Wettability modification and its influence on methane adsorption/desorption: A case study in the Ordos Basin, China

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Abstract

Wettability modification of coal rock may cause serious change in the methane adsorption/desorption behaviors. Thus, the contact angle measurement and isothermal adsorption/desorption experiment of raw coal and samples treated with surfactants (STS) were conducted to investigate the wetting properties and methane adsorption/desorption characteristics. The results indicated that the long-flame coal (LFC) has the good hydrophilicity itself, and there was no evident sign of saturated adsorption for different samples at relatively low-pressure (<8 MPa) stage. The sample treated with the wettability reversal agent (G502) had the larger methane adsorption capacity than the wetted samples (LAS, JFC, and 6501), with the latter facilitating the methane desorption. Additionally, the adsorption capacity of the air-dried samples was stronger than that of the water-containing samples, including the moisture-equilibrated, LAS, JFC, and 6501, reflecting that the better the hydrophilicity, the weaker the methane adsorption. Besides, the desorption hysteresis rate of the same sample was mainly controlled by pressure, i.e., the desorption hysteresis indicated a logarithmic decrease with the increasing pressure, but the STS clearly showed the desorption hysteresis to varying degree due to the wettability differences. The pressure drop in the low-pressure stage was difficult to drive the adsorbed methane to immediately desorb from the matrix surface, whereas even caused further adsorption or re-adsorption, meaning that the coal required a greater depressurization to enter the effective desorption stage. Finally, the positive implications of wettability modification including enhancing CBM recovery, as well as coal and methane outburst prevention and coal dust control in the mining industry were discussed.

KEYWORDS
adsorption/desorption, coalbed methane, surface free energy, surfactants, wettability

1 | INTRODUCTION

Coalbed methane (CBM) is a clean and efficient unconventional natural gas resource. The exploration and development of CBM is of great significance for the prevention and control of coal mine gas disasters, the utilization of clean energy, and the reduction of environmental pollution. The in-place CBM resource shallower than 2000 m is $29.82 \times 10^{12}$ m$^3$, and the recoverable resource is $12.51 \times 10^{12}$ m$^3$, of which the proportion of in-place resource and recoverable resource...
in low-rank CBM (VRr < 0.70%) are 34% and 40%, respectively.

Currently, China has initially achieved the large-scale commercial development of high-rank CBM in the Qinshui Basin and the eastern edge of the Ordos Basin, compared to the low-rank coal development area of the Junggar Basin, the Tarim Basin, the Ordos Basin, etc. The research on the basic theory of CBM geology and exploration in the low-rank coal has been left behind. The material composition, pore structure, surface chemistry, and other properties in low-rank coals are clearly distinguished from high-rank coals, and the former usually shows short but concentrates methane adsorption equilibrium, especially the higher initial desorption rate and desorption efficiency. However, there are also problems of lower gas content, higher water content, stronger chemical activity, and lower gas production and recovery for low-rank coals.

The key point of improving CBM recovery is to reasonably allocate the methane supply capacity and seepage ability. Low-rank coal reservoir shelters complex interactions between gas, liquid, and solid components, including the liquid-solid wettability (ie, the interaction of coal-water containing the wettability of free water and the adsorbability of vaporous water), gas-solid adsorption/desorption (ad-/desorption) (ie, coal-methane, which means the nature of methane in coals and their interaction.), and gas-liquid dissolution and displacement. The physical structure and surface properties of low-rank coals affect the specific interactions between different liquids and coal, and consequently affect the ad-/desorption behavior of methane, for example, the contact angle (CA) between coal and water can be used to judge wettability, which is mainly controlled by the material composition, oxygen-containing functional groups and surfactants.

Generally, coalbed in situ is difficult to change their composition and other properties. In recent years, wettability modification of solid surface such as coal matrix using surfactants has been intensely studied. The surfaces of coal matrix are either positively or negatively charged in the aqueous medium by ionization/dissociation of surface groups or by the adsorption of ions from solution onto a previously uncharged surface. The surfactant molecules adsorbed onto matrix surfaces alter the original wettability depending on the exposure of either hydrophobic or hydrophilic groups.

The changing wettability of coal matrix will obviously affect the physical adsorption of methane molecules, but a few researchers pay attention to the influence of wettability on CBM ad-/desorption. Previous studies have considered that the wettability has a positive correlation with the moisture content, and the increase of moisture content with the increasing wettability will significantly reduce the methane adsorption capacity, and then, this effect is no longer significant after the moisture content exceeds a certain limit. Some scholars believe that the moisture content and the oxygen content in the coal are unfavorable for methane adsorption, or the adsorbed water will result in the swelling of the coal, and the reduction of the porosity. Zhong and Li et al believe that liquid water can lead to blockage of pore-fracture channels by forming water film or droplets, thereby inhibiting methane desorption. However, several experiments had revealed that liquid water may promote methane adsorption resulting from that the water film can provide some effective adsorption sites for methane.

Though there are many published researches on the wettability modification of coal rock or the influence of moisture content on methane adsorption, the detailed characteristics and mechanism of methane ad-/desorption on samples treated with surfactants (STS) remain not fully understood. In this work, four kinds of wetting agents including the anionic surfactants, nonionic surfactants, and wettability reversal agent were chosen for wetting long-flame coal (LFC in the latest Chinese coal quality classification standard, i.e. GB/T 5751, also be called subbituminous coal according to the latest international standards ISO 11 760). We therefore studied the controlling factors of wetting difference, as well as restraint of wettability characteristics of LFC. Besides, the characteristics of methane ad-/desorption and surface free energies (SFE) of the differently treated samples including the raw and wetted coal samples were fully investigated.

2 | MATERIALS AND METHODS

2.1 | Samples and preparation

The LFC samples were collected from the Yanan Formation in middle Jurassic in the southern Ordos Basin, China. Specifically, several samples of the No.4 coal seam were taken directly from the working face of 40105 in Dafosi coal mine (Figure 1). The coal quality analysis was conducted according to the coal industry standard of the P. R. of China (GB/T 212-2008, GB/T 212-2008, GB/T 476-2001, respectively), and the results are given in Table 1.

The samples mainly were prepared for wettability and methane ad-/desorption measurements; for the former, several samples were cut to cuboid shape (~3 cm × 3 cm × 2 cm) and the surface roughness of each substrate was nearly consistent by using the PG-2 metallographic polishing machine; for the latter, the raw samples were put into a pulverizer and crushed into powder with particle sizes of 0.18-0.23 mm. Then, the part powder samples were placed in a vacuum drying at 50°C to completely dry to remove free moisture in the coal, and some others were strictly made of moisture-equilibrated samples through the standard of American Society for Testing Materials (ASTM).
2.2 Surfactants

It is no doubt that surfactants can modify the surface property, and the type of surfactants largely determines the efficiency of wettability for a given coal sample. Therefore, besides the distilled water and formation water, four kinds of wetting agents were screened in this work, whose basic properties including the name, molecular formula, and ionic property are summarized in Table 2. As anionic or nonionic surfactants,
the sodium dodecyl benzene sulfonate (LAS), cocoanot fatty acid diethanolamide (6501), and fatty alcohol-polyoxyethylene ether (JFC) could effectively reduce surface tension of solution and enhance hydrophilicity. Additionally, the 12 fluoroalkyl trimethoxy silane (G502) was chosen as wettability reversal agent for its excellent hydrophobicity. Critical micelle concentration of each surfactant (0.63% LAS, 0.61% 6501, 0.09% JFC, 1.00% G502, respectively) had been tested basing on the surface ten-
sion (Table 2). Meantime, the distilled water and production water were also chosen for comparison with surfactants.

2.3 Static contact angle measurements

Wettability can be evaluated through various methods, of which the CA measurement can be used to quantitatively assess coal wettability. Generally, solid surfaces with CAs < 90° are deemed hydrophilic, while surfaces with CAs > 90° are hydrophobic. CA value (θ) can be calculated by Young equation.

The OCA20 type of optical CA measuring device produced by German Dataphysics Company was employed in this experiment, and the static CA measurement method was applied. The droplet solution was set up to 4 μL, and the sample table was raised to touch the suspended droplets when measuring, which could avoid gravity error caused by free drop of droplets. When droplet dropped on coal surface, it stayed after 12 seconds for measuring CA. The CA of each coal sample was measured at different surface positions. Finally, the average value was taken as the final one. The image of CA in the test can be seen in Table 3.

2.4 Isothermal adsorption/desorption measurements

The methane ad-/desorption experiment was conducted using a volumetric method. The air-dry sample, moisture-equili-

| Type | Average value (°) | CA image | Testing frequency |
|------|-------------------|----------|------------------|
| G502 | 105.6             |          | 12               |
| 6501 | 39.0              |          | 12               |
| JFC  | 45.6              |          | 12               |
| LAS  | 44.0              |          | 12               |
| DW   | 49.6              |          | 12               |
| PW   | 77.8              |          | 12               |

Note:: The surface tension was measured at room temperature of 25°C and 1 standard atmospheric pressure. Because the G502 is a nonaqueous wetting reversal agent with strong hydrophobic property and huge surface tension, the surface tension cannot be obtained in this work.
simulated experimental apparatus, which is mainly composed of a host control system, thermostat system, measurement system, high-pressure gas supply system, and vacuum system.6

The characteristic parameters of methane adsorption were calculated by Langmuir isotherm model (Equation (1)).51 Usually, desorption measurements were performed as the reversible process of the adsorption measurements.52 However, because of the existence of desorption hysteresis, a desorption equation (Langmuir+C) proposed by Ma et al53 was used to calculate related desorption parameters. As showed in Equation (2).

\[ V_a = \frac{a_a b_a P}{1 + b_a P}, \]  
\[ V_d = \frac{a_d b_d P + c}{1 + b_d P}, \]

where \( V_a \) and \( V_d \) (cm\(^3\)/g) are the methane capacity in the process of ad-/desorption at accordingly pressure \( P \) (MPa); \( a_a \) and \( a_d \) (cm\(^3\)/g) are the maximum adsorption capacity in the process of ad-/desorption, respectively; \( b_a \) and \( b_d \) (1/MPa) are the reciprocal of Langmuir pressure constant that represents methane pressure at the half maximum of total adsorbed capacity; \( c \) (cm\(^3\)/g) is the residual adsorption capacity of coal sample.

The maximum equilibrium pressure was roughly set at 8.0 MPa. The temperature was set at 23°C based on the actual coal reservoir average temperature, and the ad-/desorption equilibrium time was 12 hours.

3 | RESULTS AND DISCUSSIONS

3.1 | Comparison of wetting differences

Besides the distilled and production water, different wetting agents including the 6501, JFC, LAS, and G502, as the solute for titration, were applied to the CA measurements (Table 3), and three coal samples were used for each solution. Moreover, each sample was tested for three surface locations, and the average value was taken as the final one. Measured CA values of different samples decreased in the order of G50 > PW > DW > JFC > LAS > 6501, which indicates that the G502 has the obvious hydrophobicity; however, the 6501 has the strongest hydrophilicity compared with the LAS and JFC. Additionally, the average CA of distilled water (49.6°) was significantly smaller than the production water (77.8°) with the result that the latter contains more minerals and possesses the Cl–Na\(^+\) groundwater chemical type, leading the higher salinity and surface tension of groundwater.42

The target coal samples have good hydrophilicity due to the properties of wetting agent as well as the material composition, oxygen-containing functional groups, and pore-fracture characteristics. Anionic and nonionic surfactants can effectively reduce the surface tension of a solution and enhance hydrophilicity.54 The orientation and degree of wettability changes mainly depend on the types and adsorption characteristics of surfactants.55 The surfaces of LFC are generally negatively charged.27 At low concentrations, the anion and hydrophobic agent molecules produced by the LAS and G502, respectively, are mainly laid on the matrix surface, representing that the mechanism of surfactants occurs in two ways, that is, the hydrophilic heads of surfactant adsorbed on the polar part of matrix surface with the hydrophobic tail exposed, or the hydrophobic tails of the surfactant interacted with the nonpolar part of matrix surface leaving hydrophilic heads outward.56 When the concentration is increased, the ions to be adsorbed and the previously adsorbed ions will be adsorbed by the hydrophobic interaction, resulting in an increase of adsorption capacity (Figure 2A). Also, LAS has long carbon chain and benzene ring with unfavorable hydrophilicity, but it has strong water-soluble acid groups named sulfonate, which can effectively increase hydrophilicity. The nonionic surfactant such as the 6501 and JFC does not produce ions in aqueous solution, but it usually has two-hydrophilic structure of hydroxyl group (–OH) or ether bond (R–O–R'). Therefore, the oxygen atom in the ether group easily forms a hydrogen bond with the hydrogen atom in the hydroxyl group and carboxyl group, and a plurality of hydrogen bonds can be simultaneously formed due to the large number of ether groups (Figure 2B). Cun19 considered that the alkanolamide surfactants (ie, 6501) can effectively improve the coal wettability. In regarding to the chemical formula of JFC, the larger the number of ethylene oxide adduct, the more oxygen content on the hydrophilic group of the molecule, the more hydrogen bonds can be formed with water, and the stronger the water wettability. Although the surface of LFC has many strong polar adsorption sites, there are also some nonpolar aromatic structures, that is, nonpolar adsorption sites, so the London dispersion force is also a very important contribution (Figure 2C).

In terms of the properties of coal itself, Cun19 believed that the carboxyl content has the greatest influence on coal-water (ie, the interaction between liquid water and solid coal matrix) wettability, followed by hydroxyl content. The existence of abundant hydrophilic oxygen-containing functional groups, such as the carboxyl group, hydroxyl group, carbonyl group, and ester group, in LFC samples leads to the decrease of hydrophilicity of the matrix surface. Besides, the LFC samples have the loose and porous surface structure, developed capillary pores, larger internal surface area, leading to a good hydrophilicity. In addition to the material composition, the higher ash content (8.54%), oxygen content (10.14%), and inertinite content (68.1%) in coal samples are also favorable.
for hydrophilicity. Moreover, the surface properties of samples and the developed pore-fractures also directly affect the CA value. The SEM photomicrographs finished by ZEISS EVO–MA15 electron scanning microscopy showed that the coal structure is relatively intact, and the original bedding and endogenous fractures are more developed (Figure 3A–C). There are different pores including main plant tissue pores, interstitial pores, and stomatal pores, and fractures including tensile fractures and diagenetic shrinkage fractures, some of which are filled with clay minerals (kaolinite, illite, etc) (Figure 3D–F). Therefore, these surface characteristics including the material composition, oxygen-containing functional groups, and pore-fracture distribution are beneficial to the coal wettability as a whole.6

**FIGURE 2** Types of interaction between surfactants and matrix surface of the LFC

[A] Interaction of hydrophobic groups  
[O–R]  
[H O H O H O H]  
[O R O R O R O]  
[C–O–C–N–C–O–C–N–C–O–]

[B] Hydrogen bond

[C] London dispersion force

**FIGURE 3** SEM photomicrographs of the target coal samples. (A) ×50 (magnification): horizontal bedding and endogenous fissure; (B) ×200: horizontal bedding and attached minerals; (C) ×500 horizontal bedding and breccia pores; (D) ×4000 loose fractures on the structural surface and slip surface, and the breccia pores in the broken coal matrix. (E) ×1000 clay minerals, pyrite, and tensile fractures; (F) ×1000 diagenetic shrinkage fractures and stomata groups.
3.2 | Characteristics of methane adsorption and desorption

The isothermal ad-/desorption experiment of methane at different temperatures was carried out using the 0.18-0.23 mm coal fines treated with different wetting agents. Taking the actual reservoir temperature at 23°C as an example, it is found that the adsorption capacity increases with the increasing pressure (0-8 MPa), and there is no sign of saturated adsorption (Figure 4). It was shown as well that adsorption capacity within the range of 8 MPa was in the order of G502 > air-dried > 6501 > JFC > moisture-equilibrated > LAS (Figure 4), indicating that the G502 (wettability reversal agent) facilitates methane adsorption, but other wetting agents such as the LAS, JFC, and 6501 are detrimental to methane adsorption whereas may be promoting methane desorption. The adsorption capacity of the air-dried samples is stronger than that of water-containing samples such as the moisture-equilibrated, LAS, JFC, and 6501, reflecting the moisture content or hydrophilicity is not conducive to methane adsorption, and the better the hydrophilicity, the weaker the methane adsorption, which is consistent with the author's previous research.6

As was shown on the different treated samples, the maximum adsorption capacity (Langmuir volume) corresponding to higher reservoir pressure was in the order of G502 > moisture-equilibrated > air-dried > 6501 > JFC > LAS (Figure 4 and Table 4), reflecting the effect of relatively high pressure and moisture on adsorption. Comparatively, the reciprocal of Langmuir pressure showed the opposite trend, whereas it essentially reflects the same law, that is, the smaller the reciprocal of Langmuir pressure (b, or b,c), the faster the methane adsorption rate, and the steeper the isothermal adsorption curve, which is in consistent with Zhong's research.57

The preparation of moisture-equilibrated samples could recover part of the decomposition water, combined water and adsorbed water inside the matrix.43,58 Theoretically, the water will exist in the pores of different scales inside and outside the matrix, in which gaseous water plays a role in displacement-desorption of adsorbed methane, while liquid water also has a significant effect on methane adsorption.40 Zhang et al.41 observed that water film can be formed after wettability effect with liquid water. Although the long-range interaction force between coal and methane molecules and the short-range interaction force between methane molecules and water molecules are very small, the water film could provide some effective adsorption sites for methane molecules, leading to the increasing adsorption capacity. Moreover, as for methane molecules, the increasing pressure (represent the higher reservoir temperatures) also makes the stronger activity and migration, and the increase of adsorption rate and adsorption efficiency is more than water molecules, which finally causes the phenomenon that the maximum adsorption capacity of the moisture-equilibrated samples is greater than the air-dried.

Additionally, different samples clearly showed the desorption hysteresis to varying degree (Figure 6),59-62 and the desorption hysteresis ratio (δ) was obtained according to the Langmuir model and Langmuir+C model (Equation (3)). As the pressure increases, the desorption hysteresis rate showed a logarithmic decrease. Compared with the relatively low-pressure stage, the specific pressure drop in the relatively high-pressure stage has no significant effect on methane desorption (Figures 4 and 6). The pressure drop in the relatively low-pressure stage (approximately less than the critical pressure of methane) is difficult to drive the adsorbed methane to immediately desorb from the matrix surface, whereas even causes further adsorption or re-adsorption, after which desorption and significant desorption hysteresis occurs. Furthermore, the calculated desorption hysteresis ratio for different samples decreased in the order of 6501 > G502 > moisture-equilibrated > LAS > air-dried > JFC, reflecting difference in desorption sensitivity at different pressure stages.

$$\delta = \frac{V_a - V_d}{V_a} \times 100\%.$$  (3)

3.3 | Variation of surface free energy

The surface free energy (SFE) of coal determines the difference in the methane adsorption capacity of different adsorbates.63 In general, coal is an organic solid mixture based on a polycondensation aromatic fused ring system with a macromolecular framework structure, usually in a state of force-equilibrated, but in the process of coalification, oxygen-containing functional groups, bridge bonds and side chains of coal will gradually break and fall off, resulting in volatile components and the unsaturated state of force-balanced, which causes the tendency of the carbon atoms on the surface of coal to move into the interior of coal matrix, that is, the carbon atoms obtain an additional energy named surface free energy, which could promote the adsorption of gas molecules on the surface, and the adsorption would result in the reduction of SFE.64

The LFC contains more oxygen-containing functional groups, and the interaction between (hydrophilic) functional groups and water or methane molecules largely changes the SFE. Based on the ad-/desorption experimental data, the values of a (the maximum adsorption capacity) and b (the reciprocal of Langmuir pressure constant) are obtained by fitting with the Langmuir equation, and the specific surface area (S) of methane adsorption can be obtained according to the theoretical assumption of monolayer adsorption. As shown in Equation (4).
where $S$ is the specific surface area of coal matrix in cm$^2$/g; $N$ is the number of methane molecules in the monomolecular layer adsorption saturation; $\sigma$ is the molecular cross-sectional area of methane, and its value is $13.5 \times 10^{-16}$ cm$^2$ due to the molecular diameter of methane is 0.414 nm; $N_A$ is the Avogadro constant with the value of 6.022 $\times$ 10$^{23}$; $V_m$ is the molar volume of a methane equal to 22.4 in L/mol; $V$ is the adsorbate volume in cm$^3$/g.
According to the surface chemistry principle, the concentration of methane in the matrix surface must be greater than the concentration inside the coal structure, and the concentration difference is called surface excess enthalpy ($\Gamma$) in mol/cm$^2$ (Equation 5).

$$\gamma = \frac{\gamma_0}{R} = \frac{\gamma_{\text{surf}}}{R}$$

The change in the surface tension of coal matrix body can be calculated according to the Gibbs formula, as showed in Equation (6).

$$\pi = -\gamma d\gamma + \Gamma d\Gamma = -\gamma d\gamma + \Gamma d\Gamma = -\Gamma d\ln P = -d\gamma,$$

where $\gamma$ is the SFE in $\mu$/mol; $\pi$ is the surface pressure in MPa or $\mu$/m$^2$, and it is equal to the reduced value of the SFE; $R$ is the universal gas constant equal to 8.314 (J/mol)/K; $T$ is the equilibrium temperature in K; and $P$ is the equilibrium pressure in MPa.

By integrating Equation (1), the SFE can be expressed as follows (Equation 7):

$$\pi = -\int d\gamma = \frac{RT}{V_mS} \int \frac{abP}{1+bP} \frac{1}{P} dP = \frac{aRT}{V_mS} \ln (1+bP).$$

Therefore, the SFE mainly depends on the Langmuir parameters ($a$, $b$), the specific surface area ($S$), and the temperature and pressure values of adsorption system.

According to the surface chemistry theory, the larger the SFE of coal matrix, the stronger the methane adsorbability. The Figure 7 showed that the SFE of different samples tends to decrease with increasing temperature, reflecting the sensitivity of methane adsorption to temperature variation, and the higher temperature is not conductive to methane adsorption, whether it is the sample treated with G502 or other samples treated with hydrophilic surfactants.

The variations of the SFE depending on the increase of pressure at reservoir temperature ($23^\circ$C) are shown in Figure 8, similar to the trend observed for the isotherm ad-/desorption fitting curves. Moreover, the value of SFE in the desorption process is obviously smaller than the same in the adsorption process, which corroborates the results of the isothermal adsorption curve, indicating that there is desorption hysteresis. The difference of surface energy before and after adsorption for different samples is shown in Table 4.

**TABLE 4** Fitting results of methane isothermal ad-/desorption under the temperature of $23^\circ$C

| Sample type         | Adsorption | | Desorption | | |
|---------------------|------------|---|------------|---|
|                     | $a_a$ (cm$^3$/g) | $b_a$ (1/MPa) | $R^2$ | $a_d$ (cm$^3$/g) | $b_d$ (1/MPa) | $c$ (cm$^3$/g) | $R^2$ |
| Moisture-equilibrated | 16.511     | 0.153 | 0.999    | 13.835     | 0.186 | 1.014     | 0.992    |
| Air-dried           | 15.462     | 0.299 | 0.996    | 13.832     | 0.476 | 0.138     | 0.997    |
| G502                | 26.984     | 0.225 | 0.994    | 22.745     | 0.144 | 5.569     | 0.997    |
| 6501                | 12.459     | 0.352 | 0.999    | 8.905      | 0.384 | 2.790     | 0.984    |
| JFC                 | 11.516     | 0.388 | 0.992    | 9.431      | 0.282 | 2.423     | 0.994    |
| LAS                 | 5.626      | 0.495 | 0.985    | 4.273      | 0.567 | 1.204     | 0.983    |

**FIGURE 6** Changes of desorption hysteresis ratio under different pressures

**FIGURE 7** Surface free energies of different samples varies with temperature
after methane adsorption represents the methane adsorption capacity, which corresponds to the heat released by methane adsorption. Also, the difference of SFE before and after methane desorption represents the difficulty of methane desorption, which corresponds to desorption endotherm. As was shown in Figures 7, 8, the value of SFE decreased in the following order: LAS, JFC, 6501, G502, and moisture-equilibrated, reflecting that the SFE of the hydrophilic sample treated with the surfactant (LAS/JFC/6501) is larger than that of the hydrophobic sample treated with the G502, revealing the better gas (methane) wettability for hydrophobic samples, and the LAS sample has the largest SFE representing the deficiency of methane adsorption. Particularly for the moisture-equilibrated sample, whose very small change in SFE during ad-/desorption indicates that the original moisture may hinder the methane adsorption to varying degree.

3.4 | Implications of wettability investigation

In this work, the water wettability of LFC and its influence on methane ad-/desorption were investigated by using different surfactants, which is essential for coal and methane outburst prevention as well as coal dust control in the mining industry, and also to assess enhanced CBM production from heterogeneous coal seams. Fluid-fluid displacement in coal is important for CBM extraction by fluids injection stimulation techniques such as gas, water, and heat injection.

The measured data imply that the water wettability of LFC is strongly influenced by the properties of surfactants besides the material composition, oxygen-containing functional groups, and pore-fracture characteristics. For example, the 6501 has the strongest hydrophilicity compared with other surfactants, whose CA was significantly smaller than the formation water. Therefore, the surfactant 6501 can be added in the spray water for dust removal when mining, so that the CA of the coal-water interface can be effectively reduced, and the dust-reducing effect can be greatly improved.

Moreover, gas outbursts often occur during coal mining, especially for the higher gaseous mine. The use of the wetting agent can effectively change the surface properties of the coal matrix, improve the wetting driving force in the capillary pores, and then block the methane in the pores, reduce or delay its release, and ultimately reduce the gas outbursts disasters.

In addition, more importantly, a certain gas-wetting reversal chemical can be mixed in the acidification and fracturing fluid during the development of CBM. When the active agent solution enters the formation, the wettability of reservoir rock near the well bottom or the artificial fracture can be changed into gas-wetting. After draining and depressurizing, the flow capacity of the formation fluid can gain a positive alteration due to the factors such as the wettability modification, increase of the relative permeability of gas/water, and reduction of the capillary pressure (or even transform into a driving force), leading to the reduction of liquid-lock phenomenon, and eventually allowing the fluid to flow to the wellbore, thus improving gas production.

From the microscopic point of view, the methane adsorption capacity of sample is significantly increased after applied the G502 in this research. It is experimentally proven that gas (methane) wettability of coal is lower than that of the moisture. Thus, methane adsorbed on the coal surfaces will be displaced rather easily by the moisture. In this study, 6501, LAS, and JFC can greatly improve the hydrophilicity and moisture content of coal, indicating that abundant moisture distribution could displace adsorbed methane and thus improve methane desorption rate and enhance CBM recovery efficiency.

4 | CONCLUSIONS

The following main conclusions have been reached:

1. The LFC in this work showed the good hydrophilicity itself due to the properties of wetting agent as well as the material composition, oxygen-containing functional groups, and pore-fracture characteristics.
2. The LFC sample with the wettability reversal agent (G502) had the larger adsorption capacity than the STS such as the LAS, JFC, and 6501, whereas the latter may be beneficial to promoting methane desorption. Additionally, the adsorption capacity of the air-dried samples was stronger than that of water-containing samples, reflecting the moisture content or hydrophilicity was not conducive to methane adsorption, and the better the hydrophilicity, the weaker the methane adsorption.
3. The desorption hysteresis rate was mainly controlled by pressure, i.e., the desorption hysteresis showed a logarithmic decrease with the increasing pressure, but the different samples clearly showed the desorption hysteresis to varying degree due to the intrinsic differences in wettability. The pressure drop in the low-pressure stage was difficult to drive the adsorbed methane to immediately desorb from the matrix surface, whereas even caused further adsorption or re-adsorption.

4. The variations of the SFE are consistent with the results of isotherm ad-/desorption, i.e., there is also the desorption hysteresis. The difference of SFE before and after methane desorption represents the difficulty of methane desorption, which corresponds to desorption endotherm.

ACKNOWLEDGMENTS
This work was jointly supported by the National Science and Technology Major Project (Grant No. 2016ZX05034002-001); the Excellent Supervisor Funded Program of the Ministry of Education (Grant No. 2652018235); the National Natural Science Foundation of China (Grant No. 41927801), and the Research on Exploration and Demonstration of Shale Gas in Henan Province (Grant No. 151100311000). Special thanks to the China Scholarship Council (File No. 201906400058) for providing financial assist. The authors wish to acknowledge the Editorial Office and Dr Costas K. Agalou for the help in handling the manuscript.

CONFLICTS OF INTEREST
The authors declare no conflict of interest.

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How to cite this article: Li P, Ma D, Zhang J, Huo Z. Wettability modification and its influence on methane adsorption/desorption: A case study in the Ordos Basin, China. Energy Sci Eng. 2020;8:804–816. https://doi.org/10.1002/ese3.552