

## PROTECTIVE MECHANISM OF UNBURNED PULVERIZED COAL TO COKE IN BLAST FURNACE

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### Abstract

The edge and internal morphology of coke with different contents of UPC (unburned pulverized coal) after reaction with  $CO_2$  were analyzed by SEM. The influence of UPC on CRI (coke reactivity), CSR (coke strength after reaction) and apparent porosity was also studied. The synthetic weighted mark method was used to analyze the comprehensive effect of UPC content on coke quality. The results show that because of the decrease of the content of intermediates  $C_f(O)$  and  $C(O)C_f(O)$  the restrictive step between the coke and  $CO_2$  is an interfacial chemical reaction, and it accords with the Mckewan equation  $1-(1-\alpha)^{1/3}=kt$ . The UPC has a strong effect on coke when the content of UPC is 10~20%; meanwhile, the CRI and the apparent porosity are significantly decreased by 6.8% and 9.5%, respectively, and the CSR is significantly increased by 3.8%. The UPC can effectively reduce the effect of  $CO_2$  on the edge and the internal erosion of coke; the large pores and the pulverization of coke were avoided. The results of the synthetic weighted mark method showed that the comprehensive quality of coke changed greatly when the content of unburned pulverized coal was 11.24~20.87%, which is in agreement with the experimental results.

**Keywords:** Unburned pulverized coal; Coke reactivity; Coke strength after reaction; Apparent porosity; Synthetic weighted mark method

### 1. Introduction

Coke is an important metallurgical material and has irreplaceable function in BF (blast furnace) process because of its special properties. Under the reaction conditions of BF, coke will be involved in many multiphase reactions (gas-solid reaction, liquid-solid reaction, solid-solid reaction) until reacted completely [1]. The multiphase reaction and the degradation process of coke in BF are shown in Figure 1. The research results of BF dissection at home and abroad have proved that coke loss mass caused by the boudouard reaction of coke ( $C+CO_2=CO$ ) accounted for 20~30% of the total mass of the coke, which is the main reason for the decrease of coke strength and grain size [2-8]. Because of lower temperature in the upper part of BF and lower  $CO_2$  concentration in the lower part of BF, the boudouard reaction of coke mainly occurs in the temperature range of 1000~1200°C in the cohesive

zone. A large amount of broken coke and powder will be generated if the coke degradation in this area is serious, which will seriously hinder the gas flow and affect the smooth operation of the BF.

The predecessors have done a lot of work about the change of physical and chemical properties of coke in BF, focusing on the following three aspects: (1) The evolution law of coke properties in practical BF is studied through three ways: BF dissection, coke sampling in experimental BF and BF tuyere sampling [9-12]. (2) In the laboratory, the multiphase reaction behavior of coke was studied by simulating the atmosphere, primary slag composition, and alkali metal conditions in the BF [13,14]. (3) The effect of coke on the flow law of slag iron in dead stock [15-19]. For example, Tobias HILDING et al. studied the behavior of coke with CSR (coke strength after reaction)=68.8% in experimental BF, and the results showed that the graphitization has a great effect on the degradation behavior of coke and the alkali metal has

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a catalytic effect on the reactivity of coke [20]. The physical degradation process of coke in the BF was reported by Yasuo Okuyama et al., and the study showed that coke was severely degraded at 3~5m above tuyere, and the degradation of coke was also aggravated by Si, Ca and P compounds [21]. In addition, the gasification reaction characteristics of coke with CO<sub>2</sub> were studied by Wei Huo [22,23] and Juliana G. Pohlmann [24].

On the other hand, with the widespreadness of high pulverized coal injection (PCI) rate technology, many iron and steel enterprises are pursuing high coal rate. Although improving the coal rate is helpful to reduce the cost of ironmaking, the content of UPC in BF also increases. The production of UPC in BF is inevitable. The UPC has positive and negative effects on BF smelting: (1) a part of UPC in the BF will enter into the cohesive zone and adhere to the surface of coke. Since the reactivity of UPC is higher than that of coke, the UPC will preferentially react with CO<sub>2</sub>. This will prevent the deterioration of coke to some extent, reduce coke breeze in high temperature region, and improve the permeability in the lower part of BF [25-28]. (2) A large amount of UPC will contact with liquid slag when the content of UPC is too high, resulting in an increase of the slag viscosity and in the difficulty to discharge hot metal and slag. The UPC distributed in the upper part of the tuyere raceway will seriously deteriorate the permeability of the burden. That will cause unstable pressure difference in BF and destroy the reasonable distribution of BF gas.

However, previous studies have often ignored the effect of UPC on coke in BF. The coke is the only solid material in the BF after the ore is melted at high temperature, which is very important to keep gas-liquid permeability and the activity of hearth [29]. Therefore, it is necessary to study the influence mechanism of UPC on coke. The main focus of this study is the positive influence of UPC on coke quality.

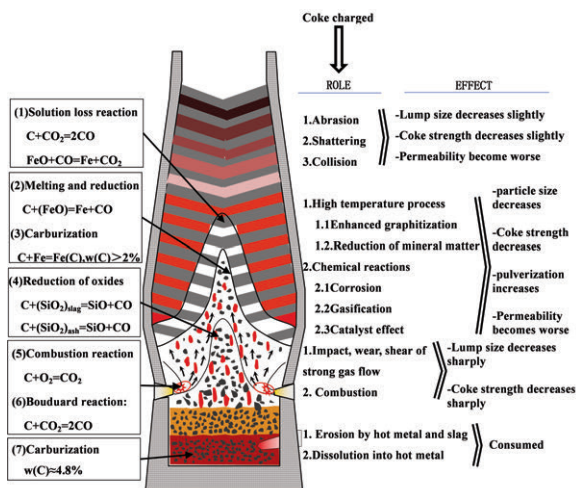


Figure 1. The degradation process of coke in BF

## 2. Experimental Section

### 2.1 Experimental materials

The experimental raw materials used in the BF were anthracite and coke. It is very difficult to obtain the UPC from the BF. Therefore, the anthracite was placed in the high-temperature heating furnace and heated to 1100°C, then pyrolyzed for 1h under anaerobic conditions in the laboratory, and then cooled to room temperature under nitrogen atmosphere to get UPC [30]. The UPC particle size less than 0.074mm accounted for 70%. The size of the coke was made into  $\Phi 18 \sim \Phi 23$ mm according to GB/T4000—2008 and dried at 175°C for 2 hours. The industry analysis of pulverized coal and coke are shown in Table 1, and the chemical composition of UPC is shown in Table 2.

Table 1. The industry analysis (in mass%)

Composition	Fc	Mad	Aad	Vad
Anthracite	79.88	0.88	11.48	7.76
Coke	86.74	0.11	12.14	1.01
UPC	85.32	0.12	13.51	1.05

Table 2. The chemical composition of UPC ash (in mass%)

	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	others
UPC	1.26	3.22	35.57	47.80	2.14	7.06	0.84	0.46	1.65

### 2.2 Experimental process and conditions

#### (1) Single sample reactivity

To compare the reactivity of UPC and coke, the experiments about the reaction of UPC or coke with CO<sub>2</sub> were carried out respectively. The UPC (4g) or coke (200g) was placed into a reaction device respectively to react with CO<sub>2</sub> for 2 hours at 1100°C, and the weight change data were recorded every 2 min.

#### (2) Mixed sample reactivity

In order to explore the effect of UPC on coke quality under the condition of CO<sub>2</sub>, the reactivity experiment of mixed sample was carried out. The coke (200g) was mixed with different contents of UPC, then placed into the reaction device to react with CO<sub>2</sub> for 2 hours at 1100°C, and the weight change data were recorded every 2 min. The experimental conditions are shown in Table 3.

The amount of UPC was calculated using the following method. According to the actual situation of the BF, that is, the coal ratio is 150 kg<sup>-1</sup> and the coke ratio is 350 kg<sup>-1</sup>. It is assumed that the combustion rate of pulverized coal injected into the BF is 100%, 90%, 85%, 80%, 75% and 70% respectively. For example, when the combustion rate of pulverized coal is 90%, the content of the UPC will be 8.57g. The



formula is as follows. In this process, the mass of coke is always 200g.

$$UPC \text{ content} = 150 \times (1 - 90\%) \times 200 \div 350 = 8.57 \text{ g} \quad (1)$$

The experimental scheme and the content of UPC are shown in Table 4.

**Table 4.** The experimental scheme

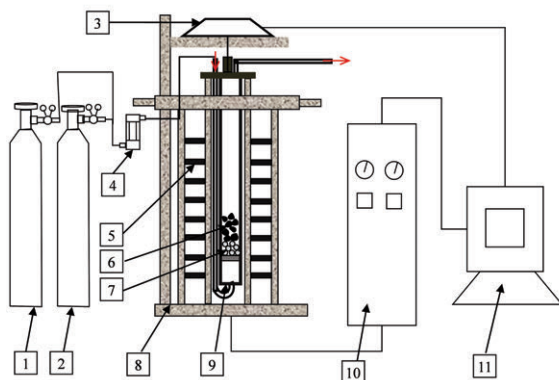
Experimental number	UPC Ratio(100-combustion rate)/ %	UPC Mass / g
0	0	0
1	10	8.57
2	15	12.86
3	20	17.14
4	25	21.43
5	30	25.71

### 2.3 Experimental equipment

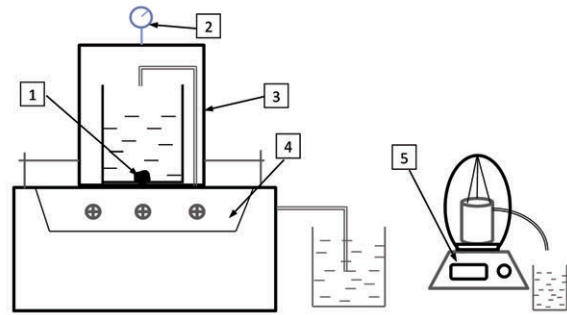
The equipment for the reactivity of sample with  $\text{CO}_2$  is shown in Figure 2. The sample was placed into the reactor which is suspended under the electronic balance. The gas was introduced from the bottom of the reactor, it passed through the sample and flowed out from the top. In this process, a layer of alumina balls with a thickness of about 100 mm was paved at the bottom of the reactor to ensure a steady flow of the gas through the sample and reduce the experimental error. The equipment can be controlled by computer, and the maximum temperature can reach 1500°C.

The micro-topography changes of coke after the reaction were observed by using the JSM-6510LV type scanning electron microscopy (SEM) made in Japan.

The apparent porosity of the coke was measured with XQK-02 type apparent pore bulk density determinator made by Sinosteel Group, as shown in Figure 3.



**Figure 2.** High temperature heating reaction device; 1—Nitrogen; 2—Carbon dioxide; 3—Electronic balance; 4—Flow meter; 5—Si-Mo bar; 6—Sample; 7—Alumina balls; 8—Heating furnace; 9—Reactor; 10—Temperature control system; 11—Computer



**Figure 3.** The measuring device for apparent porosity; 1—Coke sample; 2—Vacuum pressure gauge; 3—Vacuum cover; 4—Control cabinet; 5—Electronic balance

### 2.4 The experimental indexes

The experimental indexes included CRI (coke reactivity), CSR, and apparent porosity. The CRI and CSR were determined according to the method of GB/T4000—2008. The calculation methods of CRI (%) and CSR (%) are shown in the formulas (2) and (3), respectively.

$$CRI = \frac{(m - m_1)}{m} \times 100\% \quad (2)$$

$$CSR = \frac{m_2}{m_1} \times 100\% \quad (3)$$

Where  $m$  is the initial mass (g) of coke sample,  $m_1$  is the residual mass (g) of coke after reaction, and  $m_2$  is the mass (g) of coke larger than 10mm after the  $\bar{I}$  drum test.

The apparent porosity  $P$  (%) of coke was calculated by formula (4).

$$P(\%) = \frac{(x_3 - x_1)}{(x_3 - x_2)} \times 100\% \quad (4)$$

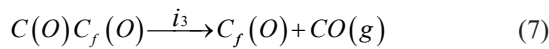
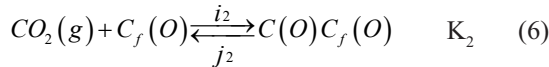
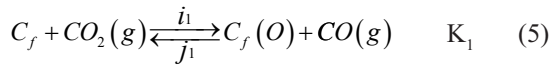
Where  $x_1$  is the mass (g) of dry coke sample,  $x_2$  is the suspension mass (g) of coke located into the apparent pore bulk density determinator, and  $x_3$  is the saturated mass (g) of coke after removing excess liquid on its surface.

## 3. Results and Discussion

### 3.1 The dynamic analysis

The research results of Zhang [31] showed that the reactivity of UPC with  $\text{CO}_2$  is about 2~4 times higher than that of coke, because of the large specific surface area of UPC. The gasification activation energy of UPC is lower than that of coke, so the reactivity of UPC is about 10 times higher than that of coke [26]. The dynamic analysis of the gasification reaction process was carried out to explore the restrictive step.

The solution loss reaction between coke or UPC with CO<sub>2</sub> is the gas-solid heterogeneous reaction. In this process, the activation point on the surface of coke or UPC continuously react with CO<sub>2</sub>. The mechanism of the solution loss reaction has been studied by predecessors, and the generally accepted mechanism is as follows [13,32-38].



Where  $K_1$  or  $K_2$  is the equilibrium constant and  $C_f$  is the carbon atom located at the activation position.  $C_f(O)$  and  $C(O)C_f(O)$  are the two types intermediate products, representing semiquinone and off plane oxygen complex, respectively.

The reaction process of UPC or coke with CO<sub>2</sub> accords with the classical unreacted core model. The reaction process follows five steps: (1) The external diffusion is that the gas reactant CO<sub>2</sub> passes through the gas-solid boundary layer and reaches to the surface of particles. (2) The internal diffusion is that the gas reactant CO<sub>2</sub> diffuses through loose ash product layer to reach the reaction interface. (3) The gas reactant CO<sub>2</sub> reacts with the particles to generate CO and ash at the reaction interface. This process consists of adsorption, interfacial chemical reaction, CO desorption, and other steps. (4) The gas product CO diffuses through loose ash layer to reach the surface of the product layer. (5) The CO diffuses into the external gas phase through the gas-solid boundary layer. The reaction mechanism process of UPC or coke with CO<sub>2</sub> is shown in Figure 4.

The following assumptions are made for the reaction process of UPC or coke with CO<sub>2</sub>: (1) the UPC or coke is an isotropic spherical particle and well distributed, (2) by literature review, during the gas-solid reaction (gasification of carbon), when the gas flow rate is over 0.83 L/min, the effect of external diffusion can be eliminated [39,40]. Also, in my preliminary work, the dioxide with the flow rates of 5 L/min and 10 L/min was used to react with the coke. The results show that the effect of external diffusion on the reaction can be completely neglected, and (3) the loss of oxygen included in oxides of UPC or coke is neglected. The restrictive step between UPC or coke and CO<sub>2</sub> may be the following two processes: (1) the CO<sub>2</sub> diffuses through loose ash product layer to reach the reaction interface. (2) the interfacial chemical reaction between CO<sub>2</sub> and unreacted core.

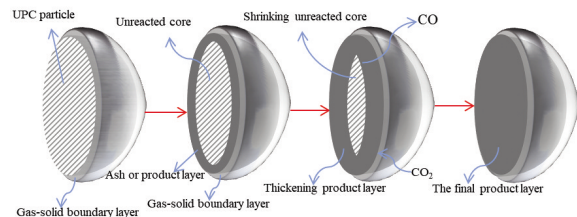


Figure 4. The reaction mechanism of UPC or coke with CO<sub>2</sub>

### 3.2 The determination of the restrictive steps

The reaction is dominated by CO<sub>2</sub>+C=2CO, so the reaction fraction  $\alpha$  is defined as follows.

$$\alpha = \frac{m_0 - m_t}{m_0 \times F_c} \quad (9)$$

Where  $m_0$  is the initial mass (g) of sample,  $m_t$  is the mass (g) of sample at time  $t$ , and  $F_c$  is the fixed carbon content (%) of sample.

(1) Assuming internal diffusion control

If the interfacial chemical reaction rate is much larger than the diffusion rate in the product layer, the interfacial chemical reaction resistance can be neglected. The reaction of UPC or coke with CO<sub>2</sub> is considered to be controlled by the internal diffusion reaction. The concentration of CO<sub>2</sub> at the edge of the coke or UPC is the same as that in the gas phase, and the distribution of gas concentration is shown in Fig. 5.

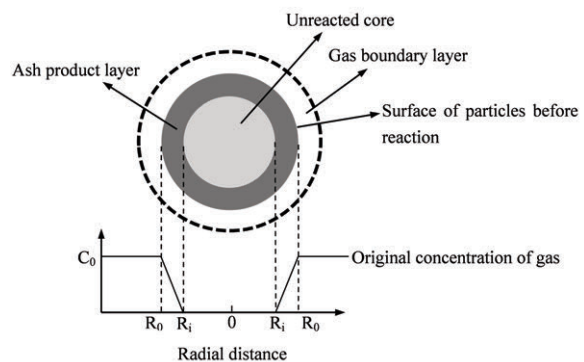


Figure 5. The concentration distribution of CO<sub>2</sub> under internal diffusion control

The diffusion process accords with the Fick law, and the reaction rate can be expressed by Ginstling–Brounshtein equation (10) [41] or Jander equation (11) [42].

$$1 - 2/3\alpha - (1 - \alpha)^{2/3} = kt \quad (10)$$

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = kt \quad (11)$$



Where the  $k$  is the reaction rate constant ( $\text{min}^{-1}$ ) and  $t$  is the time (min). The experimental data is processed according to the above formula and the results are shown in Figure 6.

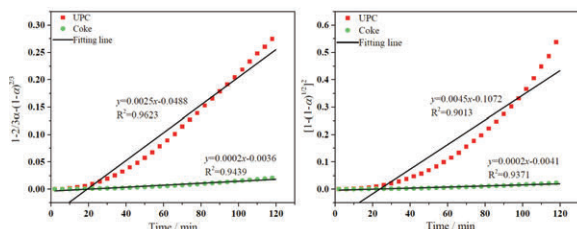


Figure 6. Reaction kinetics analysis when diffusion is restricted step

As shown in Figure 6, the linear fitting degree of UPC is 0.9623 and 0.9013, respectively. At the same time, the linear fitting degree of coke is also low, 0.9439 and 0.9371, respectively. The reason is that the internal pore structure of the coke or UPC will become larger after the reaction with  $\text{CO}_2$  at high temperature, and some independent pores are connected together, which provides a good kinetic condition for the gas diffusion. Therefore, the internal diffusion is not the restrictive step of the reaction.

(2) Assuming interfacial chemical reaction control

If the resistance of the other steps is less than that of the interfacial chemical reaction, it indicates that the interfacial chemical reaction is the restrictive step. The concentration of  $\text{CO}_2$  is the same in the gas phase, the edge of sample, and the interface of unreacted core. The gas concentration distribution is shown in Figure 7.

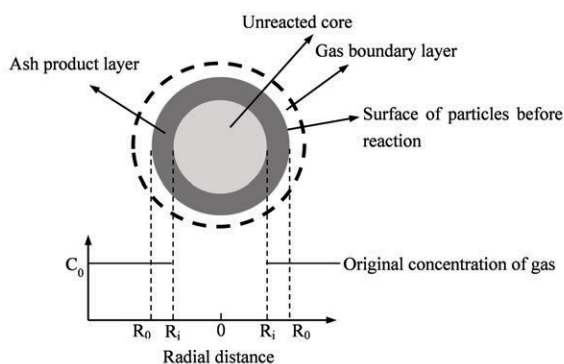


Figure 7. The concentration distribution of  $\text{CO}_2$  under interfacial chemical reaction control

It is considered that the reaction is a first-order irreversible reaction. The gasification reaction rate can be expressed by the Mckewan equation [43], as shown in the formula (12).

$$1-(1-\alpha)^{1/3} = kt \tag{12}$$

The relationship between  $1-(1-\alpha)^{1/3}$  and  $t$  is obtained by processing the experimental data according to the above equation, and the result is shown in Figure 8.

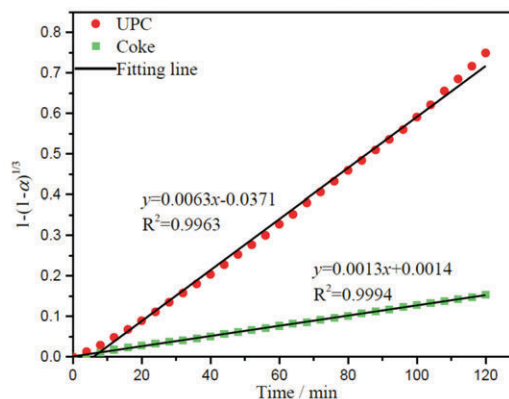


Figure 8. Reaction kinetics analysis when interface reaction or local reaction is restricted step

It is shown from Figure 8 that the correlation coefficient  $R^2 \geq 0.99$ ,  $1-(1-\alpha)^{1/3}$  has a good linear relationship with  $t$ , which shows that the hypothesis is reasonable and the interfacial chemical reaction is the restrictive step. In the process of solution loss reaction, the product of CO in the internal pores of coke or UPC is not spread to the outside of particles in time, resulting in high concentration of CO. And the reactions of (5) and (6) are reversible reactions, reducing the intermediates  $\text{C}_f(\text{O})$  and  $\text{C}(\text{O})\text{C}_f(\text{O})$  on the surface of the particles. That prevents the further generation of CO and limits the reaction to continue.

### 3.3 The effect of UPC on CRI and CSR

The CRI is the ability of coke to react with carbon dioxide, oxygen, and water vapor. The CSR refers to the ability of the coke to resist fragmentation and abrasion under the action of mechanical force and thermal stress. The results of the experiment are shown in Figure 9.

From Figure 9, it can be seen that the CRI decreases with the increase of UPC content, and the CSR increases with the increase of UPC content. When the content of UPC is 10%, the CRI is decreased by 2.3% and the CSR is only increased by 0.6%. When the content of UPC is 10~20%, the CRI and CSR change rapidly. The CRI is decreased by 6.8% and the CSR is increased by 3.8%, which shows that the UPC has great effect on coke in this content interval. The change of CRI and CSR is not significant and the UPC has little effect on coke when the content of UPC increases to 25~30%. Through the above analysis, the following conclusions can be drawn: (1) the UPC plays a good role in the protection of coke, (2) it is not that the higher the



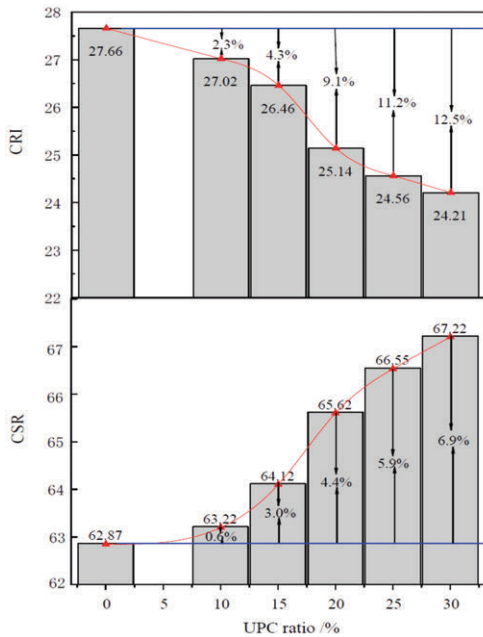


Figure 9. The effect of UPC ratio on coke reactivity and strength after reaction

content of UPC is, the more serious the effect will be on the coke. The reason is mainly attributed to these two aspects: (1) the reactivity of UPC is higher than that of the coke, so CO<sub>2</sub> will react with UPC first, (2) the UPC on the edge of the coke will react with CO<sub>2</sub> to produce residual substance, which will adhere to the surface of the coke. This can effectively prevent the CO<sub>2</sub> from further reacting with the coke.

### 3.4 The effect of UPC on the coke apparent porosity

The coke with complex structure is composed of a large number of different sizes pores and pore walls. Therefore, the CO<sub>2</sub> will enter the channels inside the coke for carbon gasification reaction, which certainly will affect the porosity of the coke. The effect of different content of UPC on the coke apparent porosity is shown in Figure 10.

### 3.5 The evaluation of indexes

The CRI, CSR, and apparent porosity can be used as indices to evaluate the quality of coke, while some index values should be as large as possible and other index values should be as small as possible. Meanwhile, the content of UPC has a significant influence on these three indices. The synthetic weighted mark method is used to determine the importance level of each experimental index. Thus, a scientific and effective experimental scheme can be selected, and the comprehensive influence of UPC content on coke quality is analyzed.

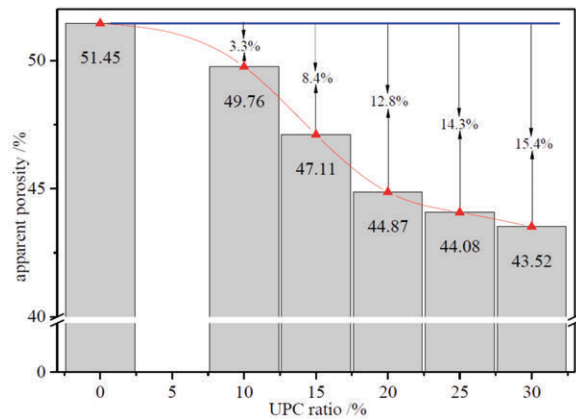


Figure 10. The effect of UPC ratio on coke apparent porosity

#### 3.5.1 The establishment of evaluation matrix

Supposing that there are n experimental schemes denoted as  $I=\{1,2,3,\dots,n\}$ , there are m experimental indices denoted as  $J=\{1,2,3,\dots,m\}$ , then the evaluation matrix is defined as  $X=(x_{ij})_{n \times m}$ .

$$X = \begin{bmatrix} 27.66 & 62.87 & 51.45 \\ 27.02 & 63.22 & 49.76 \\ 26.46 & 64.12 & 47.11 \\ 25.14 & 65.62 & 44.87 \\ 24.56 & 66.55 & 44.08 \\ 24.21 & 67.22 & 43.52 \end{bmatrix} \quad (13)$$

#### 3.5.2 Unifying the quantitative grade of the indices

In this study, the larger the values of CSR, the better, while the smaller the values of CRI and apparent porosity, the better. So the larger the final evaluation value, the better. The method was as follows:

First, in order to unify the trend demands of the various indices (CRI, CSR, and porosity), eliminate the non-commensurability among them, and obtain the matrix  $Y=(y_{ij})$ :

$$Y = (y_{ij}) = \begin{bmatrix} 0.00 & 62.87 & 0.00 \\ 0.64 & 63.22 & 1.69 \\ 1.20 & 64.12 & 4.34 \\ 2.52 & 65.62 & 6.58 \\ 3.10 & 66.55 & 7.37 \\ 3.45 & 67.22 & 7.39 \end{bmatrix} \quad (14)$$

Define the  $y_{ij}$  as shown in formula (15),  $I_1=\{\text{the smaller the index, the better}\}$ ,  $I_2=\{\text{the larger the index, the better}\}$ .



the better} and  $x_{j\max} = \max_{1 \leq i \leq n} \{x_{ij}\}$ .

$$y_{ij} = \begin{cases} x_{j\max} - x_{ij} & j \in I_1 \\ x_{ij} & j \in I_2 \end{cases} \quad (15)$$

Second, unifying the quantitative grade of the indices and eliminating the effect of dimension. We can obtain the evaluation matrix Z.

$$Z_{ij} = 100 \times (y_{ij} - y_{j\min}) / (y_{j\max} - y_{j\min}), \quad (16)$$

$i=1,2,3,\dots,n; j=1,2,3,\dots,m$

Define  $y_{j\min} = \min\{y_{ij} | i=1,2,3,\dots,n\}, y_{j\max} = \max\{y_{ij} | i=1,2,3,\dots,n\}$ .

The standardized evaluation matrix is  $Z=(z_{ij})_{nm}$ :

$$Z = (z_{ij}) = \begin{bmatrix} 0.00 & 0.00 & 0.00 \\ 18.55 & 8.05 & 21.31 \\ 34.78 & 28.74 & 54.73 \\ 73.04 & 63.22 & 82.98 \\ 89.86 & 84.60 & 92.94 \\ 100 & 100 & 100 \end{bmatrix} \quad (17)$$

### 3.5.3 Determine the subjective weight of the index

Modern ironmaking workers have a consistent understanding of the index of CSR, and believe that high CSR is beneficial to ironmaking. However, there are different views on CRI. From the perspective of BF smelting, some people think that a low CRI leads to an increase in the gasification temperature of coke. This will help to develop indirect reduction and thus to reduce the coke ratio. But the research of the company of NIPPON STEEL and SUMITOMO METAL (NSSM) has shown that the use of high reactivity carbon can reduce the temperature of BF insulation belt. This will significantly improve the reaction efficiency of BF, reduce the coke ratio and coal ratio ultimately. Therefore, based on the above analysis, the subjective weights of the experimental indices (CRI, CSR, and apparent porosity) are:  $CRI=T_1=0.2$ ,  $CSR=T_2=0.4$ , and apparent porosity= $T_3=0.4$ , respectively. Finally, the  $T=(0.2, 0.4, 0.4)^T$ .

Define:

$$\sum_{j=1}^m T_j = 1, \quad T_j \geq 0 \quad (j=1,2,3,\dots,m) \quad (18)$$

### 3.5.4 Determine the objective weight of the index

The objective weight of each index is determined by the entropy method:

$$p_{ij} = z_{ij} / \sum_{i=1}^n z_{ij}, \quad h_j = -(\ln n)^{-1} \sum_{i=1}^n p_{ij} \ln p_{ij},$$

$$U_j = (1-h_j) / \sum_{k=1}^m (1-h_k) \quad (j=1,2,3,\dots,m) \quad (19)$$

$$U = (0.25, 0.31, 0.44)^T$$

Define:

$$\sum_{j=1}^m U_j = 1, \quad U_j \geq 0 \quad (j=1,2,3,\dots,m) \quad (20)$$

### 3.5.5 The calculation of synthetic weighted mark value

The preference coefficient is 0.5, and the comprehensive weight of each index is obtained according to the formula (21):

$$W = [\alpha T_1 + (1-\alpha)U_1, \alpha T_2 + (1-\alpha)U_2, \dots, \alpha T_m + (1-\alpha)U_m]^T \quad (21)$$

$$W = [0.23, 0.35, 0.42]^T \quad (22)$$

Define:

$$\sum_{j=1}^m w_j = 1, \quad w_j \geq 0 \quad (j=1,2,3,\dots,m) \quad (23)$$

The comprehensive evaluation  $f_i$  is calculated according to the following formula:

$$f_i = \sum_{j=1}^m w_j z_{ij} \quad i=1,2,3,\dots,n \quad (24)$$

Finally, the result of synthetic weighted mark value is as follows:

$$f = [0, 16.03, 41.05, 73.78, 89.31, 100] \quad (25)$$

The relationship between the content of UPC and the synthetic weighted mark value is shown in Figure 11.

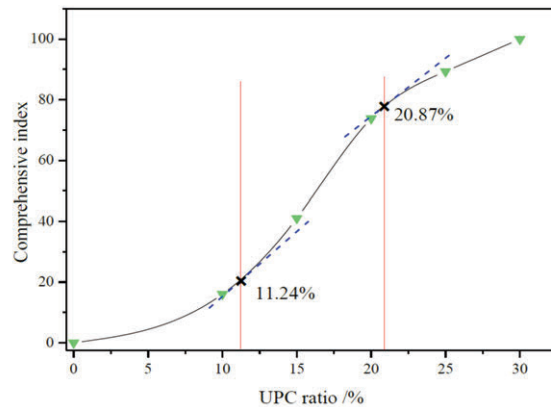


Figure 11. The relationship between UPC ratio and comprehensive index



The result shows that the higher the content of UPC, the greater the synthetic weighted mark value, which shows that the higher the content of UPC is, the better the quality of the coke in BF. However, when the content of UPC is more than 20.87%, the effect of UPC on the quality of coke gradually declines. This indicates that the protection of the coke is not improved when the content of UPC is further increased. When the content of UPC is 11.24–20.87%, the synthetic weighted mark value increases sharply, which indicates that the protective effect of UPC on the coke quality in this range value is most significant. It can be concluded from the above analysis that the higher the content of UPC, the better the coke quality. But considering the comprehensive index, it is of little significant effect on the coke to improve the content of UPC indefinitely. Therefore, it can be determined that the upper limit content of UPC in the coke is 20.87%, that is, the minimum combustion rate of the pulverized coal is 79.13%. It can be inferred that when the coke rate is kept 350 kg/t and the coal rate is increased to 160 kg/t, the minimum combustion rate of the pulverized coal needs to be maintained at the level of 80.43%.

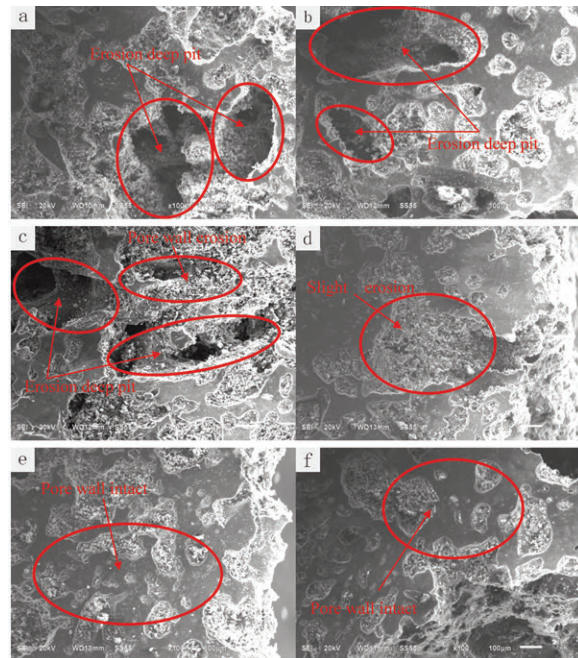
### 3.6 The microscopic analysis of coke

#### 3.6.1 The effect of UPC on external structure of coke

The edge of coke after reacting with  $\text{CO}_2$  was observed by an electron microscope, as shown in Figure 12. It can be seen from Figure 12(a), when no UPC is added to the coke, there are many deep pores in the coke edge, and the pulverization of matrix in the pores is serious. This indicates that the erosion effect of  $\text{CO}_2$  on the coke is significant. When the content of UPC is 10–15% (Figure 12(b) and (c)), there are still many erosion pits on the coke edge, but the phenomenon of pulverization has improved. As the content of UPC increased to 20–30%, the erosion of the coke edge is improved, the pores gradually become shallower and the number of pores decrease. In Figure 12(d), the matrix of coke is eroded slightly. In Figure 12(e) and (f), there are only shallow pits on the coke edge, and most of the coke is still well preserved. Through the electron microscopic observation of the coke edge, we can also get the conclusion that UPC has a certain protective effect on the coke.

#### 3.6.2 The effect of UPC on the internal structure of coke

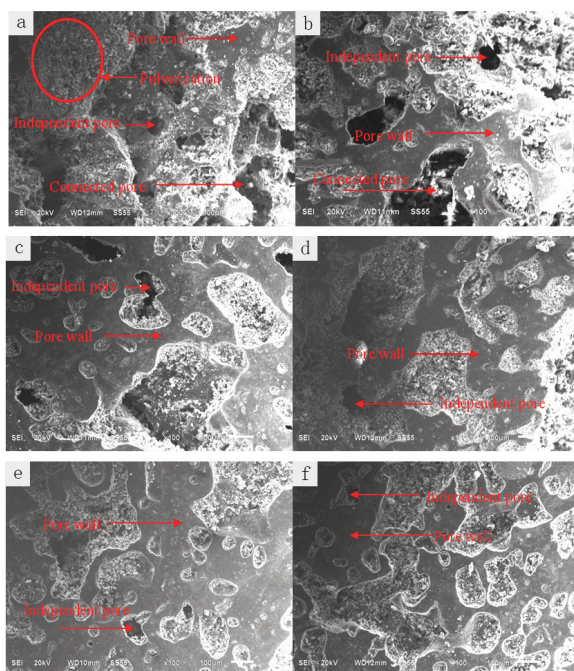
For analyzing the solution loss reaction of the coke pore wall and the matrix, the internal structure of coke after reaction is observed with an electron



**Figure 12.** The edge erosion microstructure of coke with different content of UPC. (a) UPC=0%; (b) UPC=10%; (c) UPC=15%; (d) UPC=20%; (e) UPC=25%; (f) UPC=30%

microscope. The result is shown in Figure 13. When the coke reacts with  $\text{CO}_2$ , new pores and connected pores are generated. On the whole, the deterioration degree of the interior of coke decreases with the increase of UPC content. When UPC is not added to the coke (Figure 13a), the pore wall is eroded severely and becomes loose. There is an obvious powdering phenomenon, the pore collapsed seriously. The solution loss reaction of coke is violent. There are also many macropores and connected pores, resulting in the coke structure becoming loose. When the content of UPC is 10% (Figure 13b), the erosion degree of the internal pore wall of coke is reduced, the degree of pulverization is improved, and the number of pores is decreased. But there are also many macropores and connected pores. When the content of UPC is 15–20% (Figure 13c, d), the number of independent pores is reduced, the phenomenon of connected pores disappeared, and the degree of pore wall pulverization further improved. With the further increase of UPC content (Figure 13 e, f), the internal macropores of coke almost disappeared. There are only some pits, and the coke matrix is also well preserved. Compared with Figure 13 (e) and (f), there is little difference in the internal structure of coke, which shows that the protective effect of UPC on coke is not much improved when the content of UPC increased to a certain extent. This result also confirmed the result of the synthetic weighted mark method.





**Figure 13.** The internal erosion microstructure of coke with different content of UPC. (a)UPC =0%; (b)UPC=10%;(c)UPC=15%;(d)UPC=20%; (e)UPC=25%; (f)UPC=30%

#### 4. Conclusions

The influence mechanism of different UPC content on the coke quality was studied, and the kinetic mechanism of the reaction of  $\text{CO}_2$  with coke was determined. The synthetic weighted mark method is used to comprehensively analyze CRI, CSR, and apparent porosity. The following conclusions are obtained:

(1) Because of the developed pore structure inside the coke and the high concentration of CO during the reaction process, the restrictive step of UPC or coke with  $\text{CO}_2$  is the interfacial chemical reaction, and accords with Mcewan equation:  $1-(1-\alpha)^{1/3}=kt$ .

(2) The CRI and the apparent porosity decrease with the increase of UPC and contrary to that of CSR. When the content of UPC is 10~20%, the UPC has great effect on the coke, and the CRI, CSR and the apparent porosity change greatly. CRI decreased by 6.8%, CSR increased by 3.8%, and the apparent porosity decreased by 9.5%.

(3) The UPC can effectively reduce the erosion effect of  $\text{CO}_2$  on the internal and external of coke, thus avoiding the large erosion pits on the external of coke, preventing the matrix dissolution and pore wall erosion.

(4) The higher the content of UPC is, the higher the synthetic weighted mark value. When the content of UPC is 11.24~20.87%, the synthetic weighted

mark value rises sharply, and the content of UPC in this interval has a severe effect on the coke. By this method, the minimum burning rate of the pulverized coal in BF can be determined.

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## ZAŠTITNI MEHANIZAM NESAGORENE UGLJENE PRAŠINE NA KOKS U VISOKOJ PEĆI

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### Apstrakt

Morfologija površine i unutrašnjosti koksa sa različitim sadržajem UPC (nesagorena ugljena prašina) posle reakcije sa CO<sub>2</sub> analizirani su skenirajućom elektronskom mikroskopijom (SEM). Takođe je proučavan uticaj UPC na CRI (reaktivnost koksa), CSR (čvrstoća koksa posle reakcije), kao i poroznost. Korišćen je metod sintetičkog ponderisanja da bi se analizirao sveobuhvatan uticaj koji sadržaj UPC ima na kvalitet koksa. Rezultati pokazuju da je zbog smanjenja sadržaja međuprodukta C<sub>2</sub>(O) i C(O)C<sub>2</sub>(O) restriktivan korak između uglja i CO<sub>2</sub> međupovršinska hemijska reakcija, i ona je u skladu sa Makjuanovom jednačinom  $1-(1-\alpha)^{1/3}=kt$ . UPC ima snažan efekat na koks kada je sadržaj UPC 10~20%, dok su CRI i poroznost značajno umanjeni za 6.8% i 9.5%, pojedinačno, a CSR je značajno povećan za 3.8%. UPC može efikasno da umanja uticaj koji CO<sub>2</sub> ima na površinsku i unutrašnju eroziju koksa, izbegnute su velike pore i pulverizacija koksa. Rezultati metoda sintetičkog ponderisanja pokazuju da se sveobuhvatni kvalitet koksa u velikoj meri menja kada je sadržaj nesagorene ugljene prašine 11.24~20.87%, što je u skladu sa eksperimentalnim rezultatima.

**Ključne reči:** Nesagorena ugljena prašina; Reaktivnost koksa; Čvrstoća koksa posle reakcije; Poroznost;

