorption isotherms to obtain parameters of physical significance [27–30]. Among the conventional adsorption models, the Langmuir adsorption model is widely used [21,28,30,31]. On the other hand, some scholars calculate AGC by analyzing the geological factors that affect it and establish calculation models by regression fitting because of the good spatial continuity of these factors in shale formations [32–38]. Thus, the indirect equation method is also widely applied to calculate AGC in shale formations [11,34,39]. Studies show that AGC is the result of various geological factors, and numerous scholars have conducted studies on the influence factors of gas adsorption content and concluded that it is controlled by factors like total organic carbon (TOC) content, shale mineral compositions, pore structure, formation temperature and pressure conditions [10,19,36,40–43]. Different sedimentary environments have made shale mineral compositions complex, while clay minerals, quartz, calcite, feldspar and other minerals are also important [7,44–47]. Pore structure features could significantly affect the occurrence state of shale gas and the AGC in it [48,49]. In addition, temperature and pressure are also main factors affecting AGC [20,50–52]. For shale gas in different environments, the main controlling factors are quite different, resulting in different AGC and relative proportions in adsorbed forms in shales.

As gas adsorption in organic shales is a complex multi-factor process, comprehensive qualitative evaluation of various influence factors and quantitative mathematical predication of gas adsorption content appear to be particularly important [53]. In this study, 15 samples from the drilling core in the upper Triassic Yanchang shales in the Ordos basin were carried out a series of laboratory experiments. Then systematical analysis was made about the geological factors that may affect AGC, and the main influence factors were optimized through the single-factor correlation analysis. On the basis of this, a multi-factor regression prediction model was established by SPSS software, and the reliability of the prediction model was verified by the experimental results. Finally, AGC obtained from CH4 isothermal adsorption experiments and calculated by multi-factor prediction regression models were compared. Combined with the production features, a comprehensive evaluation of shale gas adsorption capacity of Yanchang shales was further discussed. This study has important consequences for accurately assessing AGC in shales and designing effective production strategies of the Yanchang shale gas reservoir.

2. Samples and Experiments

2.1. Samples

Fifteen shale samples were obtained from well YY22 cores in the Yanchang Formation, which were taken from a burial depth ranging from 1313.11 m to 1350.64 m. Geological researches show that the Ordos Basin is one of the biggest petrolierous basins in China, and research has demonstrated it has huge shale gas potential [54]. The Yanchang Formation has the most potential strata, which are deposited in the deep-lacustrine and lacustrine depositional environment, and mainly consist of
gray-green, gray-yellow-green, and pale flesh-red feldspar and sandstone interbedded with dark-green shale and coal [54–56]. In addition, the Ordos Basin has currently the largest continental shale gas production region in China, well YY22 is one of the most important production wells, whose field analytical gas quantity range from 1.24 m$^3$/t to 2.34 m$^3$/t for the coring interval, typical representative of the Yanchang shales in the Ordos Basin.

2.2. Experiments

All samples were assessed experimentally using TOC content measurements, Vitrinite reflectance ($R_o$) analysis, rock pyrolysis analysis, X-ray diffraction (XRD) tests, Field Emission Scanning Electron Microscope (FE-SEM) observation, low-pressure nitrogen ($N_2$) adsorption, nuclear magnetic resonance (NMR) porosity experiment, pulse-decay permeability testing and $CH_4$ isothermal adsorption experiment.

A Rigaku D/max-2500PC instrument (Tokyo, Japan) was used to conduct the XRD tests. Before testing, all samples were ground into less than 0.04 mm. The TOC content was measured by the LECO CS230 carbon-sulfur analyzer (St. Joseph, MO, USA), the inorganic carbon portion was removed first and then samples were crushed to 0.15 mm particle size. Rock-eval pyrolysis was conducted on an OGE-II rock pyrolyzer (RIPED, Beijing, China) to obtain pyrolysis parameters ($S_1$ and $S_2$) after samples were crushed to 0.2 mm, then the crushed samples were heated from 300 °C to 600 °C with nitrogen as carrier gas under non-oxidative conditions. Equivalent vitrinite reflectance ($R_o$, %) values were obtained by an MPM-80-type micro-spectrophotometer at 23 °C and a relative humidity less than 70%. However, sample 12 did not have measurement points because of the poor vitrinite enrichment. Therefore, only 14 $R_o$ data were obtained. Chloroform bitumen “A” was obtained by Soxhlet Extraction method after the rock samples were crushed into powder smaller than 0.09 mm, the extraction time was 72 h, then the group components of Chloroform bitumen “A” were calculated by the method of column chromatography.

Porosity parameters of samples were conducted by the RecCore-04 low magnetic field NMR analyzer (CNPC, Beijing, China), whose test conditions as follows: echo spacing was 0.6 ms, salinity uniform was 33,000 ppm, waiting time was 5 s, the maximum echo number was 2048 and the scanning number was 64. All the operations follow the SY/T 6490-2007. Then porosity and saturation were obtained by the NMR geometric mean $T_2$ ($T_{2g}$) and producible porosity (PP) models, respectively. Permeability was measured using the PDP-200 permeability meter (Corelab, Dallas, TX, USA) according to API the RP-40 standard, under the condition of RT 26 °C, humidity 30% and simulated formation overburden pressure (maximum pressure 70 MPa). The klinkenberg permeability was measured by the pulse-decay method from unsteady state based on the transient fluid pressure transmission process [57,58]. The measurement range is 0.00001–10 mD, and the laboratory determined permeability is the apparent value depending on flow conditions, here nitrogen is the operating media.

FE-SEM observations were conducted on part of the shale samples. Ar-ion polishing was done for some samples to reduce the surface roughness of the shale samples. To create a smooth surface for clear pore observation, some selected samples were polished with Ar-ion using a Hitachi Ion Milling System IM4000 (Tokyo, Japan). The acceleration voltage was 3 KV and the use time was 3 h. The polished samples were then coated with Au to prevent electrostatic charging. The experiments were conducted using a Zeiss SUPRA 55 Sapphire FE-SEM (Carl Zeiss, Heidenheim, Germany) equipped with secondary electron, backscattered electron detectors and an energy-dispersive spectrometer. These samples were scanned by FE-SEM at a working distance of 5 mm and an accelerating voltage of 15 kV.

A Quadrasorb™ SI Surface Area Analyzer (Quantachrome, Boynton Beach, FL, USA) was used for the low-pressure $N_2$ adsorption experiments, and then a Pore Size Analyzer was used to obtain related parameters under −196 °C and relative pressure ($P/P_0$) is 0.01–0.995. Before the experiment, 60–80 mesh size samples (about 200–500 mg) were degassed at 150 °C for 20 h in a vacuum oven to remove the bound water, pore filling water, volatiles, hydrocarbons and other impurities on the surface. Powdered samples (nearly 60–80 mesh and about 15 g) were dried at 105 °C for 24 h to fully
remove moisture and impurities on the surface of the sample, and then conducted the CH$_4$ isothermal adsorption experiments with the highest temperature 120 °C and the highest pressure 18 MPa.

3. Results

3.1. Organic Geochemistry Characteristics

Figure 1a presented the OM abundance and OM maturity. It showed that TOC content was in the range of 1.37–7.44 wt % (average 5.00 wt %), $R_o$ values ranged from 0.71% to 1.06% (average 0.93%). Results indicated that these shale samples were abundant in OM and they were in the mature stage, which means large amount of oil and gas was generated, the generated gas and residual oil can coexist in shale pores. According to D. W. Van Krevelen chart, OM types were divided [59], shown in Figure 1b, the value of H/C was 0.82–1.14, O/C was 0.11–0.17, so these shale samples could be classified into type II. Due to the thermal evolution, the current range of H/C has reduced and O/C in kerogen has increased compared to the original kerogen thus the real kerogen type of organic matter is prone to sapropelic, indicating the Yanchang shales are better hydrocarbon source rocks. The results are consistent with previous studies [54].

![Figure 1.](image)

3.2. Mineral Compositions

As Figure 2 shows, there was a wide range of mineral constituents in these samples, clay minerals and quartz were two dominated compositions. The average content of the clay mineral was 48.3 wt % (24.5–60.8 wt %), the average content of quartz was 24.5 wt % (7.2–39.6 wt %), indicating that Yanchang shales were clay-rich shales. The third abundant mineral was feldspar (anorthose and orthoclase), followed by carbonates (calcite, dolomite and ferrodolomite). Pyrite was a fine-grained mineral widely distributed in shale gas reservoirs, and it was also a typical mineral for identifying the sedimentary environment for OM enrichment.
3.3. Pore Structure Characteristic

3.3.1. Pore Types

In the FE-SEM images, the Yanchang shales were very tight, and their pores were mainly micro and nano scales, with diameter ranging from 6.25 nm to 433.2 nm, displaying heterogeneous pore structures. In Figure 3a–c, the OM was associated with clay minerals, the OM pores were irregular but not developed due to the low thermal evolution degree. The intergranular pore was the dominating pore system in the Yanchang shales. They were largely developed between minerals and quartz grains, and they were typically irregular polygons (Figure 3d–f). Pyrite framboid was the most developed pyrite type in the Yanchang shale matrix, and OM were generally filled with the pyrite framboids, thus a lot of organic nanopores were developed in the intergranular organic matter. Intercrystallite pores were identified within incompletely filled pyrite framboids and quartz grains (Figure 3g,h). Fracture pores (widths 33–200 nm; lengths about 5 µm) were also observed, whose shapes were irregular elongated lines generally existing along grain rims (Figure 3i).

3.3.2. Pore Structure Parameters

The experimental N₂ adsorption/desorption isotherms of Sample 1 and Sample 7 are illustrated in Figure 4. Based on the IUPAC classification, isotherms of both of the two samples fell in Type IV (isotherms with hysteresis loop) [60], thus indicating the shale samples contained mesopores and macropores [61]. When the value of P/P₀ was less than 0.45, the adsorption branch of isotherms was coincident with the desorption branch, suggesting that small pores were accessible via a single pore throat. As the value of P/P₀ increased, the adsorption and desorption branches gradually separated, leading to the formation of a hysteresis loop at relative pressures of 0.45–1 (Figure 4), which can be attributed to the difference between the adsorption and desorption mechanism corresponding to condensation and evaporation, respectively, indicating that the studied shale samples contained mesopores [61].
calculated by the multi-point BET equation \cite{62}, and the results showed that the SSA of these shale specific surface area (SSA), pore diameter (PD) and pore volume (PV). The equivalent SSA can be attributed to the difference between the adsorption and desorption mechanism corresponding to leading to the formation of a hysteresis loop at relative pressures of 0.45–1 (Figure 4), which can be mesopores \cite{61}.

Moreover, the average PD of the studied shale samples were two peaks in the curves which fell on two intervals, respectively, and the dominant pores were in the range of 15.66–21.74 nm with a mean of 17.78 nm. The larger pore size was to the benefit of free gas transportation, and the lower pore size made for gas adsorption, which agreed with the analysis of N\textsubscript{2} adsorption–desorption isotherms from Figure 4.

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The PV at a P/P\textsubscript{0} value of about 0.98 varying in the range of 0.012–0.027 ml/g in these shale samples, and there was positive correlation between PV and SSA (Figure 5). The large SSA of shales mainly resulted from the high OM content, clay mineral content and fine grain size \cite{19}. Then, the N\textsubscript{2} adsorption and desorption isotherms of Sample 1; (b) N\textsubscript{2} adsorption and desorption isotherms of Sample 7.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{FE-SEM images of the Yanchang shale samples. (a) Organic matter with fewer pores; (b) rudimentary intergranular pores between clay minerals; (c) developed intergranular pores between organic matter and clay minerals; (d) unpolished with argon ion, intergranular pores in the clay minerals; (e) intergranular pores between quartz grains and organic matter; (f) intergranular pores and micro fracture in the calcites; (g) intercrystallite pores in the primary pyrite framboïds; (h) unpolished with argon ion, intercrystallite pores in the quartz grains; (i) micro fractures in the mineral grains.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{N\textsubscript{2} adsorption and desorption isotherms of two Yanchang shale samples. (a) N\textsubscript{2} adsorption and desorption isotherms of Sample 1; (b) N\textsubscript{2} adsorption and desorption isotherms of Sample 7.}
\end{figure}

N\textsubscript{2} adsorption isotherms can provide information on pore structure parameters, such as the specific surface area (SSA), pore diameter (PD) and pore volume (PV). The equivalent SSA can be calculated by the multi-point BET equation \cite{62}, and the results showed that the SSA of these shale
samples was in the range of 2.45–6.55 m²/g, shown in Figure 5. The large SSA of shales mainly resulted from the high OM content, clay mineral content and fine grain size [19]. Then, the N₂ adsorption volume can be used to calculate the values of PV and PD, using the Kelvin equation and BJH model [63]. The PV at a P/P₀ value of about 0.98 varying in the range of 0.012–0.027 ml/g in these shale samples, and there was positive correlation between PV and SSA (Figure 5).

![Figure 5. The positive relationship between pore volume (PV) and specific surface area (SSA).](image)

Figure 6 shows the relationship between dV/d(logD) and PD for some samples. Generally, there were two peaks in the curves which fell on two intervals, respectively, and the dominant pores were mesopores with diameters ranging from 25.3–29.5 nm, most of the pores were classified as mesopores according to the IUPAC classification [60]. Moreover, the average PD of the studied shale samples was in the range of 15.66–21.74 nm with a mean of 17.78 nm. The larger pore size was to the benefit of free gas transportation, and the lower pore size made for gas adsorption, which agreed with the analysis of N₂ adsorption–desorption isotherms from Figure 4.

![Figure 6. Pore size distribution of some shale samples.](image)
3.4. Methane Adsorption Content

Isothermal adsorption experiment was used to obtain actual AGC, which was an effective method to describe the shale gas adsorption characteristics. In this study, the experimental pressure was not that high, the relation between real adsorption content and pressure were accord with Langmuir adsorption curve, so the Langmuir model was used to calculate the AGC [1,64]. The formula is as follows:

\[ V_d = \frac{V_L P}{P + P_L} \]  

(1)

where, \( V_d \) refers to the AGC, m\(^3\)/t; \( P \) refers to the formation pressure, MPa; \( V_L \) refers to Langmuir volume, cm\(^3\)/g; \( P_L \) refers to Langmuir pressure, MPa.

Table 1 exhibited the CH\(_4\) adsorption isotherm results at 30 °C for the shale samples under various humidity (H) and increasing pressures (P) up to 18 MPa. Then, \( V_L \) and \( P_L \) were obtained based on the data of \( P \) and measured CH\(_4\) content, according to Equation (1), the formation pressure of shale samples was about 8.6–8.9 MPa, the actual AGC (\( V_d \)) of these shale samples were in the range of 0.83–1.60 m\(^3\)/t (average 1.15 m\(^3\)/t), indicating that the overall shale samples have a moderate CH\(_4\) adsorption capacity because of their lower thermal maturity.

| Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|----------|----------|----------|----------|----------|
| H = 1.05% | H = 1.25% | H = 0.95% | H = 1.02% | H = 0.78% |
| P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) |
| 0.79 | 2.4 | 0.71 | 0.29 | 0.66 | 0.29 | 0.77 | 0.27 | 0.66 | 0.32 |
| 2.04 | 0.56 | 2.10 | 0.50 | 1.97 | 0.58 | 2.04 | 0.56 | 1.93 | 0.69 |
| 3.66 | 0.73 | 3.66 | 0.66 | 3.48 | 0.77 | 3.68 | 0.77 | 4.28 | 0.98 |
| 5.72 | 0.80 | 5.80 | 0.80 | 5.75 | 0.93 | 6.18 | 0.88 | 6.35 | 1.04 |
| 9.42 | 0.82 | 9.63 | 0.90 | 9.41 | 1.04 | 9.44 | 0.90 | 9.44 | 1.12 |
| 12.59 | 0.90 | 13.35 | 0.90 | 13.09 | 1.09 | 13.28 | 0.90 | 12.59 | 1.17 |
| 16.31 | 0.88 | 16.52 | 0.90 | 16.54 | 1.07 | 16.38 | 0.96 | 16.55 | 1.19 |

| Sample 6 | Sample 7 | Sample 8 | Sample 9 | Sample 10 |
|----------|----------|----------|----------|----------|
| H = 1.04% | H = 0.86% | H = 1.14% | H = 1.25% | H = 1.25% |
| P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) |
| 0.77 | 0.37 | 0.66 | 0.35 | 0.66 | 0.32 | 0.73 | 0.27 | 0.77 | 0.45 |
| 2.15 | 0.77 | 2.04 | 0.80 | 1.97 | 0.72 | 2.03 | 0.53 | 1.77 | 0.82 |
| 3.91 | 1.00 | 3.48 | 1.04 | 3.59 | 0.98 | 3.70 | 0.72 | 3.42 | 1.04 |
| 6.57 | 1.19 | 6.29 | 1.25 | 6.24 | 1.09 | 6.40 | 0.74 | 5.69 | 1.27 |
| 9.63 | 1.25 | 9.14 | 1.33 | 9.74 | 1.19 | 9.40 | 0.80 | 9.26 | 1.41 |
| 12.59 | 1.27 | 12.59 | 1.33 | 13.35 | 1.25 | 13.28 | 0.88 | 12.59 | 1.41 |
| 16.41 | 1.27 | 16.45 | 1.35 | 16.53 | 1.25 | 16.41 | 0.88 | 15.97 | 1.46 |

| Sample 11 | Sample 12 | Sample 13 | Sample 14 | Sample 15 |
|----------|----------|----------|----------|----------|
| H = 1.04% | H = 1.14% | H = 1.30% | H = 1.18% | H = 1.18% |
| P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) | P (MPa) | CH\(_4\) (m\(^3\)/t) |
| 0.66 | 0.48 | 0.68 | 0.42 | 0.73 | 0.35 | 0.79 | 0.35 | 0.73 | 0.42 |
| 1.87 | 0.98 | 1.89 | 1.00 | 1.93 | 0.74 | 2.04 | 0.66 | 2.04 | 0.82 |
| 3.44 | 1.27 | 3.63 | 1.35 | 3.59 | 0.98 | 3.53 | 0.85 | 3.53 | 1.04 |
| 5.63 | 1.50 | 6.33 | 1.57 | 6.38 | 1.14 | 6.38 | 1.04 | 6.38 | 1.22 |
| 9.57 | 1.65 | 9.30 | 1.62 | 9.76 | 1.19 | 9.76 | 1.09 | 9.83 | 1.35 |
| 13.28 | 1.67 | 13.28 | 1.70 | 12.59 | 1.25 | 13.08 | 1.12 | 13.28 | 1.41 |
| 16.35 | 1.70 | 16.67 | 1.70 | 16.26 | 1.30 | 16.31 | 1.12 | 16.95 | 1.43 |

4. Discussions

4.1. Effect of Single Geological Factors on AGC

4.1.1. Geochemical Influence Factors

Organic Matter Abundance

Common parameters characterizing OM abundance are TOC, chloroform bitumen “A” and hydrocarbon generation potential (\(S_1 + S_2\)). As is shown in Figure 1, the Yanchang shales are rich
in OM with TOC content larger than 1.0%, and \( V_a \) has a significantly positive correlation with TOC (Figure 7). Higher TOC means better shale gas potential, because OM is the material base of shale gas generation, and OM is the most important carrier for shale gas adsorption, enhancing the adsorption capacity of shale. Sander et al. [65] also demonstrated the strong relationship between TOC and shale adsorption capacity by comparing two global shale data sets, however, he also indicated TOC alone cannot account for the differences in AGC.

Chloroform bitumen "A" is the OM extracted from the rock with chloroform, including saturated hydrocarbon, aromatic hydrocarbon, non-hydrocarbon and asphaltene. HC is the total content of saturated hydrocarbon and aromatic hydrocarbon. Studies show that \( V_a \) positively correlates with chloroform asphalt "A", the higher the content of chloroform asphalt "A" is, the higher AGC in the shale is (Figure 8).
For the main components chloroform bitumen “A”, no obvious correlation was found between $V_a$ and saturated hydrocarbon content, aromatic hydrocarbon content, as well as HC, indicating that only chloroform bitumen “A” itself affects the AGC, while its components have no obvious influence (Figure 9).

![Figure 9](image_url)

**Figure 9.** Correlations between $V_a$ and three components of chloroform bitumen “A”. (a) Correlations between $V_a$ and saturated hydrocarbon content; (b) correlations between $V_a$ and aromatic content; (c) correlations between $V_a$ and the total hydrocarbon content.

Hydrocarbon generation potential ($S_1 + S_2$) refers to the sum of residual hydrocarbon ($S_1$) and pyrolysis hydrocarbon ($S_2$), which are parameters obtained by rock pyrolysis experiment. Figure 10 shows that $V_a$ has a significantly positive correlation with all the pyrolysis parameters $S_1, S_2$ and $S_1 + S_2$. The higher $S_1$ indicates the higher residual hydrocarbon potential of the shale, so the adsorption capacity is larger; the higher $S_2$ indicates more hydrocarbons are produced from kerogen in the process of pyrolysis, which directly increase the AGC in shales; $S_1 + S_2$ represents the whole hydrocarbon generating capacity of shale, so the higher $S_1 + S_2$ is, the higher AGC in shales is.

![Figure 10](image_url)

**Figure 10.** Correlations between $V_a$ and pyrolysis parameters. (a) Correlations between $V_a$ and residual hydrocarbon $S_1$; (b) Correlations between $V_a$ and pyrolysis hydrocarbon $S_2$; (c) correlations between $V_a$ and hydrocarbon generating potential ($S_1 + S_2$).

Organic Matter Maturity

As previously concluded, the studied shales are in the mature stage. Figure 11 shows that, $V_a$ has no significant correlation with $R_o$. This is mainly because shale in the mature stage it has not yet begun to largely produce shale gas, there is still a little of residual oil in it, which makes some gas dissolved in the residual oil, influencing the adsorption of gas molecules and AGC in shale. The result is consistent with the previous conclusion [66].
Organic Matter Maturity

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![Figure 11. Relationship between $V_a$ and thermal maturity $R_o$ of the shale samples.](image)

4.1.2. Mineral Influence Factors

Clay Minerals Content

It's well known that the clay minerals content could affect the AGC [7,29,67]. In this study, $V_a$ and clay mineral content are positively correlated (Figure 12), this is maybe due to the increase of clay minerals increasing the PD and SSA of shale to some extent, so the adsorption capacity and adsorbed gas content is also increased. Gu et al. [29] further described the adsorption characteristics of main components of clay minerals and concluded that the Montmorillonite has the maximum adsorption capacity, followed by Kaolinite and Chlorite, while illite has the least.

![Figure 12. Significant positive relationship between $V_a$ and clay minerals content.](image)

Brittle Mineral Content

The brittle minerals in shale mainly include quartz, orthoclase, anorthose, etc. Due to the small SSA, the adsorption capacity of them is generally weak, but the existence of brittle minerals is propitious to produce cracks and fractures, which indirectly affect the AGC. Then, the relationship between $V_a$ and brittle mineral content in the studied shale samples shows that they are negatively correlated (Figure 13a), because the adsorption positions for gas molecules that shale can provide also decrease.
Meanwhile, quartz is found to be the most important composition in brittle minerals, and the effect of feldspar content is little in comparison with it.

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**Figure 13.** Influence of brittle minerals on AGC in shales. (a) Negative relationship between $V_a$ and the total brittle mineral content. (b) Negative relationship between $V_a$ and the quartz content. (c) No obvious relationship between $V_a$ and the feldspar content.

**Carbonate Mineral Content**

Carbonate minerals in shale samples include calcite, dolomite, dolomite and siderite, among which, calcite is the most important component. From Figure 14a, it can be seen that, $V_a$ and carbonate content have the inverse correlation relations. The reason may be that carbonate minerals are often as cementation existed in micro pores or fractures, which occupy part surface area, lower the AGC in shales, resulting in the negative correlation between $V_a$ and carbonate content. However, calcite has no obvious effect on AGC, this maybe relates to it being missing in partial samples (Figure 14b).

**Figure 14.** Influence of carbonate mineral content on AGC in shales. (a) Negative relationship between $V_a$ and the carbonate content; (b) no obvious relationship between $V_a$ and the calcite content.

**Other Mineral Content**

In the other minerals, the content of pyrite can’t be neglected in this study (2.8–5.3%). Previous research has confirmed that there is a coexistent relationship between pyrite and OM as well as AGC [5,6,33,68]. However, $V_a$ has no indistinctive positive correlation with pyrite content for the studied shale samples (Figure 15). This is mainly because iron is the primary material for OM deposition, high iron content makes for OM enriching, but the lacustrine environment where the Yanchang shale deposited is not conducive to the formation of pyrite, the content of pyrite is not at the concentrations observed in marine systems [10].
we can find that there is no obvious relationship between \( V_a \) and permeability are used to show the influence of pore-based factors.

4.1.3. Pore-Based Influence Factors

Shale reservoirs are characterized by nano-micro pores and very low permeability. It is a challenge to detect and quantify these small pores. In this study, parameters including PD, SSA, PV as well as porosity and permeability are used to show the influence of pore-based factors.

Pore Size Distribution

For the shale samples, PD is 15.7–21.7 nm and the median radius is 7.8–10.9 nm. From Figure 16, we can find that there is no obvious relationship between \( V_a \) and pore size parameters, including both average PD and median radius, which indicates the pore size distribution is not the main influence factor of AGC.

Specific Surface Area

Previous study concluded that SSA was one of the main controlling factors on adsorption behaviors [17]. In this study, SSA calculated by BET and BJH models has no obvious effect on AGC (\( V_a \) has no obvious correlation with SSA, Figure 17). The reason may be that these shale samples are in the mature stages, and the existence of residual oil will occupy part of the adsorption sites for gas molecules, which could retrain the shale gas adsorption capacity to some extent.
Figure 17. Influence of specific surface area on AGC in shales. (a) Correlation between $V_a$ and SSA based on BET model; (b) correlation between $V_a$ and SSA based on BJH model.

Pore Volume

Results show that, there is no significant linear relationship between $V_a$ and PV whether calculated based on BET model or BTH model (Figure 18). Because the OM pores are not developed due to the low thermal evolution maturity, and intergranular pores are the dominant pore types in the total Yanchang shales pores, which is not in favor of shale gas adsorption.

Figure 18. Influence of total pore volume on AGC in shales. (a) Correlation between $V_a$ and PV based on BET model; (b) correlation between $V_a$ and PV based on BTH model.

Porosity

Some previous studies considered porosity as having a positive correlation with TOC content for thermally overmature marine shales [3]. However, for the thermally early-mature Yanchang shale with strong reservoir heterogeneity, the range of porosity variation is relatively large about 3.3–4.5%, and the effect of physical property on AGC is more complex, so the linear relationship between $V_a$ and porosity is not obvious (Figure 19). In general, the porosity has little effect on the AGC in shales.
Permeability

The permeability of shale reflects the development degree of fractures to some extent [58]. From Figure 20, it can be seen that, $V_a$ and permeability only have no significant relationship. This shows that the permeability had little effect on the AGC. From the other aspect, Jia et al. [58] concluded that the gas adsorption layer may reduce the permeability by reducing the effective pore size, but the effect is limited, indicating the mysterious influence of permeability.

4.1.4. External Influence Factors

The above factors can be seen as internal factors affecting AGC in shales, while some external factors such as temperature, pressure and humidity are also important.

Temperature

By conducting the CH$_4$ isothermal adsorption experiments at different temperatures on the same shale sample, the influence of temperature on the adsorption process and AGC can be analyzed [17,69]. In this study, Sample 7 was carried out the experiments at 30, 60, 90 and 120 °C, respectively, the experimental pressure increased from 0 MPa to about 17 MPa, until the measured adsorption
gas content was no longer increased. After fitting the experimental data, the isothermal adsorption curves at different temperatures can be obtained, shown in Figure 21a, which shows the increase of temperature could inhibit the adsorption of shale gas to a certain extent. In order to directly express the relationship between AGC and temperature, $V_a$ and $T$ of shale sample 7 are fitted, from Figure 21b we can conclude that, a negative linear correlation is really existed between $V_a$ and $T$.

![Figure 21. Influence of temperature on $V_a$. (a) Isothermal adsorption curves of sample 7; (b) linear relationship between $V_a$ and temperature.](image)

**Pressure**

Given a certain experimental temperature, conduct the CH$_4$ isothermal adsorption experiment for a shale sample, the isothermal adsorption curves of can be obtained, shown as Figure 22. Results show that the measured AGC has a logarithmical relationship with pressure, when the pressure increases to a certain value, the increasing extent of AGC is not obvious and heads for a specific value $V_L$ on behalf of the maximum shale gas adsorption capacity. The reason is that when the pressure is low, the gas molecules require higher binding energy to be adsorbed, with the pressure increasing, the binding energy they required gradually reduces, the adsorption capacity gradually increases instead [70,71].

![Figure 22. Logarithmical relationship between $V_a$ and pressure.](image)

**Humidity**

Previous studies show that the effective adsorption sites for the gas molecules are fixed numbers in the inner surface of the coal, when water content or humidity in the coal is high, some adsorption sites can be occupied by the water molecules, thus adsorption sites for the gas molecules will decrease [21,72]. In this study, isothermal adsorption experiments were conducted under conditions of various humidity in shale samples (Table 1), through analysis it can be seen that, $V_a$ has no obvious correlation with humidity, indicating humidity has little effect on the AGC in Yanchang shales (Figure 23).
predicted with only one significant geological factor, thus establishing a multi-factor regression model to quantitatively predict the AGC.

4.2. Mathematical Prediction Model of AGC

4.2.1. Influence Factors Optimization

From the above analysis, the AGC in shale is comprehensively affected by various geological factors to various degrees. The factors consist of internal factors, including geochemical factors, mineral compositions, pore-based characteristics, and external factors. However, not all the geological factors are significantly correlated with the AGC. Generally, when the absolute value of the correlation coefficient |R| is larger than 0.5, it can be considered that the two variables are relatively highly correlated. Only if |R| is greater than the critical value do the influence factors really have statistical significance. Therefore, the significant influence factors can tell from the 12 geological factors displayed in Table 2.

Then we fit the linear relationships between the single influence factor and V_a. The regression equations and the coefficient of determination (R^2) are shown in Figure 7, Figure 8, Figure 10, Figure 12, Figure 13a,b, Figure 14a, Figure 21b, and Figure 22. For the influence of single factor, R^2 of V_a with TOC, S1, S2, S1 + S2, chloroform bitumen “A”, clay minerals content, quartz content, brittle minerals content, carbonate minerals content, pressure and temperature is generally low with values of 0.52, 0.60, 0.50, 0.54, 0.51, 0.48, 0.30, 0.28, 0.32, 0.39, 0.39, respectively. The results indicate that the AGC cannot be predicted with only one significant geological factor, thus establishing a multi-factor regression model to quantitatively predict the AGC is necessary.

To establish the mathematical prediction model, not all the above influence factors are useful. In this study, we optimized the main influence factors based on two principles that (1) significant correlation, |R| > 0.5 and Sig. < 0.05, these factors are displayed in Table 2; (2) no obvious relationship among the single factors, such as both chloroform bitumen “A” and S1 represent the residual hydrocarbons, so only S1 is selected; quartz is the main composition of brittle minerals, so quartz content instead of brittle content is optimized. Therefore, eight factors including TOC, S1, S2, Clm, Qz, Cam, T as well as lnP, are thought as the main influence factors affecting the AGC of the Yanchang Formation, which are further used to predict the content.

Figure 23. No obvious relationship between V_a and humidity.
Table 2. Pearson correlation coefficient (R) of $V_a$ and influence factors with statistical significance.

| Factors | $V_a$ | TOC | $S_1$ | $S_2$ | $S_1 + S_2$ | "A" | Clm | Quartz | Bm | Cam | $P$ | $\ln P$ | $T$ |
|---------|-------|-----|-------|-------|-------------|-----|-----|--------|----|-----|-----|--------|-----|
| $V_a$   | 1     | 0.722** | 0.775** | 0.709** | 0.738** | 0.711** | 0.696** | -0.546* | -0.525* | -0.567* | 0.625* | 0.626* | 0.624* |
| TOC     | 1     | 0.709** | 0.803** | 0.786** | 0.761** | 0.869** | -0.656** | -0.543* | -0.844** | 0.672** | 0.673** | 0.670** |
| $S_1$   | 1     | 0.939** | 0.969** | 0.965** | 0.725** | -0.434 | -0.495 | -0.651* | 0.942** | 0.942** | 0.941** |
| $S_2$   | 1     | 0.945** | 0.916** | 0.796** | -0.453 | -0.514 | -0.741** | 0.915** | 0.915** | 0.914** |
| $S_1 + S_2$ | 1     | 0.942** | 0.787** | -0.453 | -0.515 | -0.724** | 0.935** | 0.935** | 0.933** |
| "A"    | 1     | 0.814** | 0.518* | 0.529* | 0.567* | 0.625* | 0.626* | 0.624* | 0.625* | 0.626* | 0.624* |
| Clm     | 1     | 0.853** | 0.383 | -0.446 | -0.447 | -0.449 | |
| Quartz  | 1     | 0.204 | -0.547* | -0.548* | -0.551* |
| Bm      | 1     | -0.616* | -0.617* | -0.614* |
| Cam     | 1     | 1.000** | 1.000** |
| $P$     | 1     | 1.000** | 1.000** |
| $\ln P$ | 1     | 1.000** | 1.000** |
| $T$     | 1     | 1.000** | 1.000** |

** Significant correlation at the level of 0.01 (bilateral); * Significant correlation at the level of 0.05 (bilateral); $V_a$—Adsorbed gas content; Clm—Clay minerals; Bm—Brittle minerals; Cam—Carbonate minerals; $P$—Pressure; $T$—Temperature.

4.2.2. Establish Mathematical Prediction Model

Regression analysis is a statistical process for estimating the relationships among variables, which includes many techniques for modeling and analyzing several variables. It is widely used for forecasting and understanding that which is related to the dependent variable among the independent variables and exploring the correlative equations between them. In this study, prediction models established are multiple linear regression functions, and the optimized eight main influence factors are entered as the independent variables. Nowadays some specialized regression software has been widely used, such as the SPSS software, which packages perform multiple linear regression using least squares, the methods cover enter, stepwise, remove, forward and backward, among which, backward is proved the most effective method used for the studied shale samples. The backward regression method is to input all the independent variables first, then eliminate a variable that does not conform to the entry criteria each time, until the regression function no longer contains an independent variable that is not consistent with the criteria.

In Tables 3–5, five models are established according to the backward method, $R^2$ of each model is high up to 0.8 with small error, thus each model can be used as the prediction model, in this case, we give preference to Model 4 which has less independent variables (R is 0.885, shown in Table 4). In this model, the geological factors used to predict the AGC are TOC, $S_1$, quartz content and $T$, coefficients of each factor can be obtained from Table 5, the prediction function is as Equation (2):

$$V_a = 29.150 + 0.026 \times \text{TOC} + 0.231 \times S_1 - 0.011 \times Qz - 0.537 \times T$$ (2)

where, $V_a$ refers to the predicted AGC, m$^3$/t; TOC refers to the total organic carbon content, wt %; $S_1$ refers to the residual hydrocarbon content, %; Qz refers to quartz content, wt %; $T$ refers to the formation temperature, °C.

Table 3. Variables entered/removed $^a$.

| Model | Variables Entered | Variables Removed | Method |
|-------|-------------------|-------------------|--------|
| 1     | $T$, quartz content, carbonate content, TOC, $S_1$, clay mineral content, $S_2$ $^b$ | - | enter |
| 2     | -                 | Carbonate content | Backward (F-to-remove ≥ 0.1) |
| 3     | -                 | Clay mineral content | Backward (F-to-remove ≥ 0.1) |
| 4     | -                 | $S_2$             | Backward (F-to-remove ≥ 0.1) |
| 5     | -                 | TOC               | Backward (F-to-remove ≥ 0.1) |

$^a$ Dependent variable: $V_a$ (m$^3$/t); $^b$ tolerance reached = 0.000.
4.3.1. Comparison of AGC Obtained from Different Methods

In this study, AGC in shales was obtained by three methods, including the CH\textsubscript{4} isothermal adsorption experimental method, the single-factor correlation analysis method, and the multi-factor regression analysis method. In general, the AGC has an overall increasing trend with the increase of burial depth, unanimous for different methods (Figure 24). Except the single-factor correlation analysis, the other two methods are significantly correlated, so they are further compared. As shown in Table 6, every method naturally has advantages and disadvantages, and can complement each other when evaluating the AGC in shales.

Table 4. Model summary a.

| Model | $R$ | $R^2$ | Adjusted $R^2$ | Standard Estimate Error |
|-------|-----|-------|----------------|-------------------------|
| 4     | 0.885$^{b}$ | 0.783 | 0.686 | 0.14291 |

$^{a}$ Dependent variable: $V_a$ (m$^3$/t), $^{b}$ independent variable.

Table 5. Coefficient $^{a}$.

| Model       | $B$ (constant) | $B$: TOC | $B$: $Q_z$ | $B$: $T$ | $t$ | Significance |
|-------------|----------------|----------|-----------|---------|-----|--------------|
| (constant)  | 29.150         | 13.553   |           |         |     |              |
| TOC         | 0.026          | 0.037    | 0.187     | 0.707   | 0.060 | 0.497        |
| 4           | $S_1$ 0.231    | 0.081    | 1.414     | 2.857   | 0.019 |              |
|             | $Q_z$ -0.011   | 0.009    | 0.267     | 1.241   | 0.246 |              |
|             | $T$ -0.537     | 0.258    | -0.974    | 2.082   | 0.067 |              |

$^{a}$ predictive variable: (constant), TOC, $S_1$, quartz content, $T$.

4.2.3. Reliability Test of the Prediction Model

To verify the models’ reliability, we obtained the predicted AGC by entering the measured values of variables TOC, $S_1$, $Q_z$, and $T$ into the prediction model Equation (2), then made a correlation analysis and error analysis of the experimental values and the predicted AGC. It can be seen that, the predicted AGC has significant correlation with the experimental content, with $R$ high up to 0.897 (Figure 24a) and the relative error less than ±20% (Figure 24b), proving that the prediction model is reliable, which can be used to effectively forecast the AGC in Yanchang shales.

The multi-factor regression analysis method used in this study is of significant guidance for calculating AGC continuously. However, when apply this method to other shale reservoir, more detailed work is required and necessary to confirm the accurate relationships between AGC and influence factors, and then the targeted prediction models can be established.

Figure 24. Reliability test of prediction model of AGC. (a) Correlation analysis between actual experimental values and predicted models; (b) error analysis of the prediction model.

4.3. Comprehensive Evaluation of Shale Gas Adsorption Capacity of Yanchang Formation

4.3.1. Comparison of AGC Obtained from Different Methods

In this study, AGC in shales was obtained by three methods, including the CH\textsubscript{4} isothermal adsorption experimental method, the single-factor correlation analysis method, and the multi-factor regression analysis method. In general, the AGC has an overall increasing trend with the increase of burial depth, unanimous for different methods (Figure 24). Except the single-factor correlation analysis, the other two methods are significantly correlated, so they are further compared. As shown in Table 6, every method naturally has advantages and disadvantages, and can complement each other when evaluating the AGC in shales.
Table 6. Comparison of two main methods for evaluating the AGC.

| Method                          | Equation               | Advantages                                | Disadvantages                                      |
|---------------------------------|------------------------|-------------------------------------------|----------------------------------------------------|
| CH$_4$ isothermal adsorption    | $V_a = V_L P / (P + P_L)$ | Simple principle and mature application   | Restricted by the economic factors and spatial variation |
| experiment                      |                        |                                           |                                                    |
| Multi-factor regression          | $V_a = 28.893 + 0.026 \times$ TOC + $0.230 \times S_1 - 0.011 \times Qz - 0.532 \times T$ | Vary continuously, widely applied in areas with similar geological conditions. | Depend on data numbers, not applied to new exploration areas |

The CH$_4$ isothermal adsorption experimental method is the most direct and effective way to evaluate the AGC, including the actual AGC and the maximum adsorption capacity based on the Langmuir equation. However, it is greatly restricted by the economic factors due to the high testing cost, unable to effectively apply to large scale samples and wells. For the multi-factor regression analysis method, AGC predicted by this method varies continuously because of the spatial extension of geological factors in shale formation, not just restricted by one single well. However, due to the less core sample numbers ($N = 15$), the accuracy of prediction model needs improvements, if larger core numbers are satisfied, this method will have more universal applicability at the mature exploration area [9,36].

4.3.2. Evaluation of Shale Gas Adsorption Capacity of Yanchang Formation

As discussed above, for the AGC in Yanchang shales, the on-site analytical gas amounts are in the range of 1.24–2.34 m$^3$/t with a mean of 1.68 m$^3$/t, the actual gas absorption quantity ($V_a$) is in the range of 0.83–1.60 m$^3$/t with a mean of 1.15 m$^3$/t, indicating that the studied shale samples have a moderate gas adsorption capacity though generally lower than the marine Longmaxi shales [10]. Except for the adsorbed gas, free gas and dissolved gas are also the important occurrence states of shale gas [73]. Our previous studies have concluded that Yanchang shales have the characteristics of primary adsorbed gas (44–65%, average 58%), moderate free gas (24–45%; average 32%), and non-ignorable dissolved gas (10%) [10]. Evaluating shale gas occurrence forms and their proportions in shales especially the adsorbed one is curial to both exploration and exploitation. It is not only vital for evaluating shale gas resource potential, but also the key to analyzing production capacity, gas reservoir types, and exploitation method [74].

Shale gas exploitation mainly involves the adsorbed gas and free gas. In general, free gas content determines the primary productivity, while adsorbed gas content determines the stable production time [75,76]. Gas reservoirs with high free gas content have a higher initial recovery rate, which is conducive to economic development [75]. For Yanchang shales, adsorbed gas is the primary occurrence form, and free gas follows. The dissolved gas can also transform into free gas during exploitation, indicating that the primary productivity in the continental shale maybe low, but its stable production time may be long and thus determining the final gas production because of its larger adsorption gas ratio. The predicted trend of gas production for the Yanchang shale is similar to the gas production rate and decline trend in the Barnett Shale [77]. The initial gas production rate in the Barnett Shale is generally lower than other major shales in the US like Eagle ford, Marcellus and Haynesville [77]. Mavor [78] revealed it was due to the adsorption gas content of the Barnett Shale occupied about 60% of the total shale gas reserves.

The exploration and production of continental shale gas in China are mainly concentrated in the Ordos Basin, numbers of shale gas wells have been drilled and some of them have been successfully fractured. Among which, well LP177 was the first continental shale horizontal well in China and achieved a shale gas flow of 2000 m$^3$/d after fracturing. So far, plenty of wells have obtained industrial gas flow with the average gas content of 4000 m$^3$/d, and fracturing technology has also made breakthroughs and innovative progress. The great shale gas content and industrial gas flow demonstrate the large potential of shale gas resource in Yanchang formation in the Ordos Basin, also indicate a great prospect for further exploration and development [25]. Though the primary production
of continental shale gas is usually lower than that of predicted gas potential especially when compared to marine shale gas, the stable production time maybe longer, and with the advance of fracturing technology, the scale production can be expected in the future. Based on the above analysis, it can be concluded that under the present natural gas market, it is more economical to preferentially exploit marine shale gas than continental shale gas, the resource potential of continental shales, however, can be still substantial and should not be belittled.

5. Conclusions

The influence of geological factors on the AGC in the Yanchang shales has been analyzed based on laboratory experiments and correlation analysis then, a mathematical prediction model has been established according to the multi-factor regression analysis. Conclusions are as follows:

(1) Adsorbed gas content (AGC) in the Yanchang shales is comprehensively affected by various geological factors to different degrees. TOC, S\textsubscript{1}, S\textsubscript{2}, S\textsubscript{1} + S\textsubscript{2}, chloroform bitumen “A” and clay minerals content have significant correlations with V\textsubscript{a} at the level of 0.01 (bilateral). Quartz content, brittle minerals content, carbonate minerals content, pressure and temperature have significant correlations with V\textsubscript{a} at the level of 0.05 (bilateral). However, the coefficient of determination (R\textsuperscript{2}) of the fitted equations between the single influence actor and V\textsubscript{a} is overall lower than 0.5, can’t be used to predict the shale gas adsorption amount.

(2) A mathematical prediction model of the AGC in Yanchang shales has been established by the statistical method multi-factor regression analysis based on the SPSS software, which is the function of TOC, S\textsubscript{1}, quartz content and formation temperature. The reliability of the predicted AGC obtained from the prediction model is verified by the actual values obtained from the CH\textsubscript{4} isothermal adsorption experiment, with the coefficient of determination as high as 0.8046 and the relative error less than ±20%.

(3) AGC in Yanchang shales obtained from the CH\textsubscript{4} isothermal adsorption experimental method, the single-factor correlation analysis method, and the multi-factor regression analysis method all have a general increasing trend with the increasing depth, though unanimous for different methods. Comparison supports that CH\textsubscript{4} isothermal adsorption experimental method is the most direct and effective way to evaluate the AGC of one sample, while AGC predicted by the multi-factor regression analysis method can vary continuously and have general applicability at mature exploration area.

(4) Comprehensive assessment of shale gas adsorption capacity of Yanchang formation indicates, there is an overall moderate gas adsorption capacity. Among the three occurrence forms, the adsorbed gas occupies about 58% of the total, determining the stable production time of the Yanchang shale reservoir. Though under the present conditions, the economic benefits of the continental shale gas are not obvious, the resource potential of Yanchang formation cannot be ignored.
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