Kinetics of Hydrate Formation and Dissociation in Coal at Different Temperatures Based on Impedance Method

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ABSTRACT: In the process of coal mining, gas outburst is a challenge that must be prevented to guarantee mining safety. Forming gas hydrate in coal can reduce the original gas pressure and delay the concentricate outbursts of gas flow, which is one of the potential technologies to prevent gas outbursts in coal. In this work, we perform the formation and dissociation kinetics experiment of hydrate in the presence of coal and tetrahydrofuran (THF) at the temperature based on different geological conditions in China by means of the experimental device with the impedance measurement function. The results showed that the impedance change can qualitatively describe the kinetic characteristics of hydrate formation and dissociation in coal. The sudden change in pressure and system impedance during gas hydrate formation indicated the nucleation point at which hydrate formation started, by which the induction time can be acquired. Pressure and impedance suddenly changed at the same time, which implied that methane molecules and tetrahydrofuran (THF) molecules entered the hydrate phase at the same time. When the dissociation temperature increased to 303.15 K, the hydrate dissociation rate can be less affected by dissociation temperature if it continued to increase. This work highlights that gas hydrate formation in coal can effectively prevent gas outbursts.

1. INTRODUCTION

Gas hydrates are crystalline, ice-like solid composed of gas molecules and water molecules at low temperature and high-pressure conditions.1 Its volumetric storage capacity is high (the volume ratio of hydrate to stored gas is 1:170 under normal atmospheric pressure), and its dissociation process requires much heat (500 kJ is required for the dissociation of 1 kg hydrate).2,3 Based on these characteristics, the formation of gas hydrates can be considered for the following aspects, including CO2 capture and storage, gas storage and transportation, seawater desalination, and refrigeration.4−6 Additionally, in 2003, Wu et al.7 proposed a new theory to prevent coal and gas outbursts by forming gas hydrate in coal.

Coal is one of the three major fossil fuels. China’s identified coal reserves list top position in the world, and it will be the main energy in future years.9 With the gradual increase of mining depth, all kinds of coal mine accidents occur frequently, and ensuring its safe mining is the key to sustainable use. For coal mine accidents, coal and gas outburst has been a major disaster.10

Coal and gas outburst is a kind of geodynamic disaster caused by geostress, gas, and other factors.11,12 This kind of dynamic disaster will cause casualties, damage to equipment and facilities, and obstruction of underground ventilation, which, to a large extent, seriously threatens mining safety.13,14 In the world, China is severely subjected to coal and gas outburst accidents.15,16 According to the statistics of the State Administration of Coal Mine Safety (shown in Figure 1), about 760 coal and gas outburst accidents occurred between 2008 and 2018 in china, resulting in 2049 deaths. With coal industry regulation, coal and gas outburst accidents and deaths have decreased since 2015. However, coal and gas outburst

Figure 1. Death toll and a number of accidents for coal and mine outburst in china from 2008 to 2018.
accidents always happened every year, which is a serious threat to coal mine production safety. The main dynamic source of coal and gas outburst is gas pressure. With the deepening of mining depth, the gas pressure in the coal seam also increases gradually, which is more likely to cause accidents.\textsuperscript{17,18} Therefore, solidifying gas into gas hydrate can sufficiently reduce gas pressure, which is attributed to the prevention of coal and gas outburst.\textsuperscript{19}

The hypothesis on the possible existence of gas hydrates in coalbeds was first presented by Makogon.\textsuperscript{20} Later, Smirnov et al.\textsuperscript{21} investigated the possible formation of gas hydrate in coal by different forms of immobilized water. The study showed that methane hydrate can be formed by methane and water at the secondary adsorption position of coal. Bustin et al.\textsuperscript{22} conducted the coal bed gas hydrate formation experiments in high-volatile bituminous coal, which was tested via adsorption, X-ray diffraction, and nuclear magnetic resonance. It demonstrated that a significant proportion of the inherent moisture (nonmobile water) is available to form methane clathrate hydrates. In addition, the author successfully synthesized hydrates in coal. To sum up, through theoretical and experimental studies, it can be confirmed that hydrates can be formed in coal. Solidified mine gas in the form of gas hydrates has been a promising technology for preventing coal and gas outburst because its formation can effectively reduce gas pressure in the coal seam, and it will not be dissociated in a short time after formation. In coal, heat transfer is one of the main factors affecting the dissociation of hydrate. Thus, considering the effect of heat transfer in coal, the research that whether the dissociation process of hydrate in coal can effectively prevent coal and gas outburst is very important.

Current studies about hydrate dissociation in porous medium influenced by temperatures mainly focus on natural gas hydrate dissociation in sediments, with the aim of methane recovery from natural gas hydrate resources. Tang et al.\textsuperscript{23} investigated the influence of water temperatures and injection rates on gas production, water flow characteristics, temperature distribution, and energy ratio. Mekala et al.\textsuperscript{24} investigated the influence of two dissociation temperatures on the dissociation characteristics and gas production rates of natural gas hydrate in porous media. Chong et al.\textsuperscript{25} carried out methane hydrate dissociation experiments by thermal stimulation from 278.7 to 285.2 K and analyzed the laws of gas production, water production, and energy efficiency of hydrate dissociation. Barmecha et al.\textsuperscript{26} investigated the influence of injection water temperatures and injection water flow rates on the recovery of natural gas from the test sediment. It was found that the gas recovery rate was directly dependent upon the dissociation temperatures. Nair et al.\textsuperscript{27} studied the dissociation of methane hydrate in a confined environment at 313.15 K. It was found that the recovery rate of gas and the dissociation of hydrate were related to the particle size of sediments. Zhao et al.\textsuperscript{28} investigated the heat transfer characteristics of hydrate dissociation in sediments influenced by five different temperatures. It was found that, except for 313.15 K, the radial temperature differences increased with the increasing temperature of the air bath during the dissociation processes. The above-mentioned research studies mainly provided the theories for gas hydrate dissociation by thermal stimulation in porous media. The results showed that the temperature had a significant influence on the dissociation of hydrates. However, the characteristics of hydrates in coal are greatly different since thermal conductivity and chemical properties are different from porous media.\textsuperscript{29–31} At present, no literature studies were reported about the kinetics of hydrate dissociation in coal. Thus, it is necessary to investigate the dissociation kinetics of hydrate influenced by heat transfer in coal and to obtain the impedance in the formation and dissociation processes.

To accurately explore the process of hydrate formation and dissociation in solid media, some scholars used different detection techniques to carry out experiments. In the experiments, by detecting the electrical characteristics of hydrate formation and dissociation in rector with no windows, it can be found that electrical characteristics can indicate the reaction process of hydrates. The test principle is that the formation of hydrate will make the test area of the system basically in an insulated state, and the impedance value will be very large. In addition, the liquid increases with the dissociation of hydrate. Here, the impedance value decreases due to the enhancement of electrical conductivity in the test area. Permyakov et al.\textsuperscript{32} used the resistance method to measure sand samples containing THF hydrate, water, or ice. They reported that the temperature and the type and phase state of the fluid mainly determined the resistivity of samples. Karamoddin et al.\textsuperscript{33} investigated THF hydrate formation in the presence of electrolytic inhibitors using the measurement of electrical conductivity and analyzed the inhibition strength of these inhibitors. The results showed the hydrate nucleates when the increase of electrical conductivity in solution coincides with the sudden increase of temperature. Du Frane et al.\textsuperscript{34} found that methane hydrate (and ice) was the main current path in the mixture during the process of monitoring
the conductivity of the mixture of methane hydrate and sediment. Chen et al.\textsuperscript{35} found that there was a corresponding relationship between the impedance change and the system temperature change when monitoring CO\textsubscript{2} hydrate formation in a porous medium using impedance technology. The above studies indicated that the resistance method can accurately reflect the formation and dissociation characteristics of hydrate in solid media. In this paper, the technique of impedance measurement was also introduced to study the formation and dissociation of hydrate in coal. In our previous studies, it has been demonstrated that the hydrate can be built in the coal (shown in Figure 2). The hydrate could block off the interspace of coal, and it does not dissociate in a short time. The energy of high-pressure gas flow can be inhibited due to the hydrate in the coal.

The mining depth of existing coal mines in China ranges from 600 to 1500 m\textsuperscript{36,37} and the temperature corresponding to the depth of coal seams ranges from 294.95 to 313.15 K\textsuperscript{38,39}. Accordingly, 293.15–313.15 K was selected as the range of dissociation temperatures in this experiment.

In this study, the kinetic experiments of hydrate formation and dissociation in coal were carried out in the selected dissociation temperature range based on impedance technology. The characteristics of hydrate dissociation, rate of hydrate dissociation, and gas recovery in coal at different dissociation temperatures were investigated.

2. CALCULATION

During hydrate formation, the PR equation of state can be used to calculate the amount of methane gas consumed at any given time.\textsuperscript{40}

\[
p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}
\]

\[
a(T) = a_0 a(T_0) = 0.4572 \frac{RT_c^2}{P_c} \tag{2}
\]

\[
b = 0.0778 \frac{RT_c}{P_c} \tag{3}
\]

\[
a(T_0) = 1 + m(1 - T_0^{0.5}) \tag{4}
\]

\[
m = 0.37464 + 1.54226ω - 0.26992ω^2 \tag{5}
\]

\[
V = V_G/n \tag{6}
\]

where \(V\) refers to the molar volume of gas, \(T_s\) is the temperature contrast, \(P_c\) refers to the pressure contrast, \(P_r\) refers to the critical pressure, \(T_c\) is the critical temperature in K, and \(ω\) refers to the eccentric factor. \(R\) is the molar gas constant (\(R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}\)).

Equations 2–6 were incorporated into eq 1 using the Excel single variable to solve the equation

\[
F(V) = p - \frac{RT}{V-b} + \frac{a(T)}{V(V+b)+b(V-b)} \tag{7}
\]

The \(F(V)\) was set to 0. Then, the value of \(V\) was calculated using eq 7.

\[
(Δn_{H_4})_f = n_0 - n_t \tag{8}
\]

where \((Δn_{H_4})_f\) is the amount of methane gas consumed (mol) at time \(t\); \(n_0\) is the number of moles of gas (mol) at the beginning of the formation experiment; and \(n_t\) is the amount of methane gas (mol) at time \(t\).

At the end of the formation experiment, to measure the relationship between the gas dissolved and converted into hydrate and the gas at the initial time, gas conversion to hydrate was calculated using eq 9.

\[
\text{gas conversion to hydrate (\%)} = \frac{Δn_{H_4}}{n_0} \times 100 \tag{9}
\]

where \(Δn_{H_4}\) is the total amount of methane gas consumed at the end of hydrate formation.

With the forward difference method, the rate of hydrate formation can be calculated as follows

\[
\left(\frac{dΔn_{H_4}}{dt}\right)_t = \frac{Δn_{H_4,t+Δt} - Δn_{H_4,t}}{Δt}, \Delta t = 10 \text{ s} \tag{10}
\]

The average of these rates for formation experiments was calculated every 30 min.

During hydrate dissociation experiments, the amount of methane gas released at any given time was calculated using eq 11.

\[
(Δn_{H_4})_f = n_t - n_i \tag{11}
\]

where \(n_i\) is the amount of methane gas (mol) at time \(t\) in the dissociation process and \(n_t\) is the number of moles of gas (mol) at the beginning of the dissociation experiment.

Similarly, the dissociation rate of hydrate can be calculated by the discrete forward difference method, and the formula was as follows

\[
\left(\frac{dΔn_{H_4}}{dt}\right)_t = \frac{Δn_{H_4,t+Δt} - Δn_{H_4,t}}{Δt}, \Delta t = 10 \text{ s} \tag{12}
\]

The average dissociation rate was calculated every 30 min.

Equation 13 defined the gas recovery rate, which was based on the amount of gas consumed in the hydrate formation process to measure gas production.

\[
\text{gas recovery(\%)} = \frac{n_{\text{diss}}}{n_{\text{hyd}}} = \frac{(Δn_{H_4})_t}{Δn_{H_4}} \times 100 \tag{13}
\]

\[
f_i = x_i^* \exp\left\{-\sum_j A_{ij} \frac{f_j}{1 + \sum_i C_{ij}} + \frac{B_j}{T - C_{ij}}\right\} \tag{14}
\]

For eq 13, \(n_{\text{hyd}}\) is the amount of gas at the end of hydrate formation and \((Δn_{H_4})_t\) is the amount of gas released at time \(t\).

For eq 14, \(f_i\) is the fugacity of \(i\) in the hydrocarbon-rich liquid, \(x_i^*\) is the mole fraction of gas \(i\) in large cages, \(α = 2\) for structure II (sII), and \(a_w\) is the activity of water. Where \(β = 10.224 \text{ MPa}^{-1}\) for structure II hydrates. Where \(A_{ij}\) denotes binary parameters for the interaction between molecules in the small cages and in the large cages. Using \(X_i = 0, Y_j = 0,\) and \(Z_i = 0\) when the small cages were not being occupied.
3. RESULTS AND DISCUSSION

3.1. Impedance Characteristics in Hydrate Formation and Dissociation Processes. All of the formation experiments were conducted under the conditions of 3 MPa and 276.15 K. Table 1 summarizes the induction time, gas consumption, and gas conversion to hydrate. After the completion of hydrate formation, the hydrate dissociation experiments were carried out in the coal—THF system for five different dissociation temperatures. To ensure the repeatability of the experiments, the experiment under the same conditions was repeated three times. Figures 3–7, respectively, show curves of the changes in impedance and pressure three times for different dissociation temperatures.

As Figures 3–7 demonstrate, each experiment can be divided into two stages: formation and dissociation (time zero corresponds to the starting point of the formation experiment). The formation stage is shown in the yellow area of the figure and the dissociation stage is shown in the green area of the figure. In all experiments, it was found that the change of impedance and pressure with time showed a corresponding relationship. According to the corresponding relationship, it can be divided into six stages. Therefore, it can be inferred that impedance can sensitively reflect the material changes in the coal—THF—CH4 system.

It can be seen from Figures 3–7 that all experimental formation processes can be divided into three stages (“a”, “b”, and “c”). The dissociation processes can also be divided into three stages (“d”, “e” and “f”). In stage “a”, the system temperature decreased gradually, and the gas pressure decreased slowly. The impedance accordingly began to increase, but the increased range was small. In stage “b” (rapid growth stage), the pressure increased rapidly, and the impedance of the three channels exhibited an increasing trend with time. The last stage of the formation process is stage “c” (slow growth stage). As shown in the figure, the rate of change of gas pressure gradually decreased and then reached an equilibrium state. Correspondingly, the rate of change of impedance also gradually decreased and then reached an equilibrium state. After the hydrate formation experiments, the hydrate was dissociated in a closed environment owing to heat transfer. Similarly, it can be seen from Figures 3–7 that in the stage “d” (slow dissociation stage), the pressure did not change significantly at the initial stage and then increased slowly. The corresponding system impedance began to decrease rapidly in the stage “d”. In stage “e” (rapid dissociation stage), the gas pressure increased rapidly; the corresponding system impedance suddenly increased to a dozen times higher than that at the end of the formation of hydrate, and then rapidly dropped to near the initial formation impedance value. The last stage of the dissociation process is stage “f” (equilibrium stage of hydrate dissociation), in which the gas pressure continuously increased and then reached an equilibrium state; the corresponding system impedance also gradually reached an equilibrium.

By comparing the experiments at different dissociation temperatures, it was found that the impedance and pressure had the same trend in the same stage, but the time consumed was different. To analyze their similar changing trends, III-1st was taken as an example to illustrate. As shown in Figure 5 III-1st, in stage “a” (0–67 min), the system temperature decreased from 303.15 to 297.15 K, the gas pressure gradually decreased from 2.72 to 2.55 MPa, and the corresponding system impedance started to slowly increase from 2200 ± 260 Ω, but at a much lower amplitude. According to curves of system impedance in the process of hydrate formation and dissociation in coal, it can be concluded that the mutual transformation of coal—THF—CH4, coal—THF-hydrate—CH4, and coal—hydrate—CH4 led to obvious changes of system

Table 1. Details about Hydrate Formation in Coal Samples

| exp. no. | temperature of formation (K) | equilibrium gas pressure (MPa) | first induction time (min) | gas consumed (mol) | gas conversion to hydrate (%) |
|----------|------------------------------|-------------------------------|---------------------------|-------------------|-----------------------------|
| I-1st    | 276.15                       | 0.7                           | 0.616                     | 76.82             |
| I-2nd    | 276.15                       | 0.63                          | 0.635                     | 79.18             |
| I-3rd    | 276.15                       | 0.74                           | 0.605                     | 75.45             |
| II-1st   | 276.15                       | 0.7                           | 0.618                     | 77.14             |
| II-2nd   | 276.15                       | 0.84                          | 0.580                     | 72.42             |
| II-3rd   | 276.15                       | 0.87                          | 0.575                     | 71.74             |
| III-1st  | 276.15                       | 0.84                           | 0.581                     | 72.44             |
| III-2nd  | 276.15                       | 0.59                           | 0.579                     | 73.77             |
| III-3rd  | 276.15                       | 0.99                           | 0.540                     | 67.36             |
| IV-1st   | 276.15                       | 0.91                           | 0.559                     | 69.70             |
| IV-2nd   | 276.15                       | 0.88                           | 0.569                     | 71.04             |
| IV-3rd   | 276.15                       | 0.93                           | 0.556                     | 69.37             |
| V-1st    | 276.15                       | 1.08                           | 0.515                     | 64.29             |
| V-2nd    | 276.15                       | 1.06                           | 0.518                     | 64.63             |
| V-3rd    | 276.15                       | 1.05                           | 0.521                     | 64.97             |

Figure 3. Impedance values of three channels and pressure values during hydrate formation and dissociation in coal samples. The formation process of repeated three experiments at 276.15 K. The dissociation process for experiments at 293.15 K.
Figure 4. Impedance values of three channels and pressure values during hydrate formation and dissociation in coal samples. The formation process of repeated three experiments at 276.15 K. The dissociation process for experiments at 298.15 K.

Figure 5. Impedance values of three channels and pressure values during hydrate formation and dissociation in coal samples. The formation process of repeated three experiments at 276.15 K. Dissociation process for experiments at 303.15 K.

Figure 6. Impedance values of three channels and pressure values during hydrate formation and dissociation in coal samples. The formation process of repeated three experiments at 276.15 K. The dissociation process for experiments at 308.15 K.

Figure 7. Impedance values of three channels and pressure values during hydrate formation and dissociation in coal samples. The formation process of repeated three experiments at 276.15 K. Dissociation process for experiments at 313.15 K.
impedance. Since the phase equilibrium pressure was 3.7 MPa at 297.15 K, it can be determined that the thermodynamic conditions of hydrate formation were not satisfied in the stage “a”. At this stage, the decrease of gas pressure was due to the gradual dissolution of gas, and the slow increase of system impedance may be due to the influence of the decrease of system temperature. In addition, it was observed that the impedance in stage “a” slightly increased for II, IV, V, III-2nd, and III-3rd. This indicated that the hydrate was one of the main factors affecting the system impedance. Then, in stage “b” (67–405 min), the system temperature decreased from 297.15 to 276.75 K, and the gas pressure decreased rapidly from 2.55 to 0.89 MPa, indicating that the gas was consumed rapidly in this stage. A sudden change point appeared in the impedance curve of stage “b” at 67 min. Afterward, the impedance increased rapidly from 3100 ± 400 to 3400 ± 430 Ω in 5 min, and then the system impedance increased gradually. It can be determined that the phase state changed at the beginning of stage “b”, and the hydrate began to nucleate. Therefore, this sudden change point was the hydrate nucleation point.

It had to be noted that the gas pressure at the nucleation point for II, III, IV, and V decreased suddenly. This can be seen from the enlarged figures in Figures 4–7 (this phenomenon was also observed in the first formation experiment under four different experimental conditions, yet they were not drawn). The inflection point of the impedance curve in the process of hydrate formation indicated that the hydrate began to form. However, the sudden increase of gas consumption in the process of hydrate formation indicated that the dissolved gas began to enter the hydrate phase. According to the gas fugacity model of Ma et al., in 303.15 K, the phase equilibrium pressure of hydrate formation in CH₄–pure water system was 73.7 MPa, while the phase equilibrium pressure of hydrate formation in CH₄–20%THF system was 7.27 MPa, which indicated that THF can shift the phase equilibrium of hydrate formation to milder conditions. In addition, THF can also form hydrate under certain conditions. Furthermore, according to the experimental curves, we can see that the impedance did not change obviously before the change of the gas pressure, and the sudden change of system impedance and pressure occurred at the same time (II: 60 ± 23 min, III: 70 ± 3 min, IV: 90 ± 7 min, and V: 103 ± 7 min). This indicated that hydrate nucleation and gas consumption occurred at the same time. Therefore, based on the fact that the sudden gas consumption and hydrate formation occurred at the same time, it can be inferred that CH₄ hydrate and THF hydrate were formed together at the nucleation point.

According to the above experimental phenomena, it was analyzed that the formation of gas hydrate needed to experience four periods. First, gas began to dissolve into the liquid phase until saturation was reached. Second, the water molecules connected by a hydrogen bond formed unstable cluster structures around the dissolved gas molecules. Then, these unstable clusters gradually gathered together to form metastable agglomerates by sharing faces (this process increases the disorder of the structure arrangement). Finally, When the size of the cluster agglomerate reached a critical value, stable crystal nuclei began to form.

In the presence of THF, the structure of sII hydrate can be formed, and its basic structure units consist of 8 large cages (S¹²6⁶) and 16 small cages (S⁵²⁶). Seo et al. applied ¹³C NMR for CH₄–THF hydrate analyses to study the formation processes. Research showed that THF occupied almost all of the big cages, while methane molecules occupied a part of small cages for sII hydrate. To further understand the nucleation mechanism of mixed CH₄–THF hydrate, Wu et al. used the MD simulation method to find that when methane molecules were present in THF aqueous solution, they will provide regular cage structures (S¹²) in water, while at the same time, the large cages (S¹²⁶) were also being formed rapidly around the THF. Therefore, the presence of methane molecules and THF will jointly promote the formation of cage structures. However, Hashimoto et al. studied that the sII hydrate formed by THF provided a material basis for the entry of methane gas, which indicated that the THF hydrate and CH₄ hydrate did not form at the same time. Based on this conclusion, the THF hydrate was formed first, and impedance suddenly changed before gas pressure dropped. However, in the experiments, the system impedance and gas pressure changed at the same time; therefore, it can be proved that methane gas and THF entered the hydrate phase at the same time, which was consistent with the results of Wu et al.’s studies.

It can be seen from the stage “b” in Figure 5 III-1th that the gas pressure began to decrease from 2.55 MPa, and then the inflection point appeared at 160 min. Afterward, the gas pressure tended to balance gradually. While the system impedance increased continuously at this stage, and the inflection point appeared at 355 min, then the impedance also tended to reach an equilibrium state. In addition, in the stage “b” of all hydrate formation experiments, it can be found that the time frame for system impedance approaching an equilibrium state was from 250 to 345 min, and the time frame for gas pressure approaching an equilibrium state was from 80 to 135 min. In hydrate formation experiments for the same conditions, the gas pressure first reached an equilibrium state. This indicated that during the growth of mixed THF–CH₄ hydrate, methane gas first entered the hydrate phase. Afterward, gas pressure reached an equilibrium state. However, at this stage, the structure of the hydrate–coal system changed so that the system impedance kept increasing after gas pressure reached an equilibrium state.

In the stage “c” (405–600 min) of Figure 5 III-1th, the system temperature decreased from 276.75 to 276.15 K. Meanwhile, the gas pressure slowly decreased from 0.89 to 0.84 MPa, and finally stabilized at 0.84 MPa, which indicated that the gas is no longer consumed. The system impedance began to slowly increase from 35 000 ± 7 300 Ω after the system impedance tended to reach the equilibrium state. This indicated that the phase transformation reached an equilibrium state, and the formation of hydrate ended.

As can be seen in Figure 5 III-1th, after the hydrate formation experiments, hydrate dissociation was driven by heat transfer under confined conditions by controlling air bath temperature from 293.15 to 303.15 K. The ambient temperature of the air bath first reached the target value within a few minutes, and then the system temperature slowly reached 303.15 K. The experimental results and the corresponding experimental conditions for dissociation processes are listed in Table 2. At the dissociation temperature of 303.15 K, the three stages of impedance and pressure change in the hydrate dissociation process were 600–660 min (stage “d”), 660–930 min (stage “e”), and 930–1200 min (stage “f”), respectively. In stage “d”, the system temperature increased from 276.15 to 288.15 K, during which the gas pressure increased slowly, and the system pressure reached 0.99 MPa at 660 min. It can be concluded
that, in terms of the fugacity model of Ma et al., the hydrate was deemed to be unstable under conditions at the end of this stage. \(^{41}\) Therefore, the increase in pressure was due to hydrate dissociation. Correspondingly in stage “d”, the system impedance increased from 0.99 to 2.59 MPa, which was due to the gas production process. At the beginning of this stage, the system impedance increased rapidly, while the corresponding gas pressure also increased, which indicated that the gas hydrate was dissociated. Therefore, the hydrate formed was THF hydrate in this stage. After that, the increase of the system pressure, the THF hydrate was dissociated gradually, and the system impedance decreased.

In stage “e”, the system temperature increased slowly from 302.75 K (990 min) to 303.15 K (1200 min), the system pressure began to increase slowly from 2.59 MPa, and then reached an equilibrium state. The gas pressure was 2.81 MPa at the end of this stage. The corresponding system impedance gradually decreased from 2000 ± 180 \(\Omega\) and reached an equilibrium state at the end of the stage, indicating that the dissociation of the hydrate ended.

### 3.2. Gas Conversion to Hydrate during Hydrate Formation

Figure 8 shows the influence of temperature gradients on hydrate formation kinetics. The gas conversion to hydrate increased with increasing temperature, indicating a positive effect of temperature on hydrate formation kinetics. However, the effect was not linear, and the conversion rate increased rapidly at lower temperatures before reaching a plateau at higher temperatures.

#### Table 2. Details about Hydrate Dissociation under Coal Samples in This Study

| exp no. | temperature of dissociation (K) | equilibrium gas pressure at the end of dissociation (MPa) | total number of moles of gas recovered (mol) | recovery (%) |
|---------|---------------------------------|---------------------------------------------------------|--------------------------------------------|-------------|
| I-1st  | 293.15                          | 1.83                                                    | 0.286                                      | 46.39       |
| I-2nd  | 293.15                          | 1.96                                                    | 0.333                                      | 52.51       |
| I-3rd  | 293.15                          | 1.97                                                    | 0.306                                      | 50.63       |
| II-1st | 298.15                          | 2.85                                                    | 0.542                                      | 87.66       |
| II-2nd | 298.15                          | 2.77                                                    | 0.483                                      | 83.22       |
| II-3rd | 298.15                          | 2.75                                                    | 0.472                                      | 82.09       |
| III-1st| 303.15                          | 2.81                                                    | 0.480                                      | 82.67       |
| III-2nd| 303.15                          | 2.80                                                    | 0.489                                      | 82.63       |
| III-3rd| 303.15                          | 2.73                                                    | 0.419                                      | 77.59       |
| IV-1st | 308.15                          | 2.86                                                    | 0.457                                      | 81.89       |
| IV-2nd | 308.15                          | 2.85                                                    | 0.466                                      | 81.78       |
| IV-3rd | 308.15                          | 2.85                                                    | 0.452                                      | 81.34       |
| V-1st  | 313.15                          | 2.91                                                    | 0.414                                      | 80.26       |
| V-2nd  | 313.15                          | 2.91                                                    | 0.417                                      | 80.41       |
| V-3rd  | 313.15                          | 2.90                                                    | 0.416                                      | 79.98       |
77.2%. This indicated that the gas content of the hydrate was the highest at the end of hydrate formation under the conditions of the minimum temperature gradient. When the temperature gradient was from 313.15 to 276.15 K, the final average gas conversion rate was the lowest, which was 64.6%. This phenomenon may be due to the mass and heat transfer limitation in the process of hydrate formation under a large temperature gradient, which further limited the amount of gas into the hydrates, and finally led to the low gas conversion to hydrate. In addition, the gas conversion to hydrate was most random at the end of the hydrate formation with the temperature ranging from 303.15 to 273.15 K, while the gas conversion to hydrate was the least at the end of the hydrate formation with the temperature ranging from 313.15 to 273.15 K. It was inferred that the heat and mass transfer were relatively stable under a large temperature gradient.

**3.3. Average Rate of Hydrate Formation and Dissociation.** The average rate of hydrate formation and dissociation was calculated for all of the experiments to analyze the formation and dissociation kinetics of CH$_4$ + THF hydrate in coal using the discrete forward difference method. Figure 9 shows the comparison of the average formation rate of hydrate under different temperature gradients and the comparison of the average dissociation rate of hydrate in different temperature conditions. As shown in Figure 9, the formation reactions of all experiments experienced 600 min and the formation rate of hydrate ranged from 0 to 3 mol/min at the end of hydrate formation, which indicated that the system had reached an equilibrium state. In all hydrate formation experiments, the trends of the hydrate growth rate were similar under all experimental conditions. First of all, the average rate of hydrate formation first increased to a maximum value within 140 min, then decreased, and was finally close to 0 mol/min. It can be seen from the enlarged figure that, for experiment III, the maximum average rate of hydrate formation was the highest in the process of hydrate formation, which was $58 \times 10^{-4}$ mol/min. In addition, the average maximum rates of hydrate formation were found to be $38 \times 10^{-4}$, $46 \times 10^{-4}$, $53 \times 10^{-4}$, and $56 \times 10^{-4}$ mol/min for experiments I, II, IV, and V, respectively. From the data, it can be seen that the maximum average rates of hydrate formation for experiments III, IV, and V were similar and obviously higher than that for other experiments. This showed that when the temperature gradients are 303.15–276.15, 308.15–276.15, and 313.15–276.15 K, the influence on the peak value of the average rate of hydrate formation in coal was not obvious. The possible reason was that the hydrate formation hindered the supply of gas under a large temperature gradient. Therefore, the average rates of hydrate formation were not significantly affected by the temperature gradients. In addition, it can be seen from the enlarged figure that the higher the initial temperature, the faster the hydrate formation rate, and it had a lower effect on the hydrate formation rate when the initial temperature was higher than 303.15 K.

After the formation experiments of hydrate, dissociation experiments were carried out at different temperatures. It can be seen from Figure 9 that the change of the hydrate dissociation rate was consistent with the change of the hydrate growth rate. The rate first increased, then decreased, and was finally close to 0 mol/min. In addition, the higher the dissociation temperature, the faster the hydrate dissociation rate increased, and the higher the maximum dissociation rate would be. This can be confirmed from Figures 3–7. The higher the dissociation temperature, the faster the gas pressure increased. For experiment V, compared to other experiments, the increasing rate of system pressure was the fastest, and the time experienced for stage “d” and “e” were the shortest. For all experiments, the maximum dissociation rates of the hydrate, under temperature conditions of 293.15–313.15 K, were (6.86 ± 0.40) $\times 10^{-4}$ mol of gas/min (293.15 K), (12.11 ± 1.17) $\times 10^{-4}$ mol of gas/min (297.15 K), (17.52 ± 0.46) $\times 10^{-4}$ mol of gas/min (303.15 K), (22.91 ± 0.43) $\times 10^{-4}$ mol of gas/min (308.15 K), and (26.97 ± 0.42) $\times 10^{-4}$ mol of gas/min (313.15 K), respectively. In experiments I, II, III, IV, and V, the average gas pressure corresponding to the maximum average rate of hydrate dissociation were 0.89, 1.20, 1.54, 1.80, and 2.05 MPa, respectively, and the corresponding average gas recovery rates were 9.1, 15.0, 22.0, 32.2, and 38.0%, respectively. This was because the higher the dissociation temperature, the faster the heat transfer rate. Thus, more hydrate can be dissociated in the higher dissociation temperatures. In addition, it can be found that the hydrate dissociation rate was lower than the hydrate formation rate in coal for all experiments. This indicated that gas production was slow in the process of hydrate dissociation driven by heat transfer in coal. Moreover, Li et al. by means of numerical simulation, studied that the dissociation rate of hydrate was far less than the formation rate, and the reduction of pressure can only increase the dissociation rate to a very limited extent.

The peak stages of hydrate dissociation rate curves in these five different experimental conditions were included in their respective rapid gas production stages (the corresponding stage can be found from Figures 3–7). By comparing the different hydrate dissociation curves, it can be found that the higher the dissociation temperature was, the shorter the time taken for gas production was. However, the time taken was virtually the same for both 308.15 and 313.15 K temperatures. From this phenomenon, it can be concluded that the higher heat transfer temperature had no great influence on the time of rapid gas production.

**3.4. Gas Recovery from Hydrate Dissociation.** Figure 10 shows methane gas recovery curves in coal conducted under the different dissociation temperature conditions. As shown in Figure 10, all gas recovery rates increased with time and finally...
reached their respective maximum values. When the dissociation temperatures were 293.15, 297.15, 303.15, 308.15, and 313.15 K, the corresponding gas recovery rates were $49.8 \pm 3.1$, $84.3 \pm 2.9$, $81.0 \pm 2.9$, $81.7 \pm 0.3$, and $80.2 \pm 0.2\%$, respectively. Obviously, the final gas recovery rate was the lowest at the dissociation temperature of 293.15 K. It can be clearly demonstrated that the equilibrium pressure of the system was the lowest at the end of hydrate dissociation compared to other experiments, which is $1.8-1.9$ MPa, accounting for about 60% of the equilibrium pressures of other experiments. The reason was that the hydrate in coal was not completely dissociated at the dissociation temperature of 293.15 K.

The phase equilibrium temperature at 3 MPa was found to be 295.34 K, which can be calculated by the calculation model of Ma et al. (based on eq 14). It can be concluded that the hydrate was not completely dissociated at the dissociation temperature of 293.15 K, which can be further confirmed from the system impedance at the end of hydrate dissociation under these conditions. As shown in Figure 3, at 293.15 K, the system impedance at the end of hydrate dissociation is higher than that in other hydrate dissociation experiments, which indicated that there was still hydrate in a section of the measured impedance area. At the dissociation temperature of 293.15 K, the gas pressure also increased with the continuous dissociation of hydrate. But in this process, the system temperature was always higher than the phase equilibrium temperature; therefore, the hydrate dissociation continuously occurred. When the system temperature reached 293.15 K, at a certain time, the phase transformation among the gas phase, liquid phase, and hydrate phase would reach a dynamic equilibrium state, which indicated that the gas pressure no longer changed. Additionally, under other dissociation temperature conditions, the gas recovery rates ranged from 80.2 to 84.3%. This reason was that a part of the methane gas was dissolved into the liquid phase. In fact, this can reflect the gas solubility of methane gas in the 20%THF solution.

The phase equilibrium curves for the 20%THF–CH$_4$ system and dissociation temperature conditions are shown in Figure 11. Under the conditions of higher dissociation temperatures, it will greatly enhance the kinetics of hydrate dissociation. However, in Figure 10, when the hydrate dissociation temperature continued to increase from 303.15 K, the recovery rate of gas decreased. This indicated that the hydrate dissociation rate would be less affected by the higher dissociation temperatures. Thus, the higher the hydrate dissociation temperature, the lower the impact on the gas production process. Moreover, compared with the dissociation temperature of 293.15 K, the gas recovery was more random. In other experiments (II, III, IV, and V), when the average gas recovery rate reached 50%, the corresponding system pressures were 2, 2.08, 2.12, and 2.26 MPa, and the time consumed was 350, 225, 180, and 160 min, respectively. In addition, compared with other experiments, the gas recovery rates at the dissociation temperatures of 293.15 and 297.15 K were relatively random, indicating that lower dissociation temperatures would cause instability of the gas production process. Moreover, compared with the dissociation temperature of 293.15 K, the gas recovery was more random at 297.15 K. Zhao et al. studied the dissociation process of hydrate influenced by heat transfer in a closed reactor. The results showed that there was a dissociation boundary and a moving boundary in the hydrate dissociation process, and the dissociation delay effect of the hydrate was not obvious at lower or higher dissociation temperatures. In summary, it can be analyzed that the gas solubility of methane gas in the 20%THF solution was effectively reduced due to the endothermic effect on the hydrate dissociation process, and the absorbed heat was difficult to obtain in a short time, which hindered gas production. Under the low gas production rates, the endothermic process can be more stable, and the heat transfer process can also remain stable. At the dissociation temperature of 293.15 K, the gas production process began to be obviously influenced by the endothermic effect on the hydrate dissociation process, which caused the uneven heat transfer process because of the aggravation of the endothermic process. However, at other higher dissociation temperatures, this phenomenon can be effectively eliminated due to the higher heat transfer rates.

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4. CONCLUSIONS

In this work, the experimental device of mine gas hydrate formation and dissociation with the impedance measurement function was applied to investigate the characteristics of hydrate formation and dissociation kinetics in coal. The formation conditions of the hydrate were 276.15 K and 3 MPa, and the dissociation experiments were conducted within the temperatures ranging from 293.15 to 313.15 K. The conclusions were as follows:

(1) The characteristics of different stages of hydrate formation and dissociation can be obtained by analyzing impedance in coal. The change of impedance and system pressure can reflect the changing characteristics of coal−gas−liquid, coal−gas−liquid-hydrate, and coal−gas-hydrate in the process of hydrate formation and dissociation.

(2) In all hydrate formation experiments, the nucleation point of hydrate in coal can be determined by the change of system impedance and pressure, and the induction time of hydrate formation can also be accurately obtained. Pressure and impedance changed at the same time, which implied methane molecules and tetrahydrofuran (THF) molecules entered the hydrate phase at the same time. The gas conversion to hydrate was low when the initial temperature was high at the end of hydrate formation in coal.

(3) In all hydrate dissociation experiments, THF hydrate was dissociated first. THF hydrate reformation occurred in the hydrate dissociation process. The dissociation rate of hydrate increased with time and then decreased. The recovery rate of gas production increased with time and finally reached the maximum value.

(4) From the recovery point of view, the higher the dissociation temperature, the larger the dissociation rate of hydrate. Except for 293.15 K, hydrate in coal was completely dissociated at other dissociation temperatures. In a certain range of dissociation temperatures, the differences in the gas recovery and the time taken for gas production were observed to be decreased as the dissociation temperature increased.

(5) The formation of hydrate in coal will effectively reduce the gas pressure (the maximum pressure drop was from 3 to 0.63 MPa), and the high-pressure gas flow was not being formed in a short time.

This study verified that the curing principle of mine gas hydrate can effectively reduce the gas pressure in coal, delay the concentrative outburst of gas flow, and achieve the purpose of preventing coal and gas outburst accidents.

5. EXPERIMENTAL SECTION

5.1. Materials. In all experiments, the purity of methane gas used was 99.99%. To make it easier to form hydrates in coal, the THF solution with a mass fraction of 20% was used as the experimental solution. The outburst coal samples were selected from the Junde Coal Mine of Heilongjiang Province in China as the medium of hydration curing and dissociation.

5.2. Apparatus. The kinetic principles of mine gas hydration and dissociation in coal were studied by the impedance method, and a device with impedance electrodes was applied. Figure 12 shows the schematic diagram of the experimental device and the distribution of impedance measurement electrodes.

As seen in Figure 12a, the experimental apparatus consists of a gas pressurization system, a gas hydrate reaction system, a data acquisition system, and a temperature controlling system. The most important equipment is the high-pressure reactor with electrodes. Three pairs of electrodes are installed in a fixed cross-section of the reactor at equal intervals (shown in Figure 12b). The reactor is made of 316 stainless steel, which is equipped with an insulating sleeve closely matched with the reactor. The inner of the sleeve has a cuboid cross-section with an inner length of 100 mm, an inner width of 80 mm, and an inner volume of 1600 mL, which can withstand pressure up to 20 MPa. The upper end of the reactor contains three ports, a, b, and c, respectively. Port a was used for the gas input, port b was used for inserting temperature sensors, and port c was used for gas output and pressure measurement. The temperature sensor has a measurement range of 223.15−373.15 K with an accuracy of ±0.1 K. The pressure transducer (TRAFAG 8251type) with an accuracy of ±0.02 MPa was used at the range of 0−25 MPa. The reactor was placed in the
air bath to ensure stable temperature conditions during the experiments. The air bath power is 6.5 kW, and the temperature control accuracy is ±0.1 K. The impedance monitoring system consists of a TD1250 frequency response analyzer and a TD3691 constant potentiometer. The TD1250 frequency response analyzer generated a sine wave or square wave excitation signal during operation to be used for system testing. The analyzer is used to measure the absolute voltage of the testing. The analyzer is used to measure the absolute voltage of the testing. The analyzer is used to measure the absolute voltage of the testing. The analyzer is used to measure the absolute voltage of the testing. The analyzer is used to measure the absolute voltage of the testing. The analyzer is used to measure the absolute voltage of the testing.

5.3. Experimental Procedures. 5.3.1. Formation Experiments.

(1) S–10 mesh coal samples (average porosity of 3.48%) were sorted by a crusher and a sieve shaker.
(2) The experimental THF solution (mass fraction of 20%) was used.
(3) 523.47 g of coal samples were added to the reactor (the coal samples just reached the height of the probes), and they were evenly distributed and concentrated. Then, the configured THF solution (278 mL) was slowly poured into the experimental reactor (the solution just saturated the interspace of coal samples), and the reactor was closed. Next, the reactor was gradually heated by adjusting the air bath, and the vacuum pump was used to vacuum the reactor during the heating process.
(4) The temperature of the air bath was set to 276.15 K. When the temperature in the reactor reached 276.15 K, the methane gas was injected into the reactor up to the experimental pressure of 3 MPa (the initial pressure simulated the gas pressure in outburst coal seams).
(5) During the experiments, temperature and pressure data were recorded by the data acquisition system, and impedance data were recorded by the impedance monitoring device.
(6) The pressure in the reactor did not change significantly (the change is less than 0.002 MPa per hour), which indicated that the equilibrium conditions had been reached for this system.

5.3.2. Dissociation Experiments. The hydrate formation experiment was followed by the dissociation of hydrate. The experimental steps were as follows:

(1) The reactor remained closed all the time. After the experimental system reached an equilibrium state, the temperature of the air bath was set to 293.15 K for thermal dissociation.
(2) In the process of hydrate dissociation, impedance, temperature, and pressure data were acquired in real time using the potentiometer and sensors. When the experimental impedance, temperature, and pressure did change any longer, the hydrate dissociation was considered to be over.
(3) When the dissociation experiment was completed, the temperature of the air bath was set to 276.15 K to cool the reactor again, and the next group of experiments was carried out (the cooling gradients of different dissociation temperatures are different). The experiment of hydrate formation and dissociation were repeated three times.
(4) The dissociation temperature was set to 298.15, 303.15, 308.15, and 313.15 K, and the hydrate formation and dissociation experiment was repeated three times according to the above steps.

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Notes
The authors declare no competing financial interest.

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