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Removal of sulfur in coke oven gas by mixing ZnO-based additive into coal①

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[Abstract] A new technology for recycling EAF dust and removal of sulfur from coking oven gas was investigated. The new technology does not need to set up special equipment to treat COG (coke oven gas), and it is only acquired by mixing the ZnO-base additive into the coke coal. In the stage of pyrolysis of the coal volatile, ZnO of the additive combines with H_2S, CS_2, COS and C_2H_2SH of coal gas, forming ZnS in coal char. In the stage of coking of the coal char, Zn is gasified with S, then the gas Zn react with H_2S, CS_2, COS and C_2H_2SH, forming ZnS in coal gas and depositing as dust. After the collected ZnS dust was regenerated, it can be recycling as the additive again. The sulfur in coal gas can be completely removed if the mole ratio of the added Zn to the volatilized S is more than 1, and the sulfur in coke is also slightly decreased comparing with the coke without the additive. The EAF dust containing ZnO and Fe_2O_3 can be the base material of the desulfurizing additive.

[Key words] sulfur removal; coal gas; coking; sulfur sorbent; EAF dust
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1 INTRODUCTION

Sulfur distribution in coking process includes two parts. One part is going into COG as H_2S, CS, COS and C_2H_2SH. The other part is residual in coke as FeS, CaS, S_2 and so on. Traditionally, the removal of sulfur of COG is by spraying ammonia water into hot coal gas to form ammonium sulfate, and then the deep desulfurization of COG is specially treated at low temperatures. It needs a set of equipment as well as high operation cost. The cost of the desulfurization equipment is about 15% of the total investment of a coking plant. The operation cost for desulfurization of COG is about 15% of the cost of coke. To reduce the cost of desulfurization of COG and the secondary pollution by ammonia, development of new technology is still necessary.

The producer of coke hopes to decrease the cost for the desulfurization of COG, and even more cancels the desulfurization equipment. The environmental protection authority demands to decrease sulfur emission. The user of coke hopes that the coke is with low content of sulfur. According to the different expectation of the producer, the user and the environment official, the best way to remove sulfur of COG should be mixing some cheap desulfurizing additive into coal, which can remove sulfur of COG during coking process but has no influence on coke quality.

Furthermore, the steel industry generates a large amount of dust by EAF (electric arc furnace) which contains about 20% of Zn and 35% of Fe[1]. The EAF dust is hazardous due to their zinc, lead, cadmium and chromium contents[2]. There has been no economic technology to treat the EAF dust so far[3]. But these oxides in EAF dust are distinguished sorbents for removing sulfur from coal-derived gases[4, 5]. In the present paper, the desulfurization of COG with the processing of EAF dust is investigated.

2 THEORETIC CONSIDERATION

To achieve the removal of sulfur contained in COG during coking process by mixing desulfurizing additive into coal, it demands that the desulfurizing additive can be gasified into COG with sulfur during coking process, the gasified additive can react with sulfur contained in COG to form solid sulfide dust. The collected dust can be regenerated and recycled or used as other raw material such as the raw material for manufacturing sulfuric acid. Fig. 1 schematically shows the idea of the desulfurization of COG by mixing the desulfurizing additive into coal.

The desulfurizing additive to satisfy above demands should have the following chemical properties: 1) in low temperature stage, particularly at about 500 ℃ in coking process that the pyrolysis of volatiles in coal is quick, the desulfurizing additive can react with the sulfur of the volatile gas and form solid sulfide existing in coal char; 2) while in the high temperature stage in coking process that the coal char is coked, the formed sulfide and the desulfuring additive can be continually reduced by C, H_2 and CO into COG as metallic gas species; 3) the metallic gas species can combine with the sulfur contained in COG

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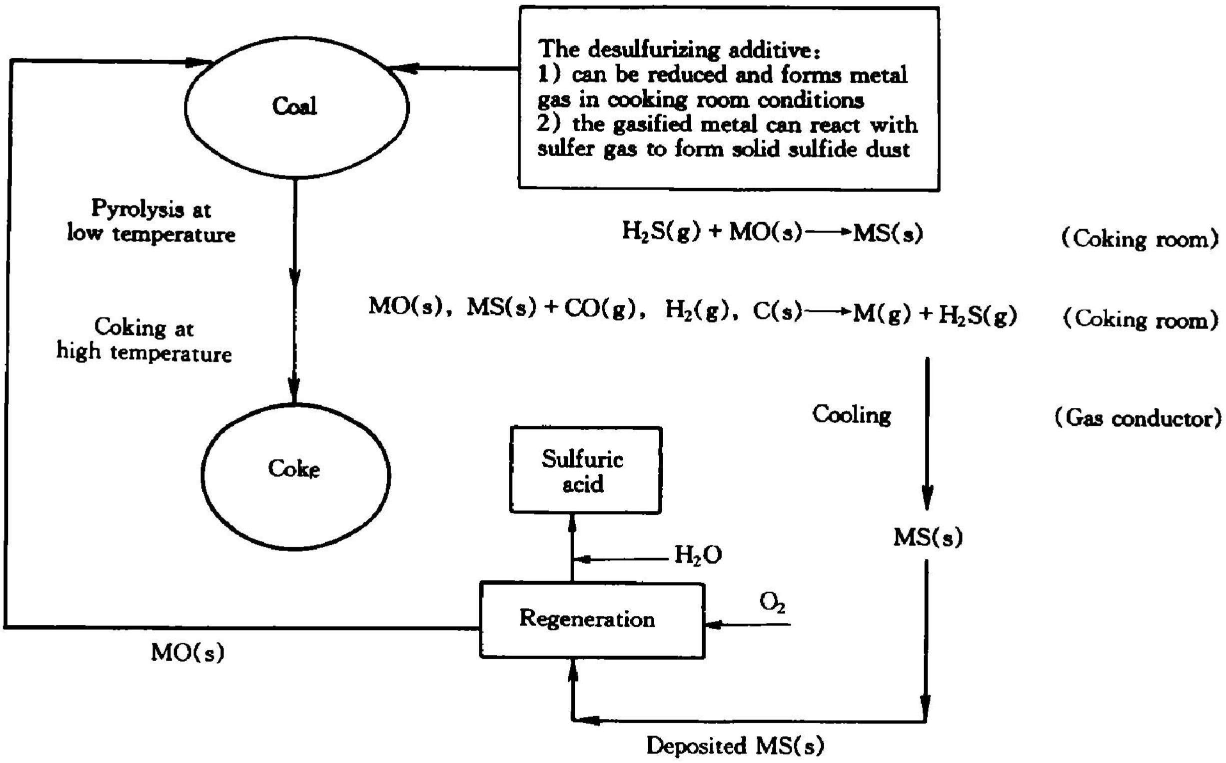

Fig. 1 Schematic diagram of sulfur removal from coal gas during coking process

and form the sulfide with high melting point temperature; 4) in addition, considering the reaction kinetics, the desulfurizing additive should have the other species which can also react with sulfur of the coal volatile gas forming solid sulfide when sulfur in coal quickly gasified at temperature about 500 ℃. The formed sulfide can be reduced by C, H_2 and CO at the coking temperature and form gas sulfide entering coal gas which is further combined with metallic gas species forming solid sulfide.

Considering chemical properties and cost, using ZnO as the effective sulfur sorbents and Fe_2O_3 as the auxiliary sulfur sorbent are proper for desulfurization of COG during coking process[6]. ZnO can absorb not only H_2S, but also COs, CS_2 and C_2H_2SH in COG[7]. The EAF dust mainly consists of ZnO, Fe_2O_3 and C. After adjusting its composition, it may be used as the desulfurizing additive of COG during coking process.

The main chemical reactions are listed as[8]:

At low temperature, before about 700 ℃ in the coking room,

$ZnO(s) + H_2S(g) + C(s) = ZnS(s) + H_2(g) + CO(g)$

$\Delta G^{\ominus} = 57\,914 - 5.56T\lg T - 116.20T$

$Fe_2O_3(s) + 2H_2S(g) + 3C(s) = 2FeS(s) + 2H_2(g) + 3CO(g)$

$\Delta G^{\ominus} = 343\,136 - 30.35T\lg T - 407.80T$

At high temperature, above 700 ℃ in the coking room,

$ZnS(s) + H_2(g) = Zn(s) + H_2S(g)$

$\Delta G^{\ominus} = 312\,936 + 48.82T\lg T - 315.72T$

$FeS(s) + H_2(g) = Fe(s) + H_2S(g)$

$\Delta G^{\ominus} = 66\,065 + 15.17T\lg T - 55.05T$

$ZnO(s) + C(g) = Zn(s) + CO(g)$

$\Delta G^{\ominus} = 370\,850 + 43.26T\lg T - 431.92T$

and there are also other reactions, for example, ZnS and FeS are reduced by C and CO forming CS_2 and COS.

At low temperature, in COG pipes,

$Zn(g) + H_2S(g) = ZnS(s) + H_2(g)$

$\Delta G^{\ominus} = -312\,936 - 48.82T\lg T + 315.72T$

$2Zn(g) + CS_2(g) = 2ZnS(s) + C(s)$

$\Delta G^{\ominus} = -780\,991 - 67.30T\lg T + 633.56T$

$Zn(g) + COS(g) = ZnS(s) + CO(g)$

$\Delta G^{\ominus} = -301\,420 - 33.65T\lg T + 235.00T$

Fig. 2 shows a calculation result of thermodynamic equilibrium by Chemisage software. The input materials are 70 g solid carbon with 0.7 g ZnO and 0.8 g Fe_2O_3, and 1.34 mol gas with the composition of 58% H_2, 6% CO, 29% CH_4, 1.3% C_2H_6, 2.5% C_3H_8, 1% N_2, 1.5% CO_2, and 0.7% H_2S[9]. Figs. 2(b) and (d) show the composition change of gas phase after its leaving the coking room. The thermodynamic simulation result shows that the added ZnO can be fully gasified if the temperature is over about 950 ℃, and sulfur in coal gas can be fully removed if Zn/S is over 1.

3 EXPERIMENTS

The experiments for the simulation of coking

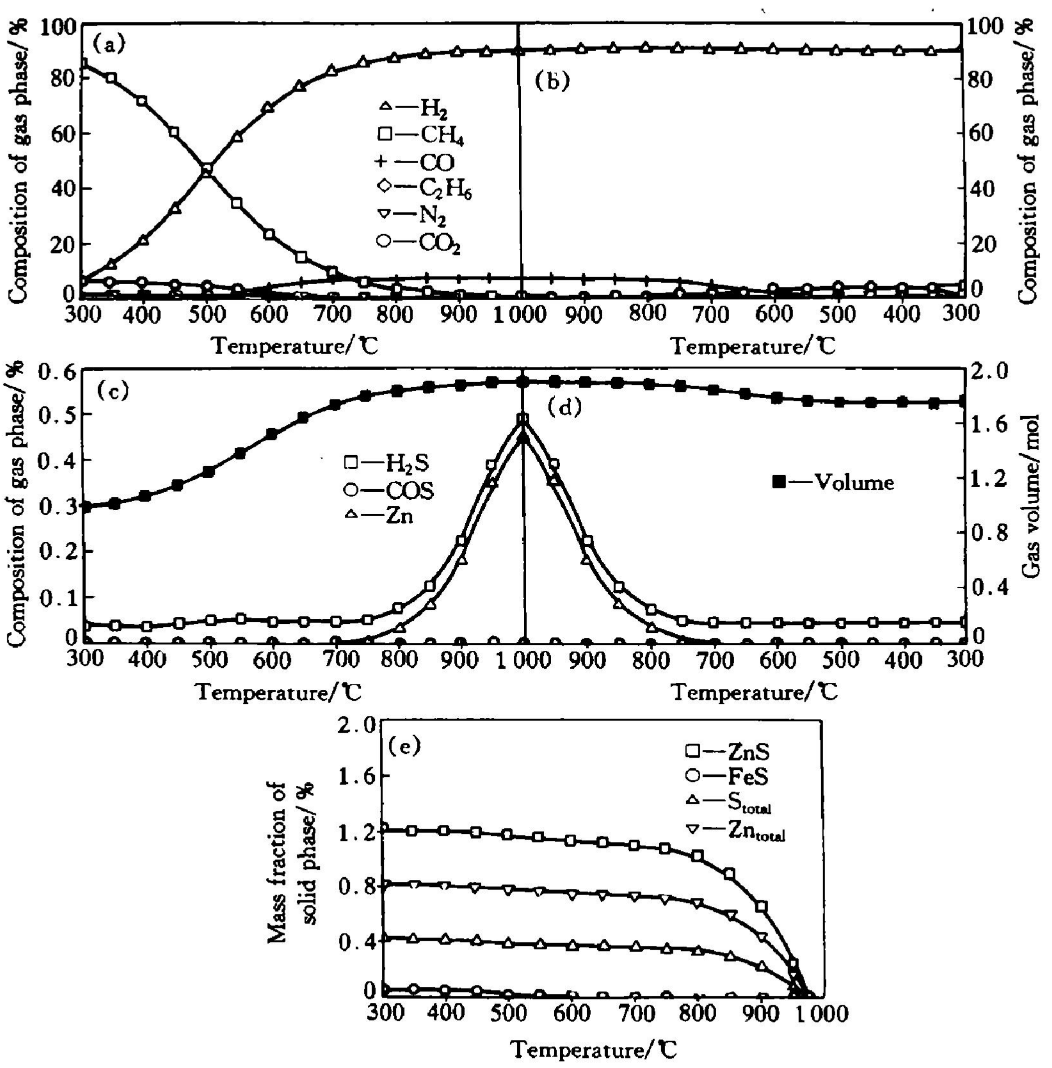

Fig. 2 Calculation results of thermodynamic equilibrium between coal gas and carbon with desulfuring additive
(a), (c), (e) —Chemical equilibrium between coal gas and coke during heating process;
(b), (d) —Chemical equilibrium of coal gas during cooling process

were carried out. The experimental apparatus is shown as Fig. 3. The coking room was made of stainless steel. Its inner diameter was 40 mm. 150 g coal was added for each run of the experiments. The coal gas was conducted out of the coking room by a stainless steel tube to a water column. The total heating time was about 15 h. The controlling temperatures of the furnace versus time are shown in Fig. 3 for simulating the temperatures at different positions of industrial coking room[10]. In Fig. 3, the temperature lines 1, 2, 3, 4 represent the controlled temperatures of the furnace. The lines 1′, 2′, 3′ and 4′ represtent the observed temperature at the center of the reactor corresponding to the controlled temperature lines 1, 2, 3 and 4 respectively. The concentration of H_2S of the coal gas before it passing water column was checked during the coking process. S and Zn of the coal char were also checked at different times in some experiments. Three kinds of the desulfurizing additives were used. The first one was chemical pure agent with 99% ZnO. The second was the mixture of chemical agent ZnO with EAF dust. The third was EAF dust. Their compositions are listed in Table 1. The composition of the used coal is 26% volatile (dry base), 9.9% ash (dry base), 0.64% S (dry base), and with 4% of moisture.

Table 1 Compositions of desulfurizing additive

Desulfurizing additive	Composition
DSZ (ZnO powder)	99% ZnO, 1% others
ZFP (ZnO + EAF dust)	42.1% ZnO, 2.5% PbO, 20.8% Fe_2O_3, 34.7% others
FZP (EAF dust)	15.3% ZnO, 3.6% PbO, 30.4% Fe_2O_3, 50.7% others

4 RESULTS

4.1 Sulfur in coal gas

Fig. 4 shows the effect of the adding amount of the desulfurizing additive DSZ, i.e. ZnO amount, on the concentration of H_2S of coal gas during heating process, where the temperature rising was controlled as the line 1 in Fig. 3 simulating the temperature at

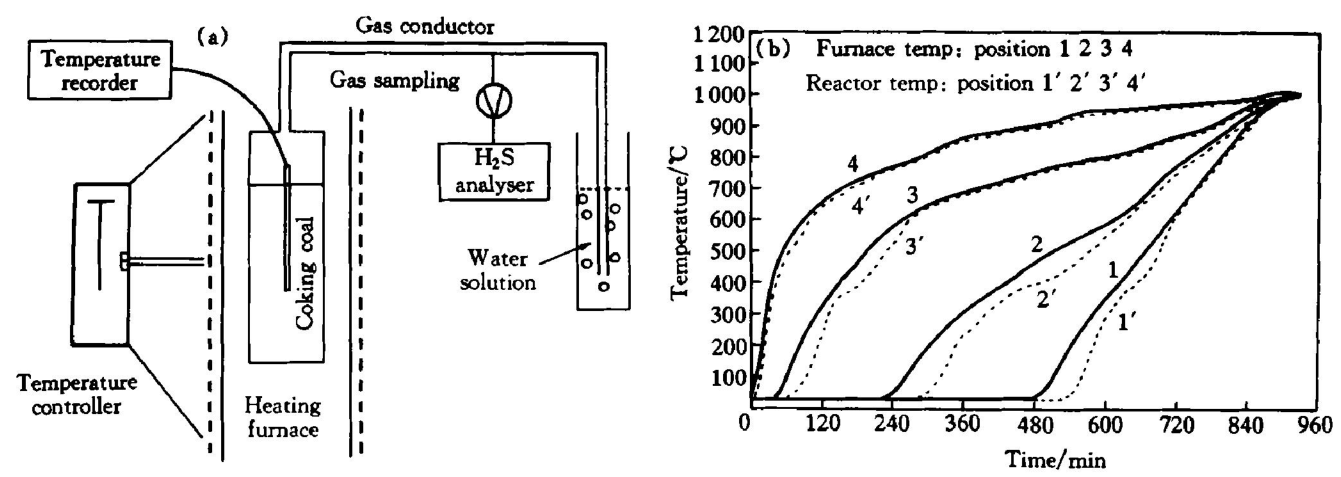

Fig. 3 Experimental apparatus and controlling temperatures for simulating temperatures at different positions of industrial coking furnace

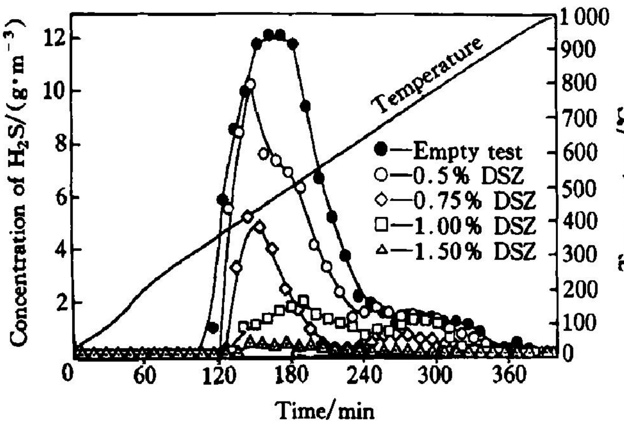

Fig. 4 Effect of amount of desulfurizing additive DSZ on H_2S concentration of coal gas
(controlling temperature as line 1 in Fig. 3)

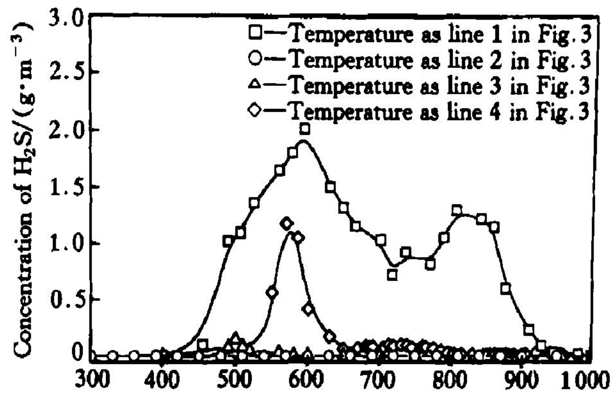

Fig. 5 Effect of heating rate on H_2S concentration of coal gas
(mixed desulfurizing additive DSZ being 1% of coal)

the center of coking room in industrial practice. It shows that the ZnO has an obvious effect on the sulfur removal of the coal gas. When the added desulfurizing additive DSZ was more than 1% in mass percent, H_2S in coal gas was only at 10^{-6} level.

Fig. 5 shows the effect of heating rate on the H_2S concentration in the coal gas when the addition amount of the desulfurizing additive DSZ was 1% in mass percent. When the heating rate was controlled as the temperature at the position 1 or 4 in coking room in industrial (line 1 or line 4 in the Fig. 3), the temperature rised quickly at about 500~ 650 ℃. At this temperature, the emission of sulfur with pyrolysis of coal was quick. Some of the gasified sulfur could not be absorbed by ZnO in time. Therefore, the H_2S of the coal gas was checked out.

Fig. 6 shows the effect of three kinds of the desulfurizing additives on the concentration of H_2S of the coal gas, the desulfurizing additives consist of different content of ZnO. At the adding amount of the desulfurizing additive of 1% DSZ, or 1.5% ZFP,

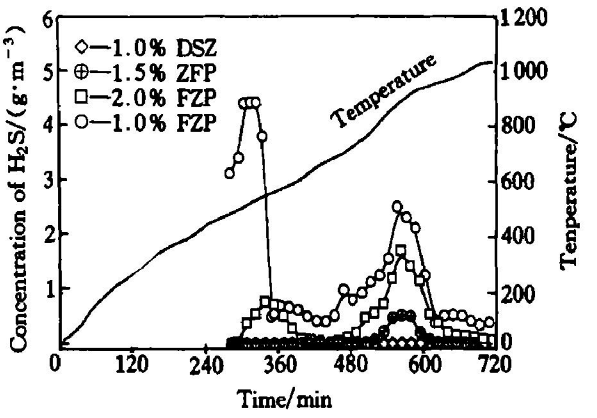

Fig. 6 Comparison of results of H_2S removal by different desulfurizing additives
(controlling temperature as line 1 in Fig. 3)

or 2.0% FZP, it could get good desulfurizing effect for the coal gas. But, for the desulfurizing additive ZFP or FZP, H_2S of the coal gas appeared at the temperature about 900 ℃. This was due to the reason of that the devolatilization rate of sulfur by reduction of FeS and ZnS formed by Fe_2O_3 and ZnO at about 500 ℃ was larger than the gasification rate of Zn from ZnS and ZnO at about 900 ℃. Although there was H_2S in the coal gas at about 900 ℃, the emission amount of H_2S is less because the amount of the coal gas was little generated at this temperature. For the cases 1% DSZ, 1.5% ZFP and 2% FZP in coal, the component ZnO was 0.99%, 0.63% and 0.31% respectively, the mole fraction of the effective desulfurizing components to the gasified sulfur from coal ($n(\mathrm{ZnO}) + n(\mathrm{PbO})) / n(\mathrm{S})$ was 1.58, 0.99 and 0.53 respectively.

4.2 Sulfur and zinc in coke

Fig. 7 shows the change of Zn and S in the coal char during coking process. if the coal mixed with the desulfurizing additive, Zn was continually gasified after the temperature rising to about 600 ℃, and there was only a little Zn residual in the coke when the temperature reached over 1 000 ℃. The gasifaction extent of Zn depended on the coking time and the final temperature. The longer of the coking time and the higher of the final temperature, the less the residual Zn in the coke. Comparing the changes of sulfur in the char in the case of the coal mixed with the desulfurizing additive and in the case without the desulfurizing additive, the mechanism of desulfurization of the desulfurizing additive is derived. The desulfurizing additive absorbed the gasified sulfur during the stage of low temperature (before about 600 ℃) and formed ZnS and FeS existing in the coal char. Then ZnS, FeS and ZnO are reduced by H_2, CO and C during the stage of high temperature (after about 600 ℃) and formed gas Zn and H_2S, COS and CS existing in hot coal gas phase. Finally, in the cooling coal gas phase, Zn(g) reacted with H_2S, COS and CS, and formed solid ZnS dust which may deposited in tar and cooling water.

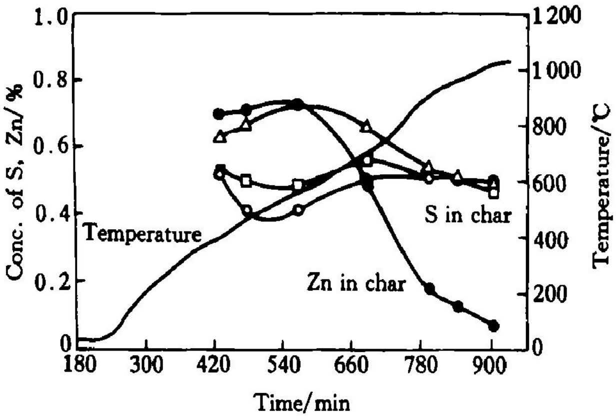

Fig. 7 Change of Zn and S contents in char during coking process

(controlling the temperature as line 1 in Fig. 3)

○—Empty test; △—1.0% DSZ;

□—1.0% FZP; ●—1.0% DSZ

Table 2 and Table 3 show the contents of S and Zn in the coke and the gasification ratio of Zn mixed into the coal in the different experimental conditions. Comparing with the empty experiment, i. e. without the desulfurizing additive mixed into the coal, the mixed desulfurizing additive not only removed the sulfur of the coal gas, but also slightly reduced the sulfur of the coke. Sulfur in coke decreased with the increase of the mixed desulfurizing additive. However, it needs to be studied about the mechanism of sulfur decrease in the coke by the desulfurizing additive.

Table 2 Effect of heating rate on contents of residual Zn and S in coke

Controlling temperature	Residual Zn / %	Gasified Zn / %	S content / %
Temp. as line 1	0.15	86.9	0.475
Temp. as line 2	0.14	88.8	0.523
Temp. as line 3	0.12	89.5	0.480
Temp. as line 4	0.10	91.3	0.494

Notes: mixing 1% DSZ into coal; sulfur content in coke was 0.497% if without desulfurizing additive mixed into coal.

Table 3 Residual Zn and S contents in coke

Amount of additive and controlling temp.	Residual Zn/ %	Gasified Zn/ %	S content / %
Empty temp. as line 1	–	–	0.497
0.5% DSZ temp. as line 1	0.084	85.3	0.516
0.75% DSZ temp. as line 1	0.14	83.7	0.485
1.0% DSZ temp. as line 1	0.15	86.9	0.475
1.5% DSZ temp. as line 1	0.24	86.0	0.426
2.0% FZP temp. as line 2	–	–	0.454
1.5% ZFP temp. as line 2	–	–	0.460

4.3 Zinc sulfide deposition

For the coking experiment of the coal with 1.0% desulfurizing additive DSZ, the collected tar contained 0.18% Zn. ZnS dust was observed on the coal gas pipes and water column. However, the distribution of ZnS in tar, cooling water and gas pipes was not determined due to the experimental scale was too small.

5 CONCLUDING REMARKS

Mixing the ZnO-based additive into coal can get better result for coal gas desulfurization of coking process. The EAF dust containing Zn can be used as the desulfurizing additive material. Fe of EAF dust remains in coke, which finally becomes hot iron in ironmaking process. Zn in EAF dust is gasified and combines with S of coal gas. There is a little Zn in coke. It is a possible way for treating the EAF dust and removing sulfur of COG.

However, the present study was carried out in laboratory. It only focused on the removal of sulfur of coal gas and the zinc gasification. More work is needed to study the effect of the desulfurizing additive on the quality of coke and tar, particularly for the distribution of the deposited ZnS among tar, cooling water and coal gas pipes by large scale experiment. If the hot coal gas is directly used as fuel gas, it will be easy to be industrialized for removal of sulfur of COG by this way. If the hot coal gas is cooled to form the tar, the technology of separation of ZnS dust from hot coal gas or tar should be studied.

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