

Article

Indirect Drying and Coking Characteristics of Coking Coal with Soda Residue Additive

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Abstract: To improve indirect drying efficiency, the effect of soda residue on the drying characteristics of coking coal were studied using a self-made indirect drying system. A tube furnace was used in the dry distillation of coal samples with soda residue, and the coke properties were analyzed. The results indicated that the soda residue has a significant influence on the increase in the heating rate of coal samples in the temperature distribution range of 90 to 110 °C. With the addition of 2%, 5%, and 10% soda residue, the drying rates increased by 11.5%, 25.3%, and 37.3%, respectively at 110 °C. The results of dry distillation show that addition of 2%, 5% and 10% soda residue decreases the carbon loss quantity by 4.67, 4.99, and 8.82 g, respectively. The mechanical strength of coke samples satisfies the industrial conditions when the soda residue ratio ranges from 2% to 5%. Soda residue can improve the active point of coke dissolution reaction and inhibit coke internal solution. Economically, coking coal samples mixed with soda residue have an obvious energy saving advantage in the drying process. Energy saving analysis found that it can reduce cost input by 20% than that of the normal drying method.

Keywords: coking coal; soda residue; indirect drying; coking characteristics; benefits

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1. Introduction

In the coking technology of drying, coal is pre-dried to reduce its moisture to less than 6% before coking [1]. This technique stabilizes coke oven operation, increases coke strength, and reduces coking heat consumption [2]. Up to now, many iron and steel enterprises have built and put into operation the coal moisture conditioning equipment and have independent intellectual property rights [3,4].

According to the form of heat source utilization, the drying technology can be divided into direct and indirect drying [5,6]. The commonly used direct drying technology includes a rotary drum dryer, a vertical tube air flow dryer, a fluidized bed dryer, etc. However, indirect drying technology has some prominent problems, such as high energy consumption, dehydration, moisture reabsorption, and production of large amounts of dust. Indirect drying technology is the transfer of heat from a heat source to a medium, which may be heat-conducting oil, steam, or air. The medium circulates in a closed loop and has no contact with the coal that needs to be dried. Compared with direct drying, indirect drying technology has many advantages: (1) no cross-contamination problem, because the material does not contact the heat transfer medium; (2) low heat loss and high thermal efficiency; and (3) equipment safety and low cost [7–10]. Therefore, the development of indirect drying equipment has been paid much attention for a long time.

At present, low drying rate is the main problem in most indirect drying devices. Therefore, increasing the drying rate is of great significance to the popularization and application of the indirect drying system [11]. At present, the methods to improve the drying rate of coking coal mainly include improving the drying equipment, increasing

the drying contact area and temperature of the drying medium, improving the distribution of the drying medium, etc. [12–14], but there are few studies on improving the drying properties of coking coal by adding additives. Most studies on improving the drying properties of materials by adding additives focus on wood, brown coal, and other materials. For example, Zhou et al. [15] added 0–5% NaCl to brown coal with microwave drying, and its effective moisture separation diffusion coefficient increased by 8.2 times. Cheng et al. [16] added activated carbon, ferric oxide, and manganese dioxide to lignite to increase the drying rate and reduce energy consumption. However, some additives may have negative effects on coke quality during coking. Thus, this method is rarely used in the study of coking coal drying. Qiu et al. [17] found that the added Fe_2O_3 decreases the plastic range and weight loss rate of the coal matrix. G. Wang [18] found that the addition of sodium salt can cause coke to crack. Stanislav [19] pointed out that in the coking process of FeS_2 , cracks are produced due to the release of gas pressure, thus reducing the coke strength. Certainly, some studies have been done to improve coke quality by selecting suitable additives. Liu et al. [20] found that adding soda residue can improve the reactivity and reduce the initial temperature of coke. K. Wang [21] proposed that calcium chloride and alumina not only have good sulfur-binding effect but can also improve the cold strength of coke. Therefore, the purpose of this study is to find a suitable additive added into the coking coal, which can improve the drying rate without affecting or even improving the coke characteristics during the coking process.

Soda residue refers to the alkaline waste slag discharged in the process of alkali preparation and alkali treatment in industrial production. The main ingredients of alkali slag include CaCO_3 , CaSO_4 , CaCl_2 , and other calcium salts, and it also contains a small amount of sulfur dioxide [22]. Compared with coking coal, these alkali slag compounds have a higher dielectric constant and can absorb energy easily. The drying time of coking coal may be shortened to a certain extent if the soda residue is mixed with the sample of coking coal after screening treatment. This will achieve the drying process to reduce other energy consumption. In addition, because soda residue is the waste produced by an alkali plant, its cost is low. This helps improve the utilization rate of waste slag, so that it can be used for coking coal drying.

Through the above research and analysis on using soda residue as a coal drying additive, the main contributions of this paper are as follows:

1. Based on the research on drying devices, an indirect, self-made coking coal drying system was set up.
2. Based on the indirect drying method, the drying characteristics, temperature, and humidity transfer characteristics of raw coking coal were studied.
3. Based on the effects of the drying temperature and alkali slag additives on the heating rate, the optimum drying temperature was determined.
4. The influence of additives on the temperature and humidity transfer characteristics of coking coal during the drying process was studied.
5. The samples of dried coking coal added with additives were tested for coking, and the influencing characteristics of the additives on coke strength, thermal reactivity, and specific surface area were studied to find out the optimal additive proportion.
6. An economic benefit analysis was conducted.

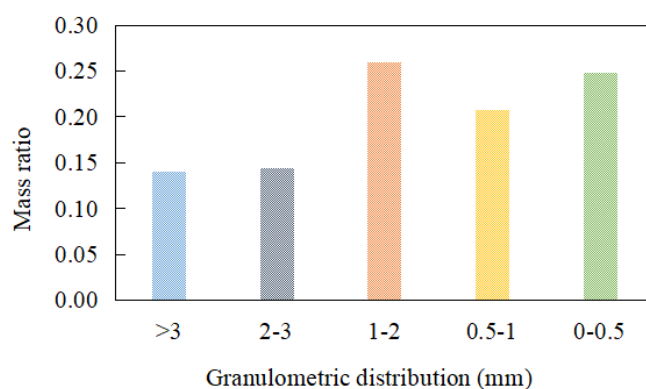
2. Materials and Methods

2.1. Materials

The raw coking coal came from the Xingtai area of the Hebei province. The particle size distribution is shown in Figure 1, and its moisture content was about 11%. The physical and chemical properties are shown in Table 1.

Table 1. The physical and chemical properties of coking coal [23].

Samples	Proximate Analysis (wt%, d)				Ultimate Analysis (wt%, daf)			
	M_{ar}	A_d	V_{daf}	F_{ad}	C	H	N	S
Xingtai	10.80	7.88	36.19	19.66	86.33	5.49	1.52	0.38

**Figure 1.** Granulometric distribution of coking coal.

The soda residue came from the Paohua alkali factory in Xintai. The components of the soda residue are shown in Table 2.

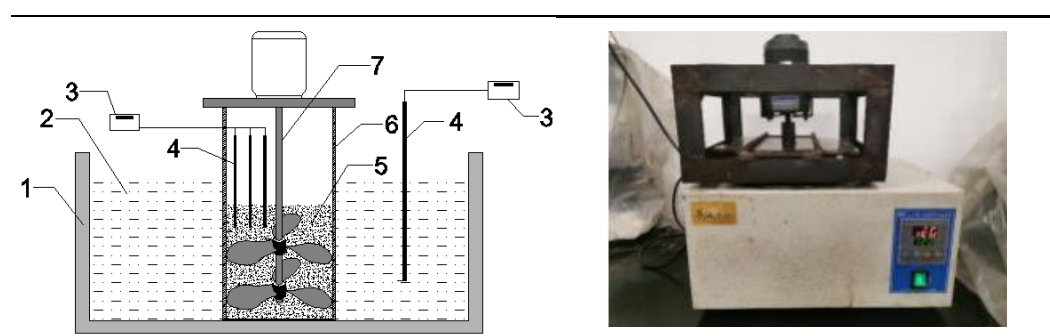
Table 2. Composition analysis of soda residue (%).

CaCO_3	Na_2CO_3	Al_2O_3	KCl	NaCl	$\text{Mg}(\text{OH})_2$	SiO_2	Insoluble
53.22	14.78	3.24	0.33	6.97	5.12	8.96	7.38

2.2. Experimental Equipment and Instruments

2.2.1. Indirect Drying Equipment

The coking coal drying experiment was mainly carried out with a cylindrical container placed in a high-temperature oil bath (Figure 2). The container was 300 mm in height and 150 mm in diameter.

**Figure 2.** Experimental apparatus for coking coal drying. 1—oil bath, 2—oil, 3—temperature display, 4—temperature and humidity sensor, 5—coking coal, 6—stainless steel container, and 7—stirrer.

2.2.2. Experimental Instruments

The platform included an electric thermostatic blast drying oven, an electronic balance, a temperature sensing and control device, a drum machine, an analysis meter of specific surface area, a data acquisition and analysis system, etc. The integrated functions of process control, online monitoring, data recording, and transmission were realized. The interface for other equipment was designed, which provided a small-scale test platform for better observation and study of coking coal drying and the coking process.

2.3. Methods

2.3.1. Preparation of Sample

During the drying process, the thickness of the coal samples was set as 15 cm and its mass 2 kg. The soda residue was crushed (<0.1 mm) and added into the raw coking coal for intensive mixing. The additive mass ratio percentages (raw coal (RC)/soda residue (SR)) were 2%, 5%, and 10%. Then the samples prepared were stored in a sealed bag for standby application.

2.3.2. Parametric Measurement

Drying Rate

The selected isothermal drying temperatures were 70, 90, 110, 130, and 150 °C, the ambient relative humidity was 65%, and the drying time was 360 min. Each test was repeated three times. The drying end point was that the coking coal mass was reduced by less than 1 mg within 1 min. According to the initial moisture content, initial mass, and mass at time t of the coking coal, the moisture content at every 5 min was calculated to obtain the drying curve and drying rate curve of the whole process. The formula for moisture content is

$$W_t = \frac{M_0 W_0 - (M_0 - M_t)}{M_t} \times 100 \quad (1)$$

where W_t is the moisture content (%) of the coking coal at drying time t , W_0 is the initial moisture content (%) of the coking coal, M_0 is the initial dry mass (g) of the coking coal, and M_t is the mass (g) of the coking coal at drying time t .

The relation expression between moisture content and drying rate is

$$D_r = \frac{W_t - W_{t+\Delta t}}{\Delta t} \times 100 \quad (2)$$

where D_r is the drying rate of the coking coal ($\text{g} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$), $W_{t+\Delta t}$ is the moisture content of the coking coal at time $(t + \Delta t)$ ($\text{g} \cdot \text{g}^{-1}$), and Δt is the drying time interval (min). $\Delta t = t_2 - t_1$, where t_1 is the coal moisture content at the initial time and t_2 is the coal moisture content at a certain moment. During the drying process, the coal moisture content was tested every 40 min. Therefore, Δt is a fixed time interval: $\Delta t = 40$ min.

Temperature and Humidity Distribution and Transfer

Moisture transfer was affected by many factors, such as coal structure, thickness of coal seam, temperature gradient, etc. In the actual process, the heat and moisture transfer in coal are often coupled with each other. The moisture transfer model under the influence of a temperature gradient is shown in Figure 3.

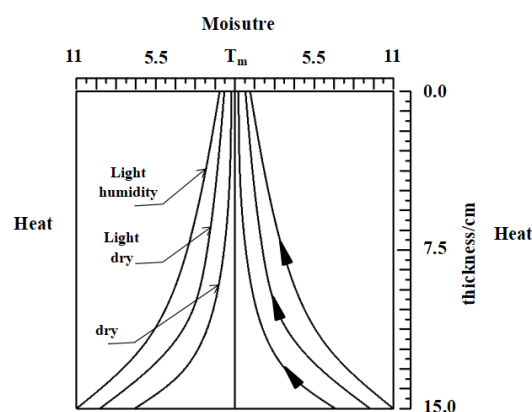


Figure 3. Moisture transfer model of coking coal during drying.

According to the moisture transfer model, the coal seam was divided into several areas vertically, from the edge near the heat to the center, which was far away from the heat during drying. Temperature and humidity sensors were used to measure the temperature and moisture change with time in each area. In the experiment, the drying time was set as 360 min, the ambient humidity was 65%, and the oil bath temperature was 130 °C.

Coking Characteristics

The dry coal samples with different proportions of soda residue added were obtained in the drying experiment. Samples of 1 kg each were loaded into the crucible, and pressure (1 KPa) was applied to the upper part to maintain the bulk density of the coal samples. Then the crucible was put into the muffle furnace for carbonization under isolated air conditions. After heating at a certain rate to 900 °C, a constant temperature was maintained for 1 h and the samples allowed to cool naturally to room temperature. In the end, the coke samples of each group were sealed and preserved.

The characteristic parameters of each coke sample were tested and studied by an industrial analysis method. The details were as follows:

(1) Cold mechanical strength

Falling strength: Coke with a diameter greater than 10 mm was let to fall freely from a height of 2 m, and the process repeated four times. A grain size greater than 10 mm was used to represent the falling strength.

Coke wear strength test: Coke with a diameter greater than 10 mm was selected to roll for 7 min at a drum with a diameter of 200 mm. The rotation speed was 30 r/min. A grain size greater than 10 mm was used to represent the wear strength.

(2) Coke thermal performance

A coke sample with a size of 3–5 mm was weighed to 30 g and put it into the corundum reaction tube. The temperature was raised to 400 °C at a rate of 20 °C/min. After 10 min of constant temperature, CO₂ was injected with a flow rate of 0.5 L/min, and the reaction time was set as 1 h. At the end of the reaction, nitrogen was injected to cool the sample to room temperature. The mass fraction of weight loss of the coke before and after the reaction is taken as the reactivity index (PRI) of the coke; the result of the parallel experiment has an error of less than 2.5%. All the reacted coke was put into the ceiling index drum and rotated 500 r at a speed of 50 r/min. After taking out the coke sample, it was sifted for 5 min on a vibrating screen machine with a 1 mm round hole. The mass percentage of the material on the sieve to the mass of the drum coke is used as the coke reaction strength (PSR). The error of the parallel experiment results should not exceed 2%.

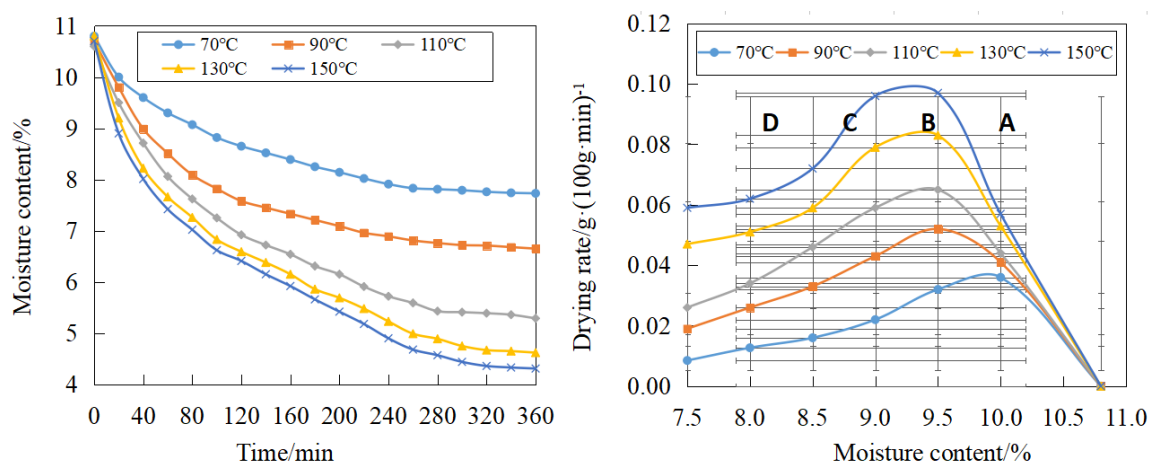
(3) Specific surface area

According to the static capacity method in GB/T19587-2004, the specific surface area of coke was measured by Basder 3H-2000PS1-type specific surface area analyzer.

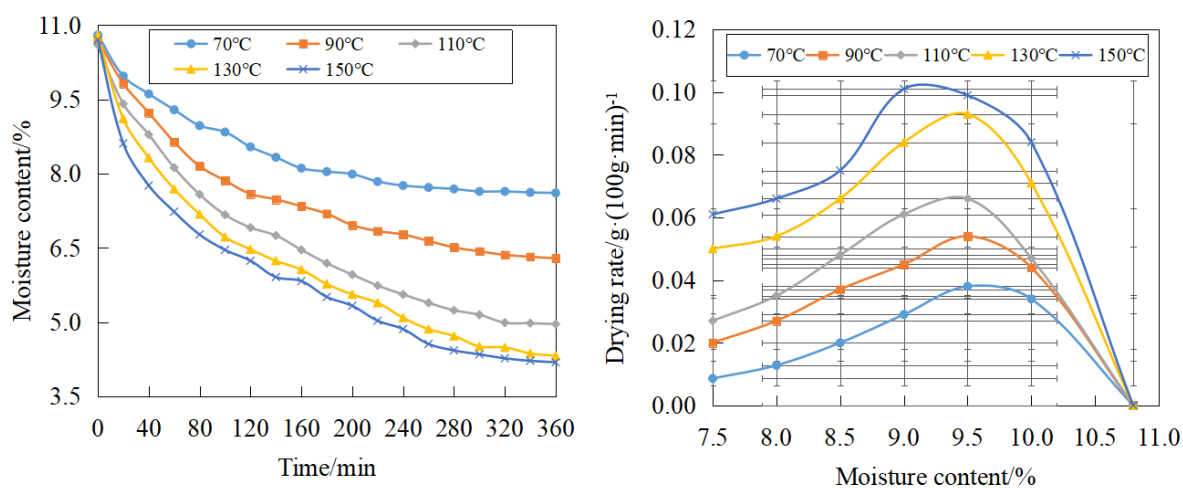
3. Results

3.1. Effects of Soda Residue on Drying Rate

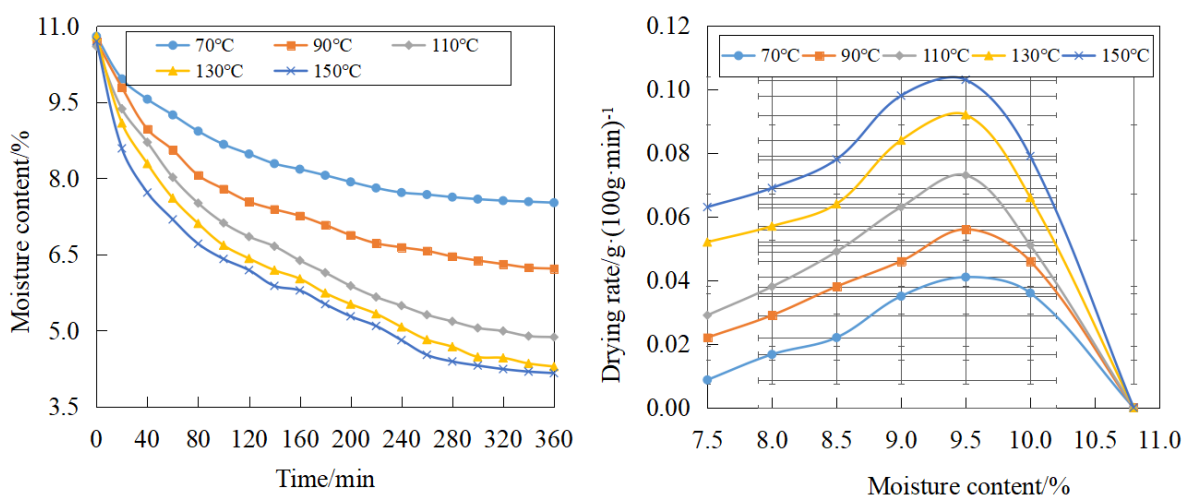
Figure 4a–d shows the moisture content change curve with the drying time of raw coking coal. The coking coal had 2%, 5%, and 10% soda residue under different temperatures. It is seen that the higher the temperature is, the shorter the drying time needed. When the drying temperature increases from 70 °C to 130 °C and 150 °C, the drying time needed to reach the same moisture content is shortened by 58.3% and 72.2%, respectively (Figure 4a). This is mainly because the higher the temperature, the more energy absorbed by the material and moisture; the faster the moisture evaporates, the shorter the time required [24]. The internal temperature of the coal sample also affects the structure of coking coal: the higher the temperature, the greater the degree of structural damage, and the easier the moisture removal [25].



(a) Raw coal (RC)



(b) RC + 2% soda residue (SR)



(c) RC + 5% SR

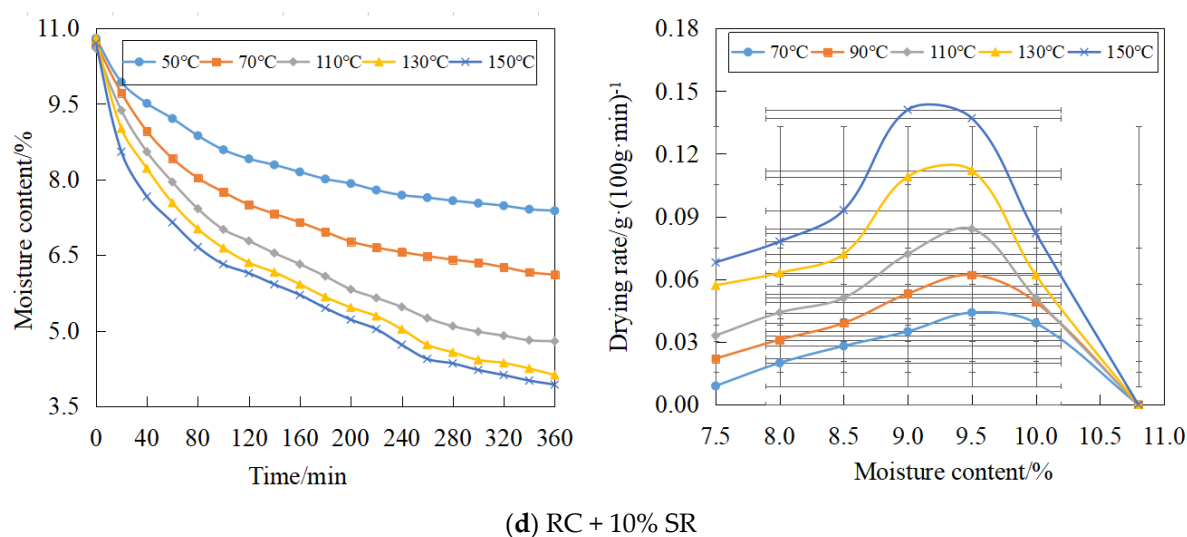


Figure 4. Coking coal drying curve and drying rate curve.

According to the drying rate curve in Figure 4a, there are four variable speed stages during drying: the rising speed stage (A); the constant speed stage (B); and the falling speed stage, which can be divided into the first stage of falling speed (C) and the second stage of falling speed (D). In the process of drying with low temperature, the heat generated per unit time in coal is basically the same as the energy required for moisture transfer. Therefore, there is a constant drying rate stage. At high temperature, the heat generated per unit time in the coal is much greater than the energy required for moisture transfer, so the drying rate increases until the free moisture content is removed. In the drying process, the evaporation of free moisture transitions to internal moisture transfer in the coal gradually. Compared with free moisture, capillary moisture in coal has a smaller dielectric constant and absorbs less energy, so the drying rate begins to decline [26]. Multiple changes occur in the slowing down stage of the drying rate, mainly due to the transition from capillary water evaporation to adsorbed water. This can be considered as a transition from the first deceleration phase to the second deceleration phase.

In Figure 4b–d, the soda residue has the most significant influence on the coking coal drying rate at 110 °C: adding 2%, 5%, and 10% soda residue, the average drying rate of coke coal increases by 11.50%, 25.3%, and 37.3%, respectively. Adding soda residue has a positive effect on promoting coking coal drying, mainly because compared with raw coal, soda residue contains chemical components with a high dielectric constant (CaCO_3 (6.1–9.1), coking coal (2/4)). These compounds absorb more energy, and thus the internal temperature of coking coal increases rapidly. In addition, the alkaline properties of soda residue can weaken the molecular force between moisture and material [27]. At the same time, calcium and sodium salts in soda residue can weaken the binding force of high polymer and C–C bond and change the pore structure of coking coal in the drying process to a large extent (reduction of pore structure) [28]. This results in reduced moisture adsorption and promotes moisture transfer. The mechanism of action is shown in Figure 5. The soda residue contains chloride, and because the radius of hydration of Cl^- (0.195 nm) is small [15], the relaxation phenomenon is easy to occur, and a large amount of the absorbed energy can be converted into internal energy, thus improving the drying efficiency.

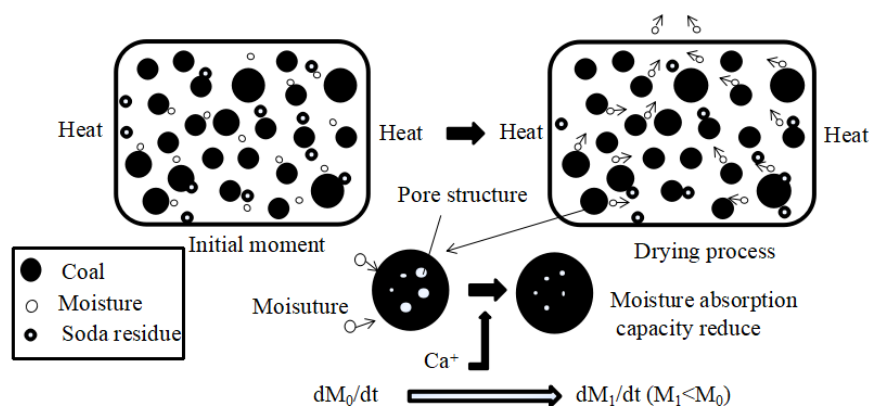


Figure 5. The influence mechanism of soda residue composition on coal moisture absorption and transfer.

3.2. Effect of Soda Residue on Temperature and Moisture Gradient during Drying

Figures 6 and 7 shows the temperature and moisture distribution characteristics of raw coking coal at each point from edge to center during the drying time range of 0 to 360 min, respectively.

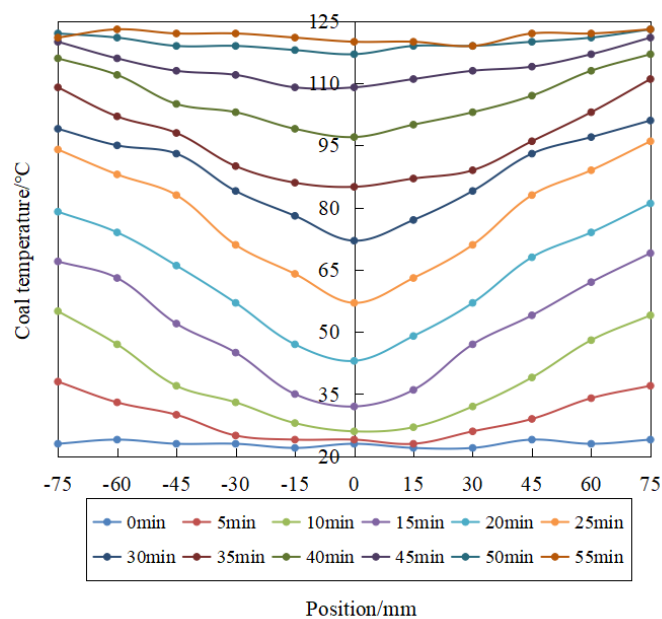


Figure 6. Characteristics of temperature distribution during the drying process.

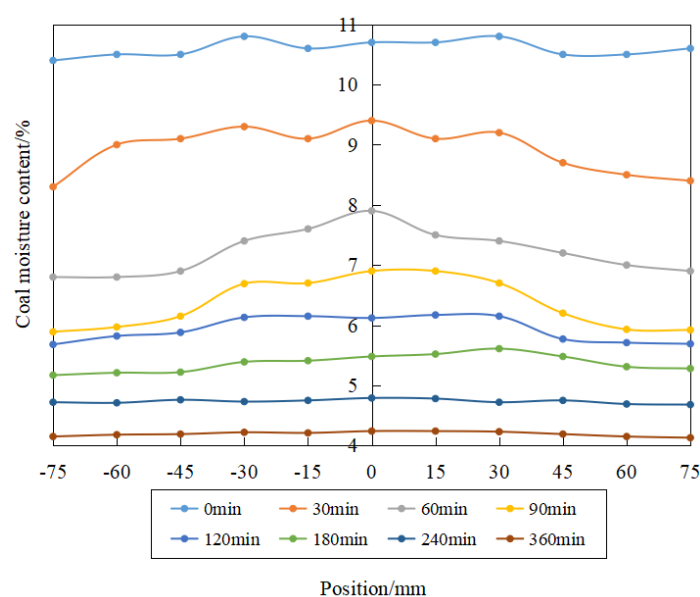


Figure 7. Characteristics of moisture distribution during the drying process.

Figure 6 shows that the temperature at the coal edge that is close to the heat source begins to rise gradually during the initial stage of drying, while the central temperature does not change. In the drying process, a temperature gradient from the edge to the center was gradually formed. This gradient reaches the maximum value when the drying time is 25 min. At this point, the temperature difference between the edge and the center is about 39 °C. As the temperature in the center increases, the temperature difference between the edge and the center shrinks. Thus, the temperature gradient at the edge and the center decreases gradually and reaches the limit when the drying time reaches 55 min. During this time, the temperature difference between the edge and the center is about 5 °C.

The moisture distribution and evaporation of coal are mainly affected by temperature. Thus, the lateral transfer process of coal moisture from the edge to the center also presents a certain gradient change. It is seen from Figure 7 that the average moisture content decreases rapidly and the moisture gradient from the edge to the center is formed gradually in 0–60 min. The moisture gradient reaches its maximum when the drying time reaches 90 min. At this point, the moisture difference between the edge and the center is 1.2%. In the drying process, the moisture gradient begins to decrease and gradually disappears.

Figures 8 and 9 show the effect of alkali slag on temperature and moisture distribution in the coal drying process, respectively. It is known that the addition of soda residue can improve the drying temperature of a coal sample and increase its moisture removal rate, but it has little influence on the temperature gradient from edge to center and no significant effect on the lateral transfer rate of coal moisture. Figure 8 shows that when 2%, 5%, and 10% soda residue was added into the coal, the temperature at the center point of the coal increased by 3, 5, and 10 °C, respectively, in 10 minutes and the temperature at the edge increased by 2 °C, 4 °C, and 8 °C, respectively. As the average temperature of coal increases, the longitudinal evaporation rate of moisture increases. From Figure 9, it is seen that when 2%, 5%, and 10% soda residue was added into the raw coking coal, the moisture content at the center point reduced by 0.3%, 0.4%, and 0.8%, respectively.

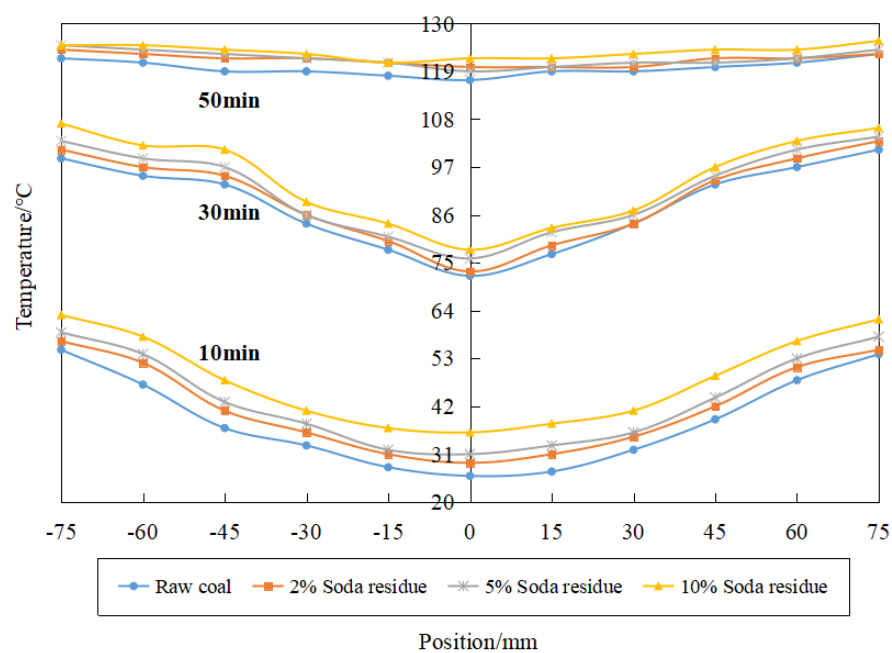


Figure 8. Effects of additives on temperature transfer from edge to center in coal.

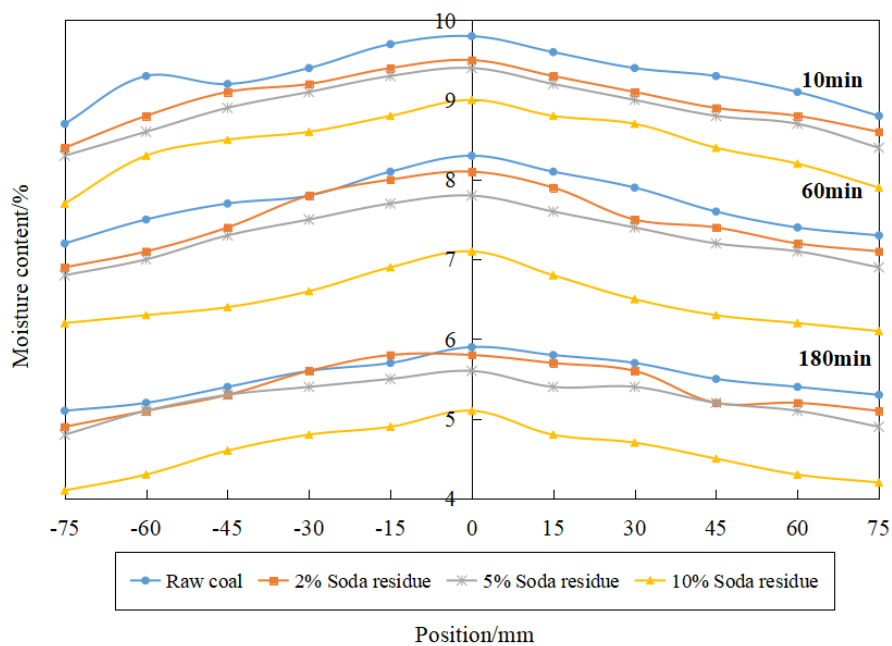


Figure 9. Effects of additives on humidity transfer from edge to center in coal.

3.3. Effect of Soda Residue on Coking Properties

3.3.1. Mechanical Strength of Coke in Cold State

Falling Strength

The falling strength of coke under different adding ratios of soda residue is shown in Table 3.

Table 3. Falling strength of different coke samples.

Coke Samples	Mass before Drop (g)	Mass after Drop (g)	Drop Strength (%)	Loss Quantity (g)
RC	400.26	395.74	98.87	4.52
RC + 2% SR	400.78	396.11	98.83	4.67
RC + 5% SR	403.82	398.83	98.76	4.99
RC + 10% SR	402.32	393.50	97.80	8.82

RC, raw coal; SR, soda residue.

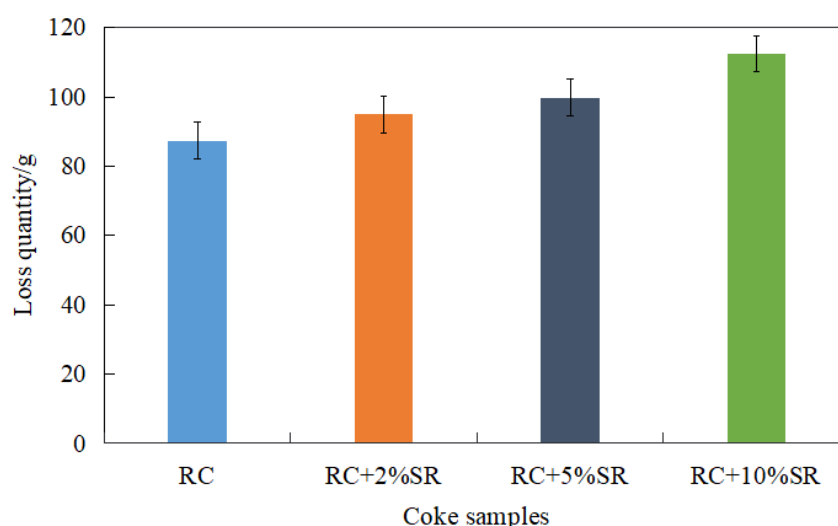
Table 3 shows that the falling strength of coke decreased after soda residue was added. This indicates that the addition of soda residue will reduce the coke falling strength. Compared with raw coal, the addition of 2%, 5%, and 10% soda residue decreases the loss quantity by 3.2%, 9.4%, and 48.8%, respectively. When the proportion of soda residue is not more than 5%, the loss quantity decreases by less than 10%. The coke falling strength is

$$RC > RC + 2\% SR > RC + 5\% SR > RC + 10\% SR \quad (3)$$

Coke Wear Strength

Figures 10 and 11 show the wear loss quantity and wear strength, respectively, for different proportions of soda residue added. Figure 10 shows that the carbon loss of coke made from raw coal is about 87.3 g when the same proportion is expanded to 1 kg of the base sample. The drum wear of coke products obtained by coal pyrolysis after the addition of soda residue is greater than that of raw coking coal. With an increase in the proportion of alkali slag, the wear strength of coke decreases continuously. When the proportion is 10%, the carbon loss reaches 112.4 g. However, when the addition ratio is less than 5%, the carbon loss does not exceed 100 g. According to Figure 11, the wear strength of coke is ranked as

$$RC > RC + 2\% SR > RC + 5\% SR > RC + 10\% SR \quad (4)$$

**Figure 10.** The loss quantity of the coke samples.

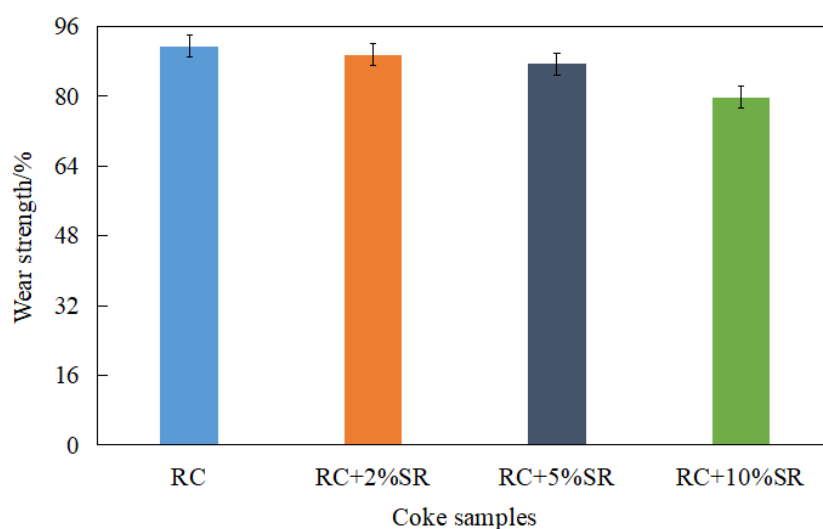


Figure 11. The wear strength of the coke samples.

3.3.2. Thermal Performance Test

The thermal properties of coke can be evaluated more accurately by studying the carbon dissolution reaction at different temperatures. The reactivity (PRI) and post-reaction strength (PSR) of raw coke (RC) and raw coke with soda residue at different carbon solution reaction temperatures (800–1200 °C) are shown in Figure 12. It is seen that the PRI of all four cokes increases rapidly with an increase in the reaction temperature. This is mainly because an increase in temperature not only increases the chemical reaction rate between coke and CO₂ but also increases the diffusion rate of CO₂ in the coke pores [29]. In addition, the addition of soda residue can further improve coke reactivity, indicating that the soda residue can increase the coke carbon dissolution reaction rate, because the metal compounds in the soda residue, such as Ca, Mg, and Na, have a strong catalytic effect on the carbon dissolution reaction of coke, which increases the gasification reaction rate of coke–CO₂ and improves the coke reactivity [30,31]. For example, at 950 °C, the reactivity of raw coke was 8.2%, which improved by 7.9% after adding 2% soda residue.

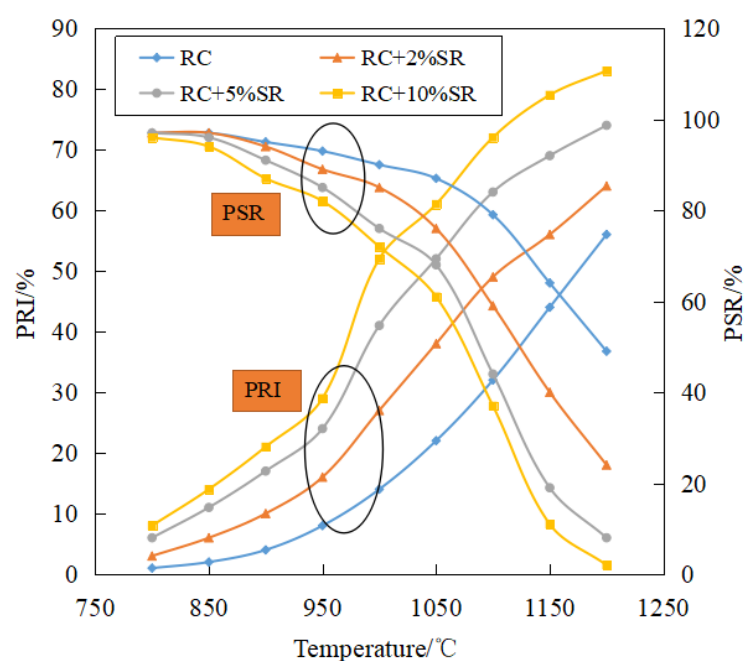


Figure 12. Thermal properties of four kinds of coke at different reaction temperatures.

In addition, with a rise in the reaction temperature, the post-reaction strength (PSR) of the four coke samples decreased slowly first and then rapidly. The turning point temperature of the degradation trend of the PSR of the four coke samples also decreased gradually. The reactivity of the four coke samples was more than 30% at four different temperature turning points. The results show that a decrease in coke strength was mainly caused by the destruction of coke skeleton structure due to the large amount of carbon loss [32]. When the carbon loss quantity of coke exceeds a certain range, the pore structure of coke is damaged; the structure becomes loose, and the cracks increase, ultimately leading to a decrease in the coke strength after the reaction.

3.3.3. Relationship between Coke Reactivity and Specific Surface Area

The specific surface area of coke after reaction was measured by nitrogen adsorption, and the influence of the carbon dissolution reaction on the stomatal structure of coke was analyzed. The relationship between the specific surface area of the five coke samples after reaction and the reactivity (PRI) is shown in Figure 13.

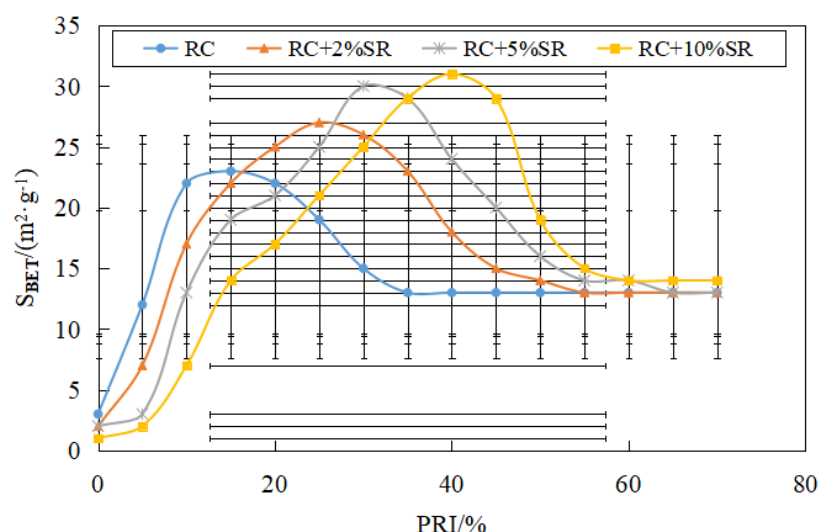


Figure 13. Effect of soda residue on specific surface area after coke reaction.

Figure 13 shows the specific surface area of the four kinds of coke before reaction (PRI = 0) differs little. However, with an increase in the reactivity, the specific surface area of the four kinds of coke increases first and then decreases. This is mainly because of the increase in reactivity. Carbon consumption leads to the formation of micropores in the coke matrix or an increase in pore size, followed by an increase in the specific surface area of coke [33]. When the reactivity is too high and carbon consumption is too much, the micropores are interconnected to form large pores, resulting in a decrease in the specific surface area of coke [34].

Compared with the four kinds of coke, the addition of soda residue can increase the maximum specific surface area after coke reaction. There is no significant difference between the specific surface area values of 2% soda residue and 5% soda residue (26 m²·g⁻¹–30 m²·g⁻¹). The maximum specific surface area corresponds to PRI increased significantly, from 10% to about 30%. This is mainly because with the addition of additives and an increase in the amount of additives, the reaction activity points increase. The coke site in contact with the soda residue is dissolved in large quantities due to catalytic action, so the loss quantity of carbon in coke increases and the reactivity increases. As the reaction goes on, the coke around the additive is consumed in large quantities, leading to coalescence of coke. A pore structure with additives at the center is formed [35]. The pore structure has little effect on the specific surface area of coke due to its large size; in the part of coke without additive distribution, the reaction is uniform because of no additive catalysis, and

the surface of coke is evenly eroded by CO₂ to form micropores, which increases the specific surface area of coke [36]. Therefore, the addition of soda residue can increase the active point of coke dissolution reaction and increase coke reactivity, but it cannot promote the formation of micropores on the coke matrix and has little influence on the specific surface area of coke.

3.4. Economic Benefit Analysis

Through the above analysis, the improvement in the drying rate and mechanical strength of coke should be taken into account. The additive proportion should not exceed 5%; thus, the additive proportion range of 2–5% is appropriate. At the same drying temperature, the drying rate increased by 11.5% and 25.3%, respectively. The economic benefits of coal drying with different adding proportions of soda residue were analyzed. The results of the analysis were shown in Table 4.

Table 4. Economic benefits comparison.

L (cm)	Sample	W ₀ (%)	W _t (%)	T (min)	Q (KW·h)	H (KJ·kg ^{−1})	C (USD·kg ^{−1})
15	RC	11	6	220	2.93	5274	0.2212
	2%SR + RC			197	2.53	4554	0.1912
	5%SR + RC			175	2.27	4086	0.1712

Note: The price of soda residue is 30.62 USD·t^{−1}.

Thinking about it economically, raw coal samples mixed with soda residue have an obvious energy saving advantage during the drying process. The total cost input is only 77–86% that of normal drying. Figure 14 shows the cost comparison. It is seen that the addition of soda residue can greatly reduce the coal drying cost.

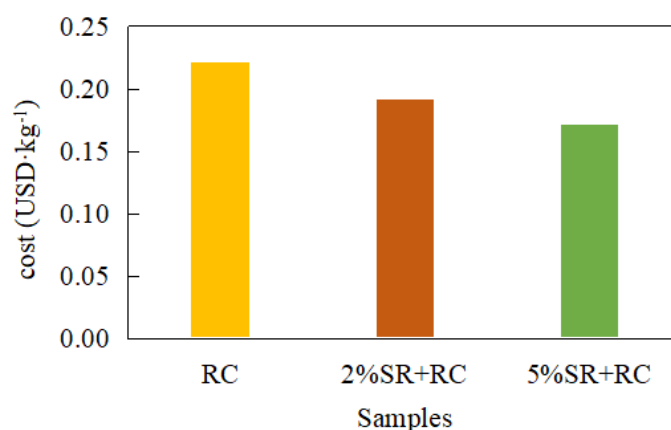


Figure 14. Effects of soda residue on the economic benefits of coking coal drying.

4. Discussion

The drying rate and coking characteristics of coking coal are affected by many factors, such as particle characteristics, temperature, raw coal characteristics, etc. R.C. Everson [37] found particle size and density influence the time required for complete conversion of the chars.

In this study, the drying rate and coking properties of coking coal were improved by mixing soda residue from alkali plants with high-moisture coking coal. On the one hand, soda residue improved the drying rate without causing other negative effects; on the other hand, the economic benefits brought by improving the drying rate were compared with those of ordinary drying methods. Therefore, it is very important to find the appropriate addition ratio. Soda residue was chosen as an additive mainly because of its characteristics.

First of all, soda residue is mainly composed of basic compounds, its dielectric constant is higher than that of raw coal because it contains components such as CaCO_3 (6.1–9.1) and coking coal (2/4)), and it can absorb more heat and convert it into internal energy. Besides, soda residue is rich in chloride, and because the radius of hydration of Cl^- (0.195 nm) is small [15], the relaxation phenomenon is easy to occur, and a large amount of the absorbed energy can be converted into internal energy, thus improving the drying efficiency.

In the process of coking, the experimental results show that the effect of soda residue on coke reactivity and cold strength is significant. With an increase in the ratio of soda residue, the pore wall of coke becomes significantly thinner and the porosity increases. A connected hole wall appears, and because the hole wall is discrete, a large number of cracks appear on the surface of the coking coal, and the carbon loss increases significantly. The experimental results show that the carbon loss is small when the soda residue content is less than 5%, which is close to that of raw coal. However, with an increase in the soda residue ratio, the coke cracks increase greatly, and the carbon loss increases sharply. When the addition ratio reaches 10%, the carbon loss is much greater than that of raw coal. The effect of the additive on steam gasification reactivity was investigated by Coetzee [38], and the results obtained for the reactivity of the parent coal were compared to that of the impregnated coal, which indicated that the addition of K_2CO_3 increases the reaction rate of large coal particles by up to 40%.

Soda residue contains a large number of alkali metal compounds. The reactivity of coke improves when soda residue is added: the higher the proportion of soda residue, the greater the reactivity of coke. This is mainly due to the catalytic action of alkali metals in the carbon solution reaction. Its catalytic mechanism was as follows:

Catalytic precursor $\text{M}(\text{CH}_3\text{COO})_n$ infiltration into coke. The high-temperature treatment and reaction, through a series of actions, form a catalytic $\text{CO}_2\text{--C}$ reaction of species intermediates (M) on the coke surface [39]. The intermediate is the determinant of catalysis; it is the high dispersion of the surface of the coke matrix, resulting in the high reactivity of coke directly. The adsorption of minerals makes a variety of minerals in the molecular form of oxides on the surface of the coke matrix to form a high dispersion. The carbon atoms at the active sites around the mineral oxides contact sufficiently, and the second migration of oxygen occurs. The reaction intermediates $\text{C}(\text{O})$ and simple substance (M) are formed, and then $\text{C}(\text{O})$ is desorbed to form CO. This results in an increase in the dissolution loss reactivity of the carbon in the coke.

This is the reaction in which fixed carbon is oxidized by CO_2 at high temperature to form CO. It is an important aspect of fixed carbon gasification. The reaction of loss carbon dissolution is a strong endothermic reaction and belongs to the gasification reaction. Bunt [40] conducted thermo-gravimetric analyses to determine the influence of the addition of an alkaline metal catalyst and found that catalyst addition significantly increases the reaction rate of the carbon conversion. There is an opportunity to possibly improve on the fluidized-bed/large particle gasifier throughput by speeding up the time needed for the rate-limiting CO_2 gasification reaction in a catalyzed system comprising fine discard coal agglomerates containing an alkaline additive. According to the dissolution loss kinetics, the effects of chemical reaction or stomatal diffusion rate on coke dissolution and degradation were considered. Soda residue contains lots of alkali metal compounds. The alkali metal vapor absorbed on coke has significant degradation effect on the high-temperature metallurgical properties of coke, which has a catalytic effect and significantly increases gasification reactivity, and the catalytic limit of potassium vapor and sodium vapor was about 5% and 3%, respectively. Wang [18] found that the destruction of the aromatic ring structure with dense and stable carbon structure in coke by the alkali metal vapor adsorption process was the essential cause of coke reactivity increase and fracture.

Finally, the significance of the soda residue additive in increasing the drying rate of coking coal and energy saving was proved according to the analysis of economic benefits.

At present, the treatment methods of alkali plant slag mainly include incineration, neutralization method, wet air oxidation method (WAO), chemical oxidation method, biological method, etc., but they all have some disadvantages, such as high cost and low utilization rate. For every 1 t soda ash to discharge 0.3 t of soda residue, a plant with an annual capacity of 800,000 t soda residue is produced. The annual cost of disposing waste residue is about 10 million RMB.

Taking the 6 m top-charged coke oven as an example, the annual consumption of dry coal is 1.24 million tons. According to the drying experiment results, the drying rate increased by 11.5% when the mass ratio of alkali slag was 2%. Calculation shows that the amount of alkali slag consumed for every 1 ton of coal dried is about 20 kg.

Of course, the soda residue used for coal drying is the waste residue after the desulfurization and denitrification pretreatment process in the caustic plant. It contains no sulfide and nitrogen oxides. Thus, for the mixture of soda residue and coal sample at high temperatures, the coking process will not increase the emission of nitrogen oxides and sulfur compounds.

Next, it is of great significance to study the influence of various compounds of alkali slag on the drying characteristics of coking coal. Perhaps the change in coking coal properties is the result of the interaction of various compounds at high temperatures. In addition, different compounds may have different influencing mechanisms.

5. Conclusions

By studying the influence of soda residue on the drying and coking characteristics of coking coal, the following conclusions were drawn:

1. The soda residue has the most significant influence on coking coal drying rate at 110°C. Adding 2%, 5%, and 10% soda residue, the average drying rate of coke coal increases by 11.50%, 25.3%, and 37.3%, respectively.
2. The addition of additives can improve the drying temperature of a coal sample and increase its moisture removal rate, but the additive has little influence on the transverse temperature and humidity transfer gradient of coking coal from edge to center.
3. The addition of soda residue reduces the coke falling strength. The effect of adding 10% soda residue was the most obvious: the loss quantity was as high as 8.82 g. When the proportion of soda residue was not more than 5%, the loss quantity decreased by less than 10%; this range meets industrial requirements.
4. The reactivity of coke increases with an increase in soda residue. With the increase in the reactivity, the specific surface area of coke increased first and then decreased; the maximum specific surface area corresponding to PRI increased with an increase in soda residue quantity. The addition of soda residue can increase the active point of the carbonization reaction and improve the reactivity of coke.
5. Adding 2–5% soda residue, the coking coal sample mixed with soda residue has an obvious, energy saving advantage in the drying process. The total cost input is only 77–86% that of normal drying.

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