

Study on the thermal kinetics of anthracite oxidation induced by water and associated pyrite

Caiping Wang

Xi'an University of Science and Technology

Xiadan Duan

Xi'an University of Science and Technology

Zujin Bai

Xi'an University of Science and Technology

Yang Xiao (✉ xiaoy212@163.com)

Xi'an University of Science and Technology <https://orcid.org/0000-0002-3960-9708>

Jun Deng

Xi'an University of Science and Technology

Research

Keywords: Associated pyrite, Coal spontaneous combustion, Oxidation kinetics, Apparent activation energy, Mechanism model

Posted Date: June 22nd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-37092/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Pyrite and water in coal have considerable influence on coal spontaneous combustion and threaten the safety of mine production gravely. To reveal the influence mechanism of water and associated pyrite on oxidation kinetics of coal–oxygen composite reaction, the pyrite of 0%, 1%, 2%, 4%, 6% and the moisture of 1%, 5%, 10%, 15% and 20% were mixed with the coal samples to obtain 25 coal samples. Thermogravimetric analysis technology was conducted to explore the changes of mass and characteristic temperatures of coal samples treated with water and associated pyrite during the low–temperature oxidation, and kinetic analysis of the oxidation process was discussed based on multiple heating rates (5 °C/min, 10 °C/min and 15 °C/min). The results show that water and associated pyrite had a great influence on coal in oxygen absorption and weight gain stage ($T_3 \sim T_5$), and there was a proportion range with the largest synergistic oxidation contribution. The apparent activation energy of the coal sample appeared changes, but the mechanism model did not, indicating that water and pyrite could affect the oxidation process of the coal sample externally. When water and associated pyrite exhibit synergistic interaction, there have a range that water was 10~15% and associated pyrite was 2~4% had the largest promotion and contribution to anthracite oxidation. The results have important scientific value and practical guiding significance for the further study on prediction, prevention and control of high sulfur anthracite spontaneous combustion.

1. Introduction

Coal utilities are currently the major source of electricity in China, and in foreseeable future, coal will continue to be main energy and important industrial raw materials all over the world, and still plays an important role in economic development (Xu et al. 2018; Xie et al. 2020). At present, low–sulfur coal is widely exploited and utilized; so, coal of high sulfur may have a significant role to play in future. Sulfur in coal can be divided into organic sulfur and inorganic sulfur; meanwhile, the main form of inorganic sulfur is pyrite (FeS_2) (Yang et al. 2019). In actually anthracite mining process, the content of pyrite increased under the influence of mining depth. At the same time, it was affected by the infiltration of surface and groundwater in the mining process. The air leakage caused by water exploration and release provided enough oxygen for anthracite, which lead to the spontaneous combustion of high–sulfur anthracite (Huang 2013). Burning high–sulfur coal would produce carbon dioxide and sulfur dioxide, they were the main sources of greenhouse gases and acid rain, respectively (Gu et al. 2017; Liang et al. 2019). In order to ensure production safety, reduce energy loss and whilst minimising the impact on the environment, we need to study the influence of water and associated pyrite on coal oxidation process.

Sulfur is promising storage medium, which can be used for thermal energy storage at high temperature with a lower cost, and has good charge–discharge performance at high temperature (Jin et al. 2020; Nithyanandam et al. 2018). As for the influence of pyrite on CSC, studies have found that pyrite has a great influence on low temperature oxidation in humid environment (Arisoy and Beamish 2015; Arisoy et al. 2017). In the past decades, numerous researches have been carried out in learning the effect of pyrite on low–temperature coal oxidation. According to the Fenton reaction, FeS_2 in coal reacts with oxygen

and water, the resulting H_2SO_4 and $\text{Fe}(\text{OH})_3$ colloids make a difference to CSC (Arisoy et al. 2017; Doulati et al. 2008; Li 2007; Yu et al. 2013). At the same time, the reaction gives off heat, which accumulated continuously and further increased the macroscopic calorific value of coal, promoted coal sample oxidation, and finally caused CSC. In recent years, Deng et al. (2015), Wang et al. (2020) found that pyrite has a significant effect on the spontaneous combustion of coal. The addition of 2.0 mass% FeS_2 exerted a prominent promoting effect on gas coal oxidation, the 5~7% FeS_2 had a great impact on anthracite. Yang et al. (2019) found that temperatures corresponding to the maximum weight loss and peak temperatures of coal samples were lowered with higher pyrite content, also calculated the apparent activation energy (E_a) using Flynn–Wall–Ozawa (FWO) method, it was conclude that coal with higher pyrite content was more prone to spontaneous combustion.

Zhang et al. (2020a) have found the external moisture content has a significant impact on coal quality variation in the process of oxidation. The increase of moisture content would make the TG and DSC curve of CSC showing hysteresis, and inhibit the coal oxidation, which is not conducive to CSC (Jia et al. 2020). In addition, water-immersed coal can affect coal initial heat release temperature and heat release in the low temperature oxidation process, compared with raw coal, it was more likely to spontaneously ignite (Zhong et al.2015; Qin et al. 2018; Qiao et al. 2018). Tang et al. (2017) calculated the activation energy of bituminous coal immersed for 30~90 days using Arrhenius Formal, and found that the coal sample released more heat at the low temperature stage, with lower activation energy and easier oxidation than raw coal. At the same time, the structure of coal sample will change to some extent after water immersion.

Domestic and foreign scholars have made some progress in the study of CSC which affected by water and pyrite, and accumulated a good research foundation. However, hardly study on oxidation kinetics effect of water and pyrite on CSC, such as the thermogravimetry, temperature and kinetics in the process of low temperature oxidation. Therefore, on the basis of previous studies, this paper investigated the influence of water and associated pyrite on anthracite mass and characteristic temperature in low temperature oxidation through TG–DTG experiments. In addition, based on the synergistic effect of water and pyrite, the kinetic characteristic parameters of coal oxidation process were calculated and the most probable function was determined. Meanwhile, the mechanism of its effect on anthracite oxidation reaction was revealed, the optimal influence ratio range was also determined; which provided a key support for further inhibiting the oxidation process of pyrite bearing coal from the perspective of thermal reaction.

2. Experiments And Methods

2.1. Sample preparation

Taking the anthracite of Baijiao Coal Mine (Sichuan Province, China) as the research object, the fresh and unoxidized coal samples collected from the site were transported to the laboratory in sealed packaging of

multi-layer plastic and nylon bags. Meanwhile, the fresh coal samples crushed and ground to less than 200 mesh, and each coal sample was ca. 100g.

In order to accurately study the effect of external moisture on coal oxidation at low temperature, the coal sample was dehydrated. The specific method was to dry the coal samples in vacuum at 30°C for 48 hours. Due to the lower internal moisture of Baijiao anthracite, the influence of internal moisture was not considered. So, different moisture was added to the coal samples after many calculations and experiments. Mixture well and leave in a cool, airtight place for a week until moisture was absorbed. Finally, coal samples with external moisture content of 1%, 5%, 10%, 15% and 20% were obtained. Pyrite was crushed to 0.075mm and added to the samples in order to gain anthracite samples with pyrite content of 0%, 1%, 2%, 4% and 6%.

The coal samples with pyrite content were orthogonal to the samples with water content; at the end, 25 coal samples with different moisture and pyrite were obtained, respectively W1P0, W1P1, W1P2, W1P4, W1P6, W5P0, W5P1, W5P2, W5P4, W5P6, W10P0, W10P1, W10P2, W10P4, W10P6, W15P0, W15P1, W15P2, W15P4, W15P6, W20P0, W20P1, W20P2, W20P4, W20P6; wherein W represents water and P for pyrite.

2.2. Elemental analysis and proximate analysis

Samples underwent technical and element analysis via a 5E-MAG6700 (Kaiyuan, Changsha, China) proximate analyser and Vario ELIII (Elementar, German) organic element analyser before experiments. The moisture (M_{ad}), ash (A_{ad}), volatility (V_{ad}), fixed carbon (FC_{ad}), and element content were presented in Table 1.

2.3. TG-DTG experiment

The TG-DTG experiments were carried out from 30 to 400 °C, at heating rates of 5, 10 and 15 °C/min in air and N₂ atmosphere of 50 mL/min, and the experimental sample volume was 5mg. The TG-DTG curves of coal samples with different water and pyrite were obtained, which showed the different characteristics of coal oxidation at low temperature.

2.4. Kinetic methods

In the study of coal oxidation kinetics, the rate of coal weight loss (gain) can be expressed by differential method and integral methods.

$G(a)$ represents the integral of the reaction mechanism function, as shown below.

$$G(\alpha) = kt \quad (1)$$

$f(\alpha)$ represents the differential form of the reaction mechanism function:

$$d\alpha / dt = kf(\alpha) \quad (2)$$

According to Arrhenius formula, the relationship between reaction constant and temperature (absolute temperature) is:

$$k = A \exp(-E_a / RT) \quad (3)$$

The experiment adopts non-isothermal temperature rise, so $T = T_0 + \beta t$. The simultaneous Eqs. (1–3), are summarized to obtain the kinetic expression of the solid–gas two phase under non-isothermal heating conditions (Hu et al. 2008):

$$d\alpha / dt = \frac{A}{\beta} f(\alpha) \exp(-E_a / RT) \quad (4)$$

Where, R is the universal gas constant, 8.314 J/(mol·K); β is the heating rate, K/min; E_a is the apparent activation energy; α is the conversion rate of coal at time, t ; A is the pre-exponential factor.

(1) Achar differentiation

Integrate both sides of Eq. (1) and take the logarithm to get:

$$\ln \frac{d\alpha}{f(\alpha)dT} = \ln \frac{A}{\beta} - \frac{E_a}{RT} \quad (5)$$

(2) Group-Redfern integral method

$$n=1, \ln \left[\frac{G(\alpha)}{T^2} \right] = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \quad (6)$$

$$n \neq 1, \ln \left[\frac{1-(1-\alpha)^n}{T^2} \right] = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \quad (7)$$

In this paper, $n = 1$. Eq. (4) and Eq. (6) were fitted linearly respectively to calculate the apparent activation energy and the pre-exponential factor.

3. Results And Discussion

3.1. Characterization of coal samples

Through proximate and elemental analysis of raw coal (YM), and 25 experimental coal samples, indexes of each element, moisture and ash were obtained, as shown in Table 1. In raw coal, the content of C was higher, while H was lower; it indicated that Baijiao anthracite had a high degree of metamorphism. Meanwhile, the lower content of O in raw coal, which was only 1.51%, suggested the oxygen condition of spontaneous combustion of raw coal was relatively low (Song et al. 2019).

With the increase of moisture content, the content of O and H increased accordingly, and it was greatest when water content was 1~5%. Hence, the increased of moisture content will lead to the increase of oxygen-containing functional groups. According to Table 1, it could be concluded that the increase of pyrite content would increase sulfur in coal, which may enhance the environmental impact of sulfur oxide (SO_x) release. Conversely, the impact on other elements was small. The V_{ad} showed a trend of decrease after the first increase, this was because the water in coal and pyrite would have a synergistic reaction, with the increased of water, the production such as CO_2 will increase. The variation was strongest at about 10% moisture. After that, the water film and vapor pressure (Arisoy et al. 2017; Yu et al.2013) would be produced due to excessive water, and the changing effect will be weakened.

Table 1 Coal samples analysis

Sample	Elemental analysis (%)					Proximate analysis (%)			
	C	H	O	N	S	M_{ad}	A_{ad}	V_{ad}	FC_{ad}
YM	90.47	3.21	1.51	2.80	2.01	1.40	26.02	8.85	63.73
W1P0	89.69	3.61	1.71	2.85	2.14	2.32	25.49	9.10	63.39
W1P1	88.96	3.49	1.59	2.75	3.21	2.30	25.34	9.01	63.35
W1P2	88.43	3.45	1.35	2.52	4.25	2.29	24.92	9.23	63.56
W1P4	86.25	3.58	1.24	2.59	6.34	2.34	25.54	8.92	63.20
W1P6	84.69	3.48	1.2	2.34	8.29	2.21	25.8	8.98	63.01
W5P0	86.98	5.82	3.01	2.21	1.98	6.27	24.96	9.49	60.15
W5P1	87.00	5.58	2.98	2.19	2.25	6.30	24.22	9.28	60.20
W5P2	85.96	5.36	2.78	2.12	3.78	6.28	24.19	9.38	60.15
W5P4	84.26	5.29	2.68	2.09	5.68	6.27	24.04	9.58	60.19
W5P6	82.32	5.3	2.78	2.01	7.59	6.19	24.19	9.54	60.08
W10P0	84.51	6.54	4.26	2.8	1.89	9.73	24.01	9.02	57.24
W10P1	83.77	6.52	4.21	2.75	2.75	9.80	24.18	9.01	57.01
W10P2	83.25	6.01	4.32	2.83	3.59	9.68	24.22	8.89	57.21
W10P4	81.71	5.95	4.01	2.65	5.68	9.59	24.21	8.80	57.40
W10P6	80.13	5.69	3.73	2.32	8.13	9.46	24.31	9.04	57.19
W15P0	83.08	7.61	5.45	2.18	1.68	14.95	22.30	8.82	53.93
W15P1	82.35	7.52	5.42	2.12	2.59	14.89	22.47	8.75	53.89
W15P2	82.59	7.21	5.38	2.10	2.72	14.58	22.66	8.98	53.78
W15P4	80.05	7.09	5.28	1.99	5.59	14.99	22.36	8.69	53.96
W15P6	78.35	7.01	5.16	1.89	7.59	15.01	22.19	8.78	54.02
W20P0	80.83	8.94	6.66	2.08	1.49	19.59	20.96	8.31	51.14
W20P1	80.5	8.54	6.56	2.02	2.38	19.60	20.99	8.29	51.12
W20P2	79.95	8.21	6.4	2.12	3.32	19.55	18.16	8.19	54.10
W20P4	78.49	8.01	6.23	1.98	5.29	19.45	17.99	8.40	54.16
W20P6	76.07	8.75	6.01	1.58	7.59	19.44	18.06	8.30	54.20

3.2. Characteristics temperatures

The TG and derivative–TG (DTG) curves during coal oxidation process were presented in Figs. 1–3. It should be illustrated that this paper took the heating rate of 10°C/min as an example to research the influence of water and associated pyrite on TG–DTG curve. As shown in Fig. 1, coal generally have five temperature points during the oxidation process at low temperature: T_1 , T_2 , T_3 , T_4 , and T_5 , correspondingly to the temperatures of the maximum evaporation of water and desorption of gases, minimum weight loss on TG curve, coal sample began to gain weight, maximum oxidization mass gain, ignition point, respectively (Deng et al. 2017; Yang et al. 2018; Zhao et al. 2019a). Combined with the change of weight loss rate of TG–DTG curve, coal oxidation process could be divided into four stages: water evaporation and desorption stage ($T_1\sim T_2$), dynamic equilibrium stage ($T_2\sim T_3$), oxygen absorption and weight gain stage ($T_3\sim T_5$), and thermal decomposition stage (after T_5) (Zhao et al. 2019b).

The characteristic temperatures of all samples were presented in Fig. 2, the temperatures of the maximum evaporation of water and desorption of gases of 25 coal samples ranged from 90 °C to 110 °C. Under the different moisture content and with the increase of pyrite, T_1 was reduced, although the change was nonlinear. When the moisture content increased, the critical temperature displayed a trend of increasing first and then decreasing. This was because the increase of water content leads to the increase of water evaporation in the early stage of low–temperature oxidation and the longer evaporation time. However, it was not the higher the moisture content, the higher the critical temperature. There was a critical moisture content in this experiment, which was 10~15%.

With the increase of pyrite which in different water content, the variation trend of T_2 was different. When pyrite content was less than 6%, with the increase of moisture content, the T_2 first fall and then rose and then decreased, reached the lowest value at 5%, and reached the highest temperature when the water content was 10~15%. According to Fig. 2, the dry cracking temperature of 25 coal samples were about 105~126 °C, and the increase of pyrite content would raise the temperature to a certain extent.

Started from T_3 , the oxidation of coal became intense, which was the starting of oxygen absorption and weight gain stage of coal sample. The variation of T_3 was shown in Fig. 3a, under the 20% of moisture content, the temperature of coal samples was lower when pyrite content was 2~4%. Meanwhile, with the increase of moisture content, the trend of T_3 was different, among which the coal samples with water content of 10% and 15% had lower temperature. The change of temperature was affected by many factors, on one hand, the products $\text{Fe}(\text{OH})_3$ colloid under reaction of pyrite and oxygen in damp environment (Arisoy et al. 2017; Yu et al. 2013) filled the coal inner pore and prevented coal oxidation; on the other hand the reaction of pyrite and water produced H_2SO_4 , a large amount of H^+ liquid film made the coal molecules in an oxygen–rich environment and active groups advanced to participate in reaction (Zhang et al. 2020b).

By observing T_4 of 25 coal samples, it was viewed that the temperature was within 278~330°C, and temperature variation was nonlinear. W10P2, W1P2 and W1P0 had smaller T_4 in all coal samples. Due to the comprehensive effects of pyrite and O_2 reaction products, water and oxygen complex and other factors, the temperature of maximum oxidization mass gain was not the same.

T_5 was the temperature represented the maximum value of sample mass ratio, which the number of active groups and the adsorption amount of oxygen in the coal reached the maximum. Notably, as presented in Fig. 3b, when moisture content was greater than 1%, T_5 was first decreased, then increased and last decreased with the increase of pyrite content, and it was smaller when the pyrite content was 2~4%. When pyrite content less than 6%, T_5 was first rose and then fall and finally rose with the raise of moisture content, and was lower at 10~15%. The reason for this was the reaction between water and pyrite could give off heat, when water content was 10~15%, it could fully react with the 2~4% pyrite. Under the influence of heat release, the active groups that were originally not involved in coal oxygen reaction at a lower temperature also began to participate in the reaction and reached the ignition temperature in early. T_5 was within the range of 368~388°C, especially the temperature of coal samples W1P0, W5P6 and W20P6 were relatively low (Fig. 2).

3.3. Variation of coal mass

In order to further research the impact of water and associated pyrite on coal low temperature oxidation, the mass changes in different stages on the TG curve were observed, date in Table 2 shown the mass change of two stages (Deng et al.2018a).

Table 2 Mass variation of coal samples at different stages in the heating process

Sample	Water evaporation and desorption		Oxygen absorption and weight gain		
	T_2 (°C)	ΔM_1 (%)	T_3 (°C)	T_5 (°C)	ΔM_2 (%)
W1P0	114.1	0.12	127.7	368.2	2.14
W1P1	116.7	0.13	135.9	371.3	2.20
W1P2	113.3	0.16	133.1	377.1	2.22
W1P4	118.1	0.19	137.2	370.7	2.24
W1P6	118.7	0.18	134.2	378.7	2.25
W5P0	109.0	0.14	130.1	387.7	2.17
W5P1	109.8	0.16	131.0	374.7	2.22
W5P2	108.3	0.17	126.1	379.3	2.36
W5P4	122.5	0.21	130.2	374.6	2.30
W5P6	112.4	0.16	132.4	369.4	2.20
W10P0	120.0	0.18	131.5	383.9	2.23
W10P1	115.5	0.20	133.9	373.8	2.36
W10P2	123.6	0.24	133.5	374.4	2.46
W10P4	113.8	0.25	126.7	386.5	2.47
W10P6	119.0	0.24	128.7	378.6	2.36
W15P0	110.8	0.19	134.6	375.8	2.36
W15P1	118.0	0.21	130	375.6	2.43
W15P2	116.8	0.26	128.9	373.0	2.49
W15P4	116.3	0.24	131.0	380.6	2.46
W15P6	109.5	0.19	134.3	372.7	2.30
W20P0	117.7	0.14	133.7	380.3	2.18
W20P1	115.0	0.19	136.3	372.1	2.35
W20P2	122.0	0.17	142.5	379.9	2.36
W20P4	126.4	0.18	135.6	373.8	2.34
W20P6	116.9	0.22	133.5	369.5	2.38

Note: ΔM_1 : The loss ratio of water evaporation and desorption stage; ΔM_2 : The loss ratio of oxygen absorption and weight gain stage

3.3.1. Mass change during evaporation and desorption stage

As shown in Table 2, under the different moisture content, as pyrite increased, the mass changes in the water evaporation and desorption stage was first increased and then decreased and finally increased, and the mass was the largest when the water content was 10~15%; meanwhile, the maximum change was achieved when pyrite was 2~4% (Fig. 4a). After T_1 , larger active group in coal began to react with oxygen and generate CO and CO₂, at this time, the reaction rate of pyrite with O₂ was also accelerated, which made the gas generation and consumption rate achieve balance. Finally, the mass changes of coal became stability. The variation of coal mass affect by many factors, such as the evaporation of coal water, the production of water–oxygen complex and the generation of pyrite with oxygen.

Observing the mass changes of 25 coal samples in water evaporation and gas desorption stage, discovered the mass changes of coal samples ranged from 0.12 to 0.26%, among which the mass changes of coal sample W15P2 was the largest, followed by W10P4, 0.25%, and then mass variation of W10P2, W10P6 and W15P4 were 0.24%. Therefore, when pyrite content was 2~4% and water was 10~15%, it had the strongest ability to promote the oxidation of coal in the water evaporation and desorption stage.

3.3.2. Mass change during oxygen absorption and weight gain stage

Under different moisture content, with the rise of pyrite content, the sample mass generally showed a trend of increasing first and then decreasing and last increasing, and the weight gain was the largest when water was 10~15%. At the same time, the weight gain was the largest when the pyrite content was 2~4% (Fig. 4b). Coal oxidation is a complex chemical interplay and temperature is the most crucial factor affecting the reaction process. After T_3 , coal samples entered into a violent oxidation stage, and the oxygen uptake increased continuously. In the process of oxidation, 2~4% pyrite reacted with 10~15% water in the coal, eventually advancing the oxidation process and lowering the temperature. Therefore, the mass variation of 2~4% pyrite and 10~15% moisture coal samples will also be large at this stage. Meanwhile, 15% moisture was the critical water content in this paper. When the water content was lower than 15%, due to the swelling effect of water on coal, the pores inside the coal and water–oxygen complex generated in the initial stage of coal oxidation increased, which accelerated the oxidation reaction of coal samples (Liu et al. 2016). On the contrary, when the water was too large, the formation of liquid film prevented the coal oxidation, at the end, the variation of coal samples gradually decreased.

The mass change of 25 coal samples in oxygen absorption and weight gain stage was ranged from 2.14~2.49%. The larger mass change of coal samples was: W15P2 > W10P4 > W15P4, W10P2, W10P6. The results showed that the synergistic effect of pyrite 2~4% and moisture 10~15% was the strongest in promoting the oxidation of coal at the oxygen absorption and weight gain stage.

3.4. Kinetic parameters

The coal oxidation reaction was the sum of complex primitive reactions. Activation energy was a very important kinetic parameter in coal oxidation, which can reflect the coal reaction difficulty to a certain extent. A great deal of work has been done (Qi et al. 2015; Deng et al. 2018b) in the study of oxidation reaction kinetics to obtain different methods for solving E_a , A and deducing the most probable mechanism function. In this paper, Achar differential method and Coatsal–Redfern integral method were used for kinetic analysis and calculation of coal oxidation reaction, and Bagchi method was used to infer the reaction mechanism function. The experimental data and the 18 solid reaction mechanism functions in the Table 3 were substituted into Eq. (5) and Eq. (7). The fitting curves of $\ln[G(a)/T^2]$ and $\ln[(da/dT)/f(1/T)]$ of different coal samples in the oxygen absorption and weight gain stage were obtained. The fitting curves of some coal samples were shown in Fig. 5.

Due to technical limitations, Table 3 is provided in the Supplementary Files section.

Table 4 summarized the differential and integral results of sample W1P0 under 18 mechanism functions at 10 °C/min.

Table 4 Differential and integral kinetic parameters of W1P0 under different mechanism functions

Function	$f(\alpha)$			$G(\alpha)$		
	R	E_a (J/mol)	A	R	E_a (J/mol)	A
1	/	/	/	/	/	/
2	/	/	/	/	/	/
3	/	/	/	/	/	/
4	0.978	194988	895522	0.981	193042	772540
5	0.910	159820	654311	0.932	108927	458521
6	0.852	201542	895621	0.821	156982	805692
7	0.935	215982	698548	0.952	189651	785692
8	0.896	201896	589652	0.856	202590	586348
9	/	/	/	/	/	/
10	/	/	/	/	/	/
11	0.896	218974	658921	0.895	198653	569899
12	/	/	/	/	/	/
13	/	/	/	/	/	/
14	0.893	159352	489235	0.935	158935	485635
15	0.932	189621	459863	0.893	186325	489658
16	/	/	/	/	/	/
17	/	/	/	/	/	/
18	/	/	/	/	/	/

Note: / is directly exclude, as have the lower fitting degree from the differential or integral phase

By comparing integration and differentiation, the mechanism function with a larger fitting degree and a similar slope was taken; E_a and A were finally calculated according to the curve. The average apparent activation energy and pre-exponential factor of each coal sample were finally obtained in the oxygen absorption and weight gain stage, as shown in Table 5. Accordingly to the average apparent activation energy, the most probable mechanism function was finally determined, which was $n = 4$ Avrami-Erofeev.

From Table 5, it could be found that E_a was first decreased and then increased, and minimal at 2% pyrite. Besides, E_a was the minimum when sample water was 10~15%, coal samples needed the small energy for oxidation in this content and were more prone to chemical reactions (Fig.6). While the moisture content was 15%, the apparent activation energy started to increase, which implied that 15% was the

sample critical point of the oxidation activity. On the whole, it could be concluded that when the coal sample was synergistically affected by water and pyrite, E_a decreased as a whole, and the oxidation activity increased. There were critical content points of water and pyrite, which were 15% and 2%, respectively. In addition, it suggested that the chemical reaction of water and pyrite on coal active groups brings changes, which was manifested as the changes of apparent activation energy in the oxidation process. In this stage, coal molecules needed less energy to complete the coal oxygen adsorption reaction.

Due to technical limitations, Table 5 is provided in the Supplementary Files section.

Based on the analysis of sample probable mechanism, the mechanism function of different water and pyrite coal samples did not change during this stage. It implied that although water and associated pyrite can promote the process of coal oxidation, the reaction mechanism was not changed; water and pyrite can affect the degree of coal oxidation, but it does not fundamentally change the oxidation mechanism.

3.5. Reaction mechanism

Low temperature oxidation of coal sample is a complex chemical reaction. When coal contains different water and associated pyrite, the coal characteristics will change correspondingly, such as the increase of oxygen-containing functional group and volatile component. All of these will affect coal oxidation, and finally present the changes of characteristic temperatures, coal weight, and so on, in the oxidation process. It can be found from the study that, as shown in Fig. 7, water and pyrite can react chemically and give off heat in coal. Under the comprehensive action of reaction heat and moisture wetting heat, the speed of coal water evaporation was accelerated, made the critical temperature reduce and coal sample began to release heat and gases. At the initial stage of oxidation, the water in the coal sample continued to evaporate, and the oxidation reaction was relatively gentle and the heat generation and gases was less. Meanwhile, under the influence of pyrite, T_2 had a certain increase, coal samples from T_3 began a strong coal reaction. Under the dual action of water and pyrite reaction product $\text{Fe}(\text{OH})_3$ colloid to fill the pore structure of coal samples, blocked coal oxygen reaction, water and oxygen complex and H_2SO_4 acid solution to promote coal oxygen reaction, T_5 was in advance. At the same time, when water was 10~15% and pyrite was 2~4%, the oxidation of anthracite required the least activation energy and the strongest oxidation reaction.

4. Conclusion

Coal spontaneous combustion has always been a difficult problem all over the world. Water and associated pyrite is of significance for coal mining, transport and utilizing. The influence of water and associated on coal oxidation had investigated through TG-DTG experiment and dynamic calculation. It was found that water and associated pyrite could not change the oxidation reaction mechanism of coal, but could accelerate or delay coal oxidation process, and it had a great influence on the oxygen

absorption and weight gain stage (126~388 °C). Coal oxidation process affected by water and associated pyrite was consistent with the $n = 4$ Avrami–Erofeev equation. It was also observed that the synergistic effect of water 10~15% and pyrite content 2~4% had the strongest effect on coal oxidation. In summary, the content of water and pyrite will affect the spontaneous ignition time of anthracite coal seam, we should pay close attention to the content of water and associated pyrite during mining.

Declarations

Acknowledgment

This work was supported by the National Key Research and Development Plan of China (No. 2018–YFC–0807900), the National Natural Science Foundation of China (No. 5197–4234), Shaanxi Provincial Innovative Talent Promotion Plan–Youth Science and Technology Rising Star Project (No. 2019KJXX–0500), Xi'an University of Science and Technology Outstanding Youth Fund (2019YQ2–03), and Shaanxi University Youth Outstanding Talent Support Program.

Conflicts of interest

The authors declare that they have no conflict of interest.

References

1. Arisoy A, Beamish B (2015) Mutual effects of pyrite and moisture on coal self–heating rates and reaction rate data for pyrite oxidation. *Fuel* 139: 107–114
2. Arisoy A, Beamish B, Yoruk B (2017) Moisture moderation during coal self– Fuel 210: 352–358
3. Doulati AF, Jodieri SB, Moradzadeh A, Soleimanet E, Ansari JM (2008) A combined mathematical geophysical model for prediction of pyrite oxidation and pollutant leaching associated with a coal washing waste dump. *Int J Environ Sci Technol* 15(4): 517–526
4. Deng J, Ma XF, Zhang YT, Li QW, Zhu WW (2015) Effects of pyrite on the spontaneous combustion of coal. *Coal Sci Technol* 2(4): 306–311
5. Deng J, Li B, Xiao Y, Ma L, Wang CP, Laiwang B, Shu CM (2017) Combustion properties of coal gangue using thermogravimetry–Fourier transform infrared spectroscopy. *Appl Therm Eng* 116: 244–252
6. Deng J, Ren LF, Ma L, Lei CK, Wei GM, Wang WF (2018a) Effect of oxygen concentration on low–temperature exothermic oxidation of pulverized coal. *Thermochim Acta* 667: 102–111
7. Deng J, Bai ZJ, Xiao Y, Shu CM (2018b) Effects on the activities of coal microstructure and oxidation treated by imidazolium–based ionic liquids. *J Therm Anal Calorim* 133: 453–463
8. Gu Y, Yperman J, Vandewijngaarden J, ReggersG, CarleerR (2017) Organic and inorganic sulphur compounds releases from high–pyrite coal pyrolysis in H_2 , N_2 and CO_2 : Test case Chinese LZ coal. *Fuel* 202: 494–502

9. Hu ZY, Gao SL, Zhao QF, Shi QZ, Zhang TL, Zhang JJ (2008) Thermal analysis kinetics. Science Press, Beijing
10. Huang HJ (2013) Experimental study on coal spontaneous combustion characteristic parameters affected by pyrite sulfur. Dissertation, Xi'an University of Science and Technology
11. Jia YG, Lou HZ, Liu J, Qu GN (2020) Experimental study on thermal characteristics of spontaneous combustion process of coal with different moisture. J China Coal Soc <https://doi.org/10.13225/j.cnki.jccs.2019.1080>
12. Jin KY, Wirz RE (2020) Sulfur heat transfer behavior in vertically-oriented and nonuniformly-heated isochoric thermal energy storage systems. Appl Energy <https://doi.org/10.1016/j.apenergy.2019.114287>
13. Li ZJ (2007) Investigation on the mechanism of spontaneous combustion for sulphide ores and the key technologies for preventing fire. Dissertation, Central South University
14. Liu JF, Peach CJ, Spiers CJ (2016) Anisotropic swelling behaviour of coal matrix cubes exposed to watervapour: Effects of relative humidity and sample size. Int J Coal Geol 167:119–135
15. Liang XH, Wang QH, Luo ZY, Eddings E, Ring T, Li SM, Lin JJ, Xue S, Han L, Xie GL (2019) Experimental and numerical investigation on sulfur transformation in pressurized oxy-fuel combustion of pulverized coal. Appl Energy <https://doi.org/10.1016/j.apenergy.2019.113542>
16. Nithyanandam K, Barde A, Lakeh R B, Wirz R E (2018) Charge and discharge behavior of elemental sulfur in isochoric high temperature thermal energy storage systems. Appl Energy 214: 166–177
17. Qi GS, Wang DM, Zheng KM, Xu J, Qi XY, Zhong XX (2015) Kinetics characteristics of coal low-temperature oxidation in oxygen-depleted air. J Loss Prevent Proc 35: 224–231
18. Qin BT, Song S, Qi XY, Zhong XX, Song C (2018) Effect of soaking process on spontaneous combustion characteristics of long-flame coal. J China Coal Soc 43(5): 1350–1357
19. Qiao L, Deng CB, Zhang X, Wang XF, Dai FW (2018) Effect of soaking on coal oxidation activation energy and thermal effect. J China Coal Soc 9: 2518–2524
20. Song YW, Yang SQ, Xu Qin, Cai JW, Hu XC, Song NW, Zhang ZC (2019) Effect of low-temperature oxidation of coal with different metamorphic degrees on coal quality characteristics and outburst comprehensive index. Process Saf Environ Prot 132:142–152
21. Tang YB, Li YF, Xue S, Wang JF, Li RC (2017) Experimental investigation of long-term water immersion effect on spontaneous combustion parameters and microscopic characteristics of bituminous. J China Coal Soc 42(10): 2641–2648
22. Wang CP, Bai ZJ, Deng J, Shu CM, Li QW (2020) Effects of FeS₂ on the characteristics of coal oxidation at low temperatures. Process Saf Environ Prot <https://doi.org/10.1080/00102202.2020.1753715>
23. Xu J, Tang H, Su S, Liu JW, Xu K, Qian K, Wang Y, Zhou YB, Hu S, Zhang AC, Xiang J (2018) A study of the relationships between coal structures and combustion characteristics: The insights from micro-Raman spectroscopy based on 32 kinds of Chinese coals. Appl Energy 214: 46–56

24. Xie HP, Wu LX, Zheng DZ (2019) Prediction on the energy consumption and coal demand of China in 2025. *J China Coal Soc* 44(7): 1946–1960
25. Yu JL, Tahmeasebi A, Han YN, Yin FK, Li XC (2013) A review on water in low rank coals: The existence, interaction with coal structure and effects on coal utilization. *Fuel Process Technol* 106: 9–20
26. Yang Y, Deng J, Zhang YN (2018) Oxidation characteristics of coal by STA–FTIR experiment. *J China Coal Soc* 43(04): 134–143
27. Yang FQ, Lai W, Song YZ (2019) Determination of the influence of pyrite on coal spontaneous combustion by thermodynamics analysis. *Process Saf Environ Prot* 129: 163–167
28. Zhong XX, Kan L, Xin HH, Qin BT, Dou GL (2015) Thermal effects and active group differentiation of low–rank coal during low–temperature oxidation under vacuum drying after water immersion. *Fuel* 1236: 1204–1212
29. Zhao JY, Deng J, Song JJ, Shu CM (2019a) Effectiveness of a high–temperature–programmed experimental system in simulating particle size effects on hazardous gas emissions in bituminous coal. *Safety Sci* 115: 353–361
30. Zhao JY, Deng J, Chen L, Wang T, Song JJ, Zhang YN, Shu CM, Zeng Q (2019b) Correlation analysis of the functional groups and exothermic characteristics of bituminous coal molecules during high–temperature oxidation. *Energy* 185: 136–147
31. Zhang XY, Zhang YL, Wang JF, Hao HD, Wu YG, Zhou CS (2020a) Study on the effect and mechanism of foreign moisture on coal spontaneous combustion. *J Fuel Chem Technol* 48(1): 1–10
32. Zhang HR, Niu J, Yin X, Guo YX, Cheng FQ (2020b) Role of inherent pyrite in coal on physicochemical structure of activated carbon and adsorption capacity. *Fuel*
<https://doi.org/10.1016/j.fuel.2019.116527>

Figures

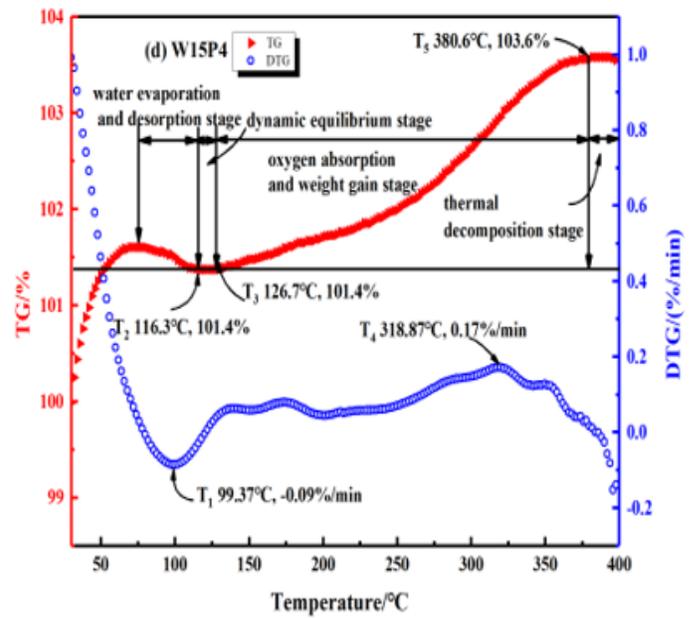
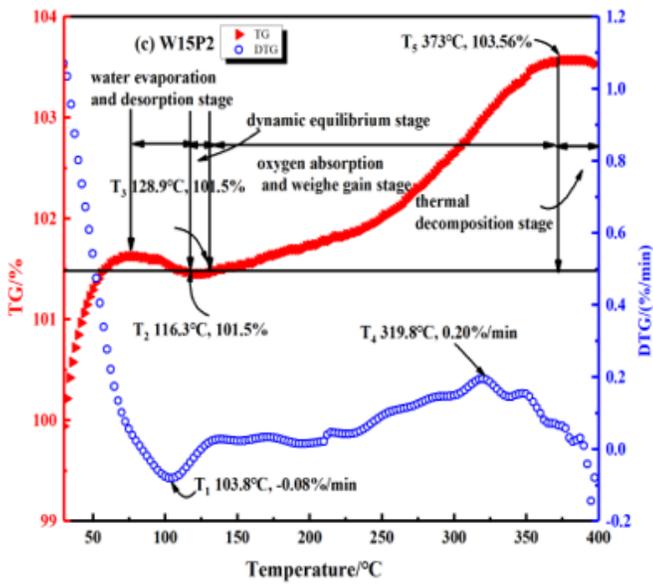
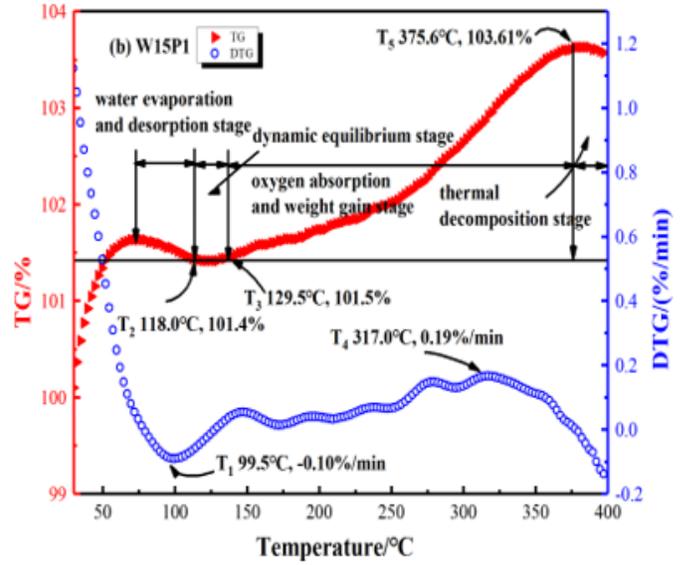
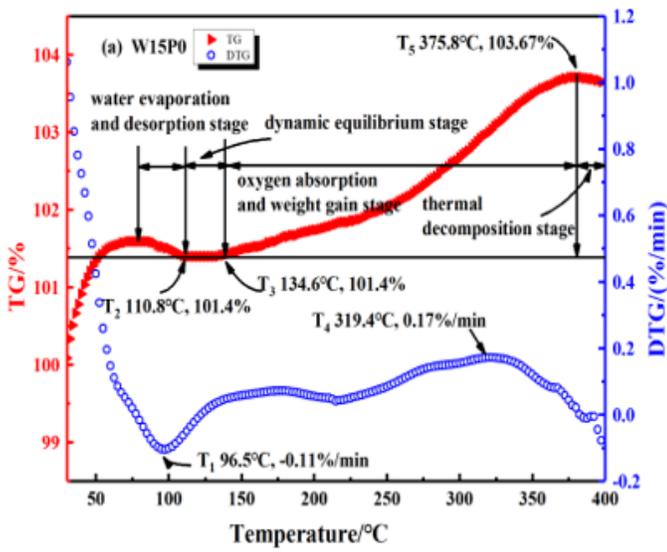


Figure 1

TG-DTG curve of some coal samples

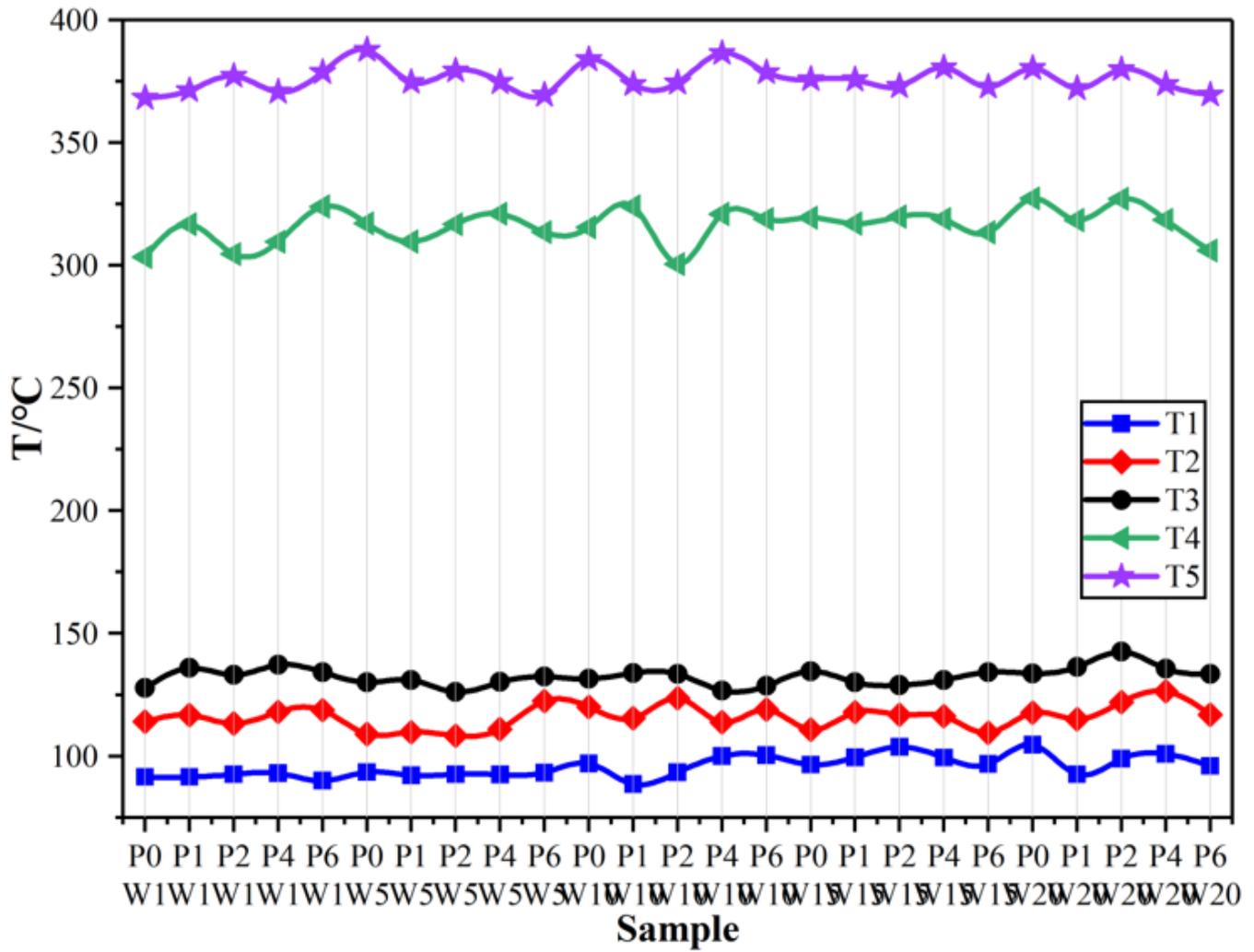


Figure 2

Characteristic temperatures of 25 coal samples

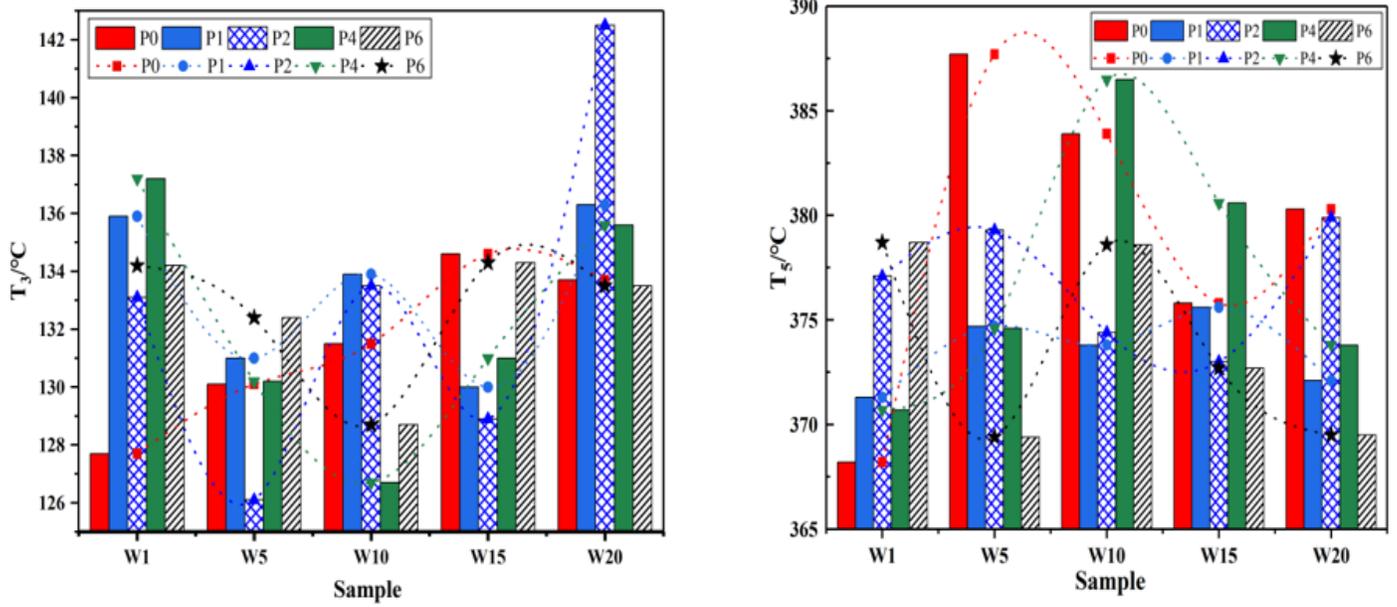


Figure 3

Characteristic temperature under different moisture and pyrite content

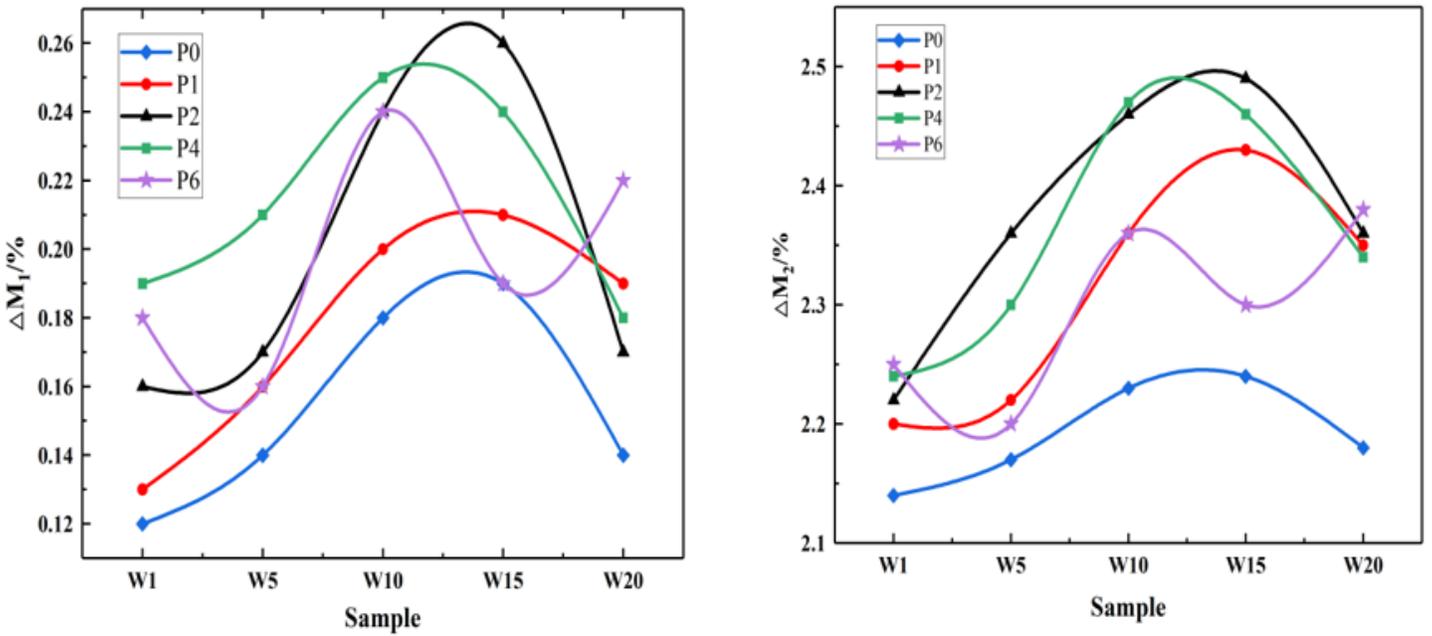


Figure 4

The mass variation of coal samples at different stages in the heating process

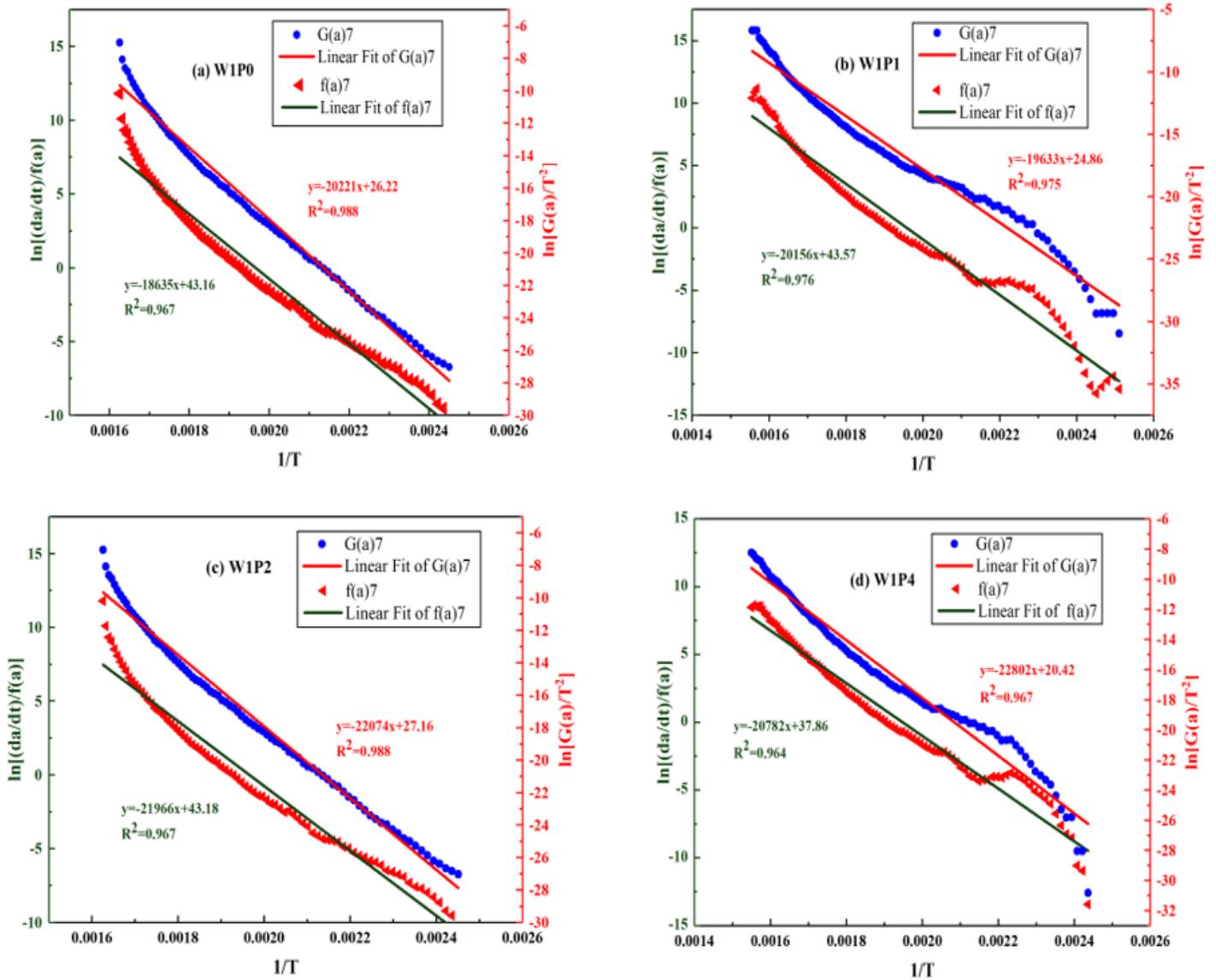


Figure 5

Oxygen absorption and weight gain stage $\ln[G(a)/T^2]$, $\ln[(da/dt)/f(a)]$ and $1/T$ fitting curve of some coal samples

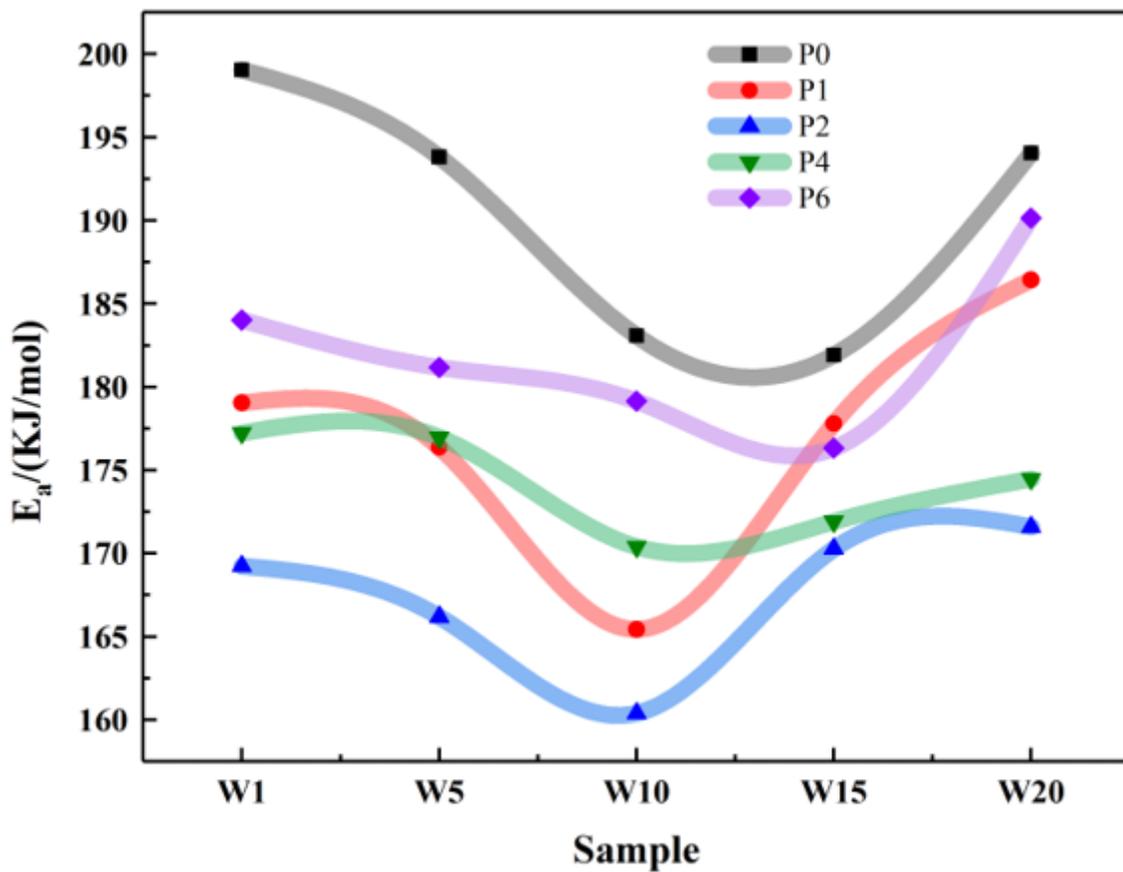


Figure 6

Changes of apparent activation energy of pyrite in coal sample oxidation process

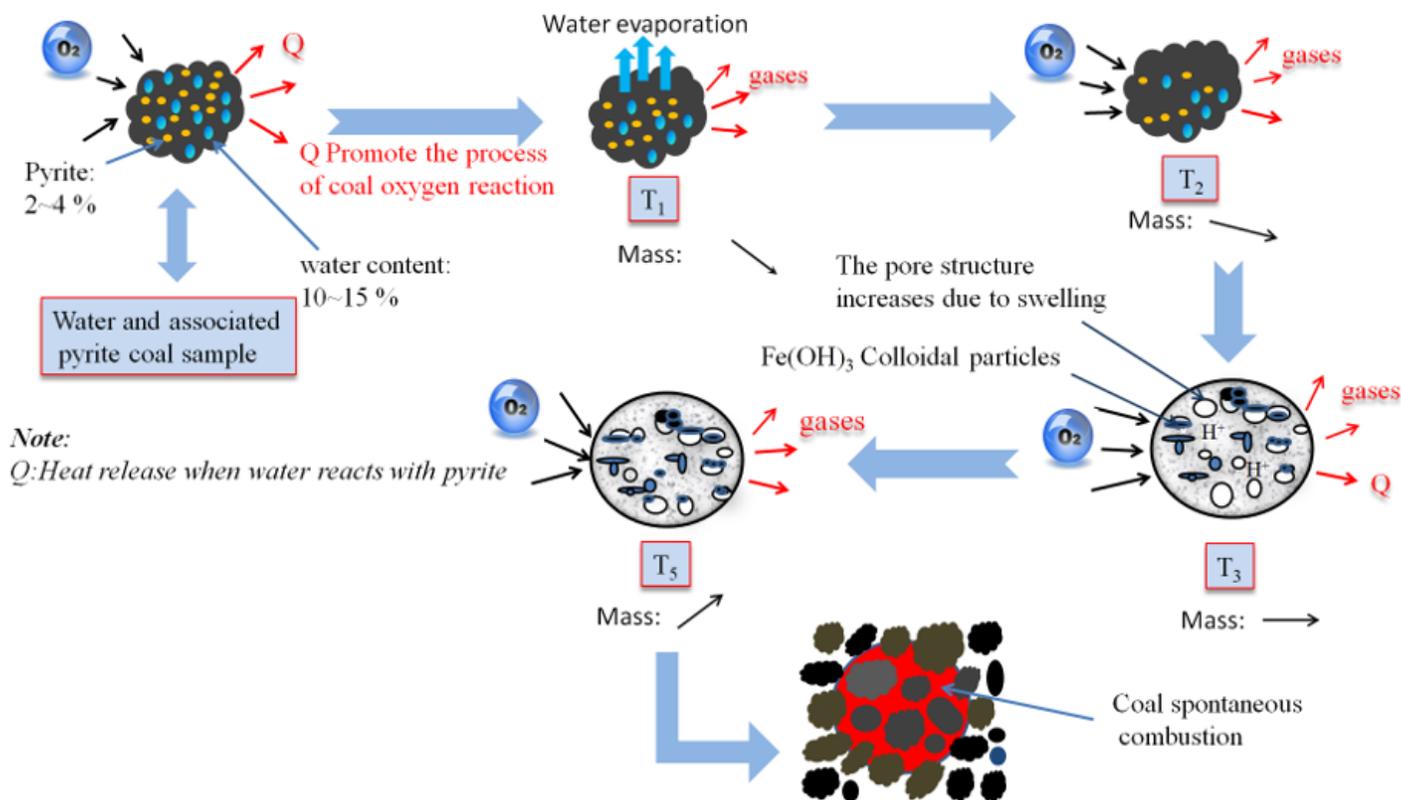


Figure 7

Effect of water and associated pyrite on spontaneous combustion of coal

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table3Commonsolidreactionmechanismfunctions.docx](#)
- [Table5Dynamicparametersofdifferentcoalsamples.docx](#)