Effective removal of sulfur from high-sulfur coal prior to use by dry chlorination at low temperature

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ABSTRACT

Desulfurization of high-sulfur coal prior to use by dry chlorination under various conditions was investigated. The contents of total carbon, total sulfur, pyritic sulfur, sulfate and organic sulfur of the coal were 72.48, 5.95, 1.08, 0.66 and 4.22 wt.%, respectively. It was found that the chlorination temperature and particle size had a great influence on sulfur removal. The optimal chlorination temperature and particle size for sulfur removal was 350 °C and 48–75 μm, respectively. Under optimal conditions, sulfur content in the chlorinated coal was 1.12 wt.%. The removal percentages of total sulfur, pyritic sulfur, sulfate and organic sulfur were 67.7, 93.0, 65.6 and 61.6, respectively, indicating that a high proportion of organic sulfur, pyritic sulfur and inorganic sulfur were removed by dry chlorination. Meanwhile, the fixed carbon did not lose appreciably. It was speculated that the removal of organic sulfur by dry chlorination at 350 °C proceeded mainly based on the equation $2R\text{—}S + Cl_2 = 2R\text{—}Cl + S_2Cl_2$. The chlorinated coal thus obtained could be used in production of various carbon-containing materials such as metallurgical coke after a complete dechlorination pretreatment at 500–600 °C.

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1. Introduction

Coal is one of main economical sources of energy in the world. With the gradual depletion of low-sulfur coal, interest in the utilization of high-sulfur coal, because of its lower price, continues to grow as the demand for energy increases. However, the use of high-sulfur coal may cause many problems such as corrosion and acid rain due to the emission of a large amount of sulfur oxides and hydrogen sulfide in the environment. According to an estimation of the Chinese Research Institute of Environment, the total economic loss due to acid deposition in China was 116.54 billion RM Yuan in 1995 and 176.42 billion RMB Yuan in 2000 [1]. Therefore, the removal of sulfur from the coal is imperative prior to its utilization. For iron-steel making industry, coking process cannot remove sulfur from coal and it combines with molten iron in blast furnace. The sulfur sediments on the iron crystal surface make steel more brittle and decrease its plasticity property. Thus, sulfur content in the coal used in making metallurgical coke must be reduced to a level less than 1.5 wt.% [2]. Sulfur in coal exists in the forms of inorganic and organic sulfurs. The inorganic sulfurs are present mainly in the forms of disulfides (pyrite and marcasite) and

sulfate (mainly calcium, iron and barium). The organic form, which is bound directly to the organic coal matrix, generally exists in forms of thiols, sulfides, disulfides, thiophenes and cyclic sulfides [3]. It has been reported that in coal the iron has bonded with organic sulfurs in aromatic and aliphatic systems [4]. Wet flue gas desulfurization processes and dry injection processes are widely used in the coal desulfurization of power industry. However, their high capital and/or operating costs, low sorbent utilization, reduced availability of the power generating plant, and the production of significant volume of waste sludge make them expensive for high sulfur coal application [5]. Thus, the desulfurization of high-sulfur coal is an unsolved problem so far. The removal of sulfur from high-sulfur coal prior to its combustion could result in significant reduction in the emission of the precursors of acid rain. A number of physical, microbial, chemical, pyrolytic, and radiation assisted oxidative methods of desulfurization have been reported. Physical processes such as froth flotation and magnetic force separation can only remove a portion of pyritic sulfur but cannot reduce organic sulfur [6–9]. Microbial desulfurization of coal was usually carried out with chemolithoautotrophic bacteria such as *T. thiooxidans* and *T. ferrooxidans* [10]. However, neither of the microorganisms for leaching of organic sulfur from coal is effective [11]. Coal pyrolysis can remove most of sulfur, including inorganic and organic forms, but it requires rigorous operating conditions. For example, the treatment temperature is generally higher than 600 °C [12,13]. Chemical desulfurization and demineralization based on the treatment of coal with various oxidizing agents, ferric sulfate

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and hydrogen peroxide, are effective to remove ash and pyritic and sulfate sulfur, but yield only small reduction of organic sulfur [12,13]. Many attempts have been made to remove organic sulfur. For instance, Pittsburgh No. 8 coal (USA) was leached with 0.49 M hypochlorite at 90 °C for 2 h, which resulted in 37% reduction in total sulfur and 14% reduction in organic sulfur [14]. Desulfurization of high-sulfur coal with aqueous chlorine was reported [15,16]. It was found that 90% of coal pyrite and approximately 40% of organic sulfur were removed [15]. Thus aqueous chlorination was more effective to remove organic sulfur than other methods. After aqueous chlorination, coal weight increased due to the combination of chlorine with coal matrix [15]. This part of chlorine could not be removed by simple washing [15]. Thus, the leached coal must be dechlorinated because the chloride forms corrosive HCl(g) upon combustion of the coal. The chlorinated coal can be effectively dechlorinated by heating at 500 °C in oxygen-free nitrogen [15]. In addition, treating the chlorinated coal at 300 °C to 500 °C in water steam is an effective method for removing chloride [15]. It was observed that coal was completely dechlorinated by water steam after aqueous chlorination at 600 °C [15]. The proposed reaction for dechlorination from chlorinated high-sulfur coal was as follows. $RCl(s) + H_2O(g) = ROH(s) + HCl(g)$. HCl(g) thus produced can be recovered as a chemical product. The dry chlorination by using fluidizing bed at around 1000 °C has been widely applied in the production of $TiCl_4$ and $ZrCl_4$ from TiO_2, ZrO_2-containing minerals. Such industrial dry chlorination is also likely to be efficient for coal desulfurization considering the excellent desulfurization efficiency achieved by using aqueous chlorination. Thus, the aim of the present work is to investigate coal desulfurization by dry chlorination under various conditions. Similar work has never been reported so far to the best of our knowledge.

2. Experimental

2.1. Materials

The high-sulfur coal used in this work was obtained from Yunnan province of China. The coal was crushed, dried, ground and sieved. The particle size of coal powder used in this work was usually 49–75 μm. The characterization of the high-sulfur coal sample was listed in Table 1. The 99.99% (v/v) of chlorine and 99.99% (v/v) of argon gas were used in this work. The powder of activated carbon of analytical grade was used in this work and its particle size ranged from 75 to 106 μm. The powder of sodium chloride of analytical grade was used in this work and its particle size ranged from 106 to 149 μm.

Table 1
Characterization of original high-sulfur coal.

Parameters[a]	Content (wt.%)
Total carbon (TC)	72.48
Fixed carbon (FC)	70.05
Moisture (M_d)	1.15
Ash (A)	16.48
Volatile matter (V)	12.33
Pyritic sulfur (S_p)	1.08
Sulfate sulfur (S_s)	0.66
Organic sulfur (S_o)	4.22
Total sulfur (S_T)	5.95

[a] Parameters were obtained for the coal powder with particle size ranging from 48 to 75 μm.

2.2. Experimental apparatus and procedure

The chlorination experiments were carried out in a horizontal tubular furnace (Fig. 1).

The length of the heating zone of furnace is 60 cm. A quartz glass tube with an outside diameter of 48 cm was inserted in the furnace. About 4 grams of weighed solid high-sulfur coal was usually mechanically mixed with 7.13 wt.% of NaCl powder and 4.43 wt.% of activated carbon powder. The solid mixture was then loaded on a quartz boat and the quartz boat was then placed inside the quartz tube. The quartz boat was located in the center of furnace. Then the furnace temperature was raised meanwhile an argon gas with a flow rate of 100 mL/min was passed through the quartz tube. When the furnace temperature was raised to a usual value of 350 °C and maintained at this temperature for 30 min, the argon gas was stopped and dry chlorine with a usual flow rate of 200 mL/min was passed through the quartz tube for a pre-set time, which was usually 2 h. At the end of reaction, the power of the furnace was shut down and the boat was cooled down to room temperature under an atmosphere of argon. Then the chlorinated coal in the boat was simply washed with 500 mL of deionized water and dried at 104 °C for 2 h. The chlorinated coal thus obtained were used to determine its weight W_R (g) and the content of left sulfur ($[S]_R$) (wt.%). The removal percentage of S, which was denoted as "S removal", was calculated based on the following equation.

$$\text{S removal} = \frac{W_O[S]_O - W_R[S]_R}{W_O[S]_O} \times 100\% \tag{1}$$

where W_O was the weight of dried original coal employed (g); $[S]_O$ the content of S from dried original coal (wt.%). The percentage of
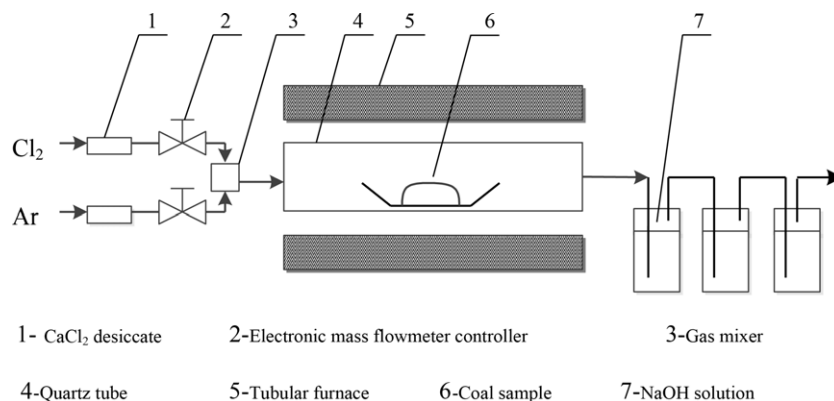

Fig. 1. Schematic diagram of the experimental apparatus for chlorination of high-sulfur coal. (1) $CaCl_2$ desiccate; (2) electronic mass flowmeter controller; (3) gas mixer; (4) quartz tube; (5) tubular furnace; (6) coal sample; (7) NaOH solution.

weight increase of coal, which was denoted as "Weight increase", was calculated based on the following equation.

$$\text{Weight increase} \approx \frac{W_R - W_C - W_O}{W_O} \times 100\% \tag{2}$$

where W_C was the weight (g) of added activated carbon in the experiment. The flow rates of chlorine and argon were controlled using electronic gas mass flow meter controllers made by MKS Company (USA). The 99.99% (v/v) chlorine and 99.99% (v/v) argon gases were used in the experiments. All gases were passed through anhydrous $CaCl_2$ columns to reduce water content before entering flow meters. Then the two gases were mixed in a gas mixing vessel, which is made of Teflon, before entering the reactor.

2.3. Chemical analysis

The coal samples analyzed in this work included original high-sulfur coal and the chlorinated coal. The Eschka analytical procedure described in Chinese state standard method [17] was used to determine total sulfur in coal samples. The sulfur forms in coal samples were determined according to Chinese state standard method [18]. Proximate analyses of coal samples were performed according to Chinese state standard method [19]. The contents of total carbon in coal samples were determined according to Chinese state standard method [20]. The contents of chloride ion in coal samples were determined according to Chinese state standard method [21].
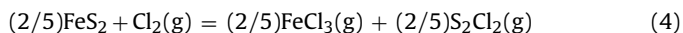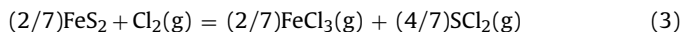
3. Results and discussion

3.1. Characterization of high-sulfur coal

The content of total carbon in the original high-sulfur coal used in this work is 72.48 wt.% (Table 1). The contents of pyritic sulfur, sulfate sulfur, organic sulfur and total sulfur were 1.08, 0.66, 4.22 and 5.85 wt.%, respectively (Table 1). It should be noted that the contents of organic sulfur and total sulfur in the coal were extremely high. The XRD (M21X, MAC Science) patterns of the original coal were presented in Fig. 2(a). The possible species of inorganic sulfur identified in the original coal was FeS_2 (Fig. 2(a)). eta-Fe_2O_3 was also identified (Fig. 2(a)). The contents of ash and volatile matters of the original coal were 16.48 and 12.33 wt.%, respectively (Table 1).

3.2. Possible reactions of desulfurization by dry chlorination

The inorganic sulfurs in coal are present mainly in the forms of disulfides (pyrite and marcasite) and sulfate (mainly calcium, iron and barium). Only disulfides in coal can be removed by dry chlorination based on the following reactions [22].

$$(2/7)FeS_2 + Cl_2(g) = (2/7)FeCl_3(g) + (4/7)SCl_2(g) \tag{3}$$

$$(2/5)FeS_2 + Cl_2(g) = (2/5)FeCl_3(g) + (2/5)S_2Cl_2(g) \tag{4}$$

SCl_2 is more volatile than S_2Cl_2 [22]. SCl_2 decomposes at 59 °C [23]. The boiling point of S_2Cl_2 is 136.5 °C [23]. Thus S in FeS_2 from coal can be removed by vaporization during dry chlorination. The organic sulfur is bound directly to the organic coal matrix. It is well known that sulfur-containing organic compounds are chlorinated by the following reactions.

$$2R–S + Cl_2 = 2R–Cl + S_2Cl_2 \tag{5}$$

$$R–S–R' + Cl_2 = R–S–Cl + R' \tag{6}$$

It was speculated that some organic sulfurs from the high-sulfur coal were perhaps removed in the forms of S_2Cl_2 or/and R–S–Cl by vaporization during dry chlorination. The saturated organic
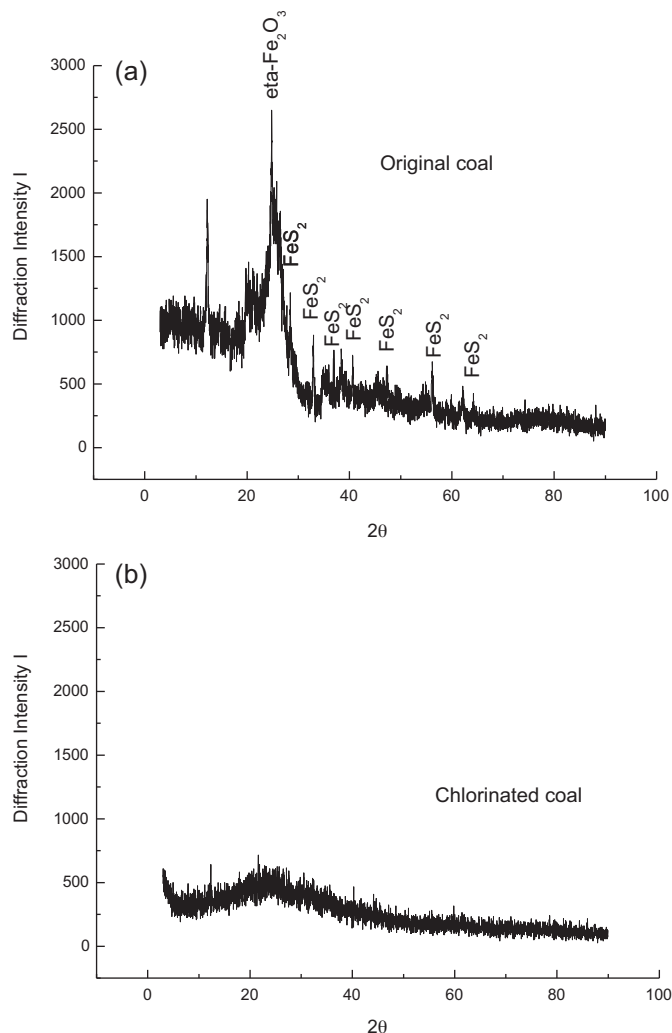

Fig. 2. XRD patterns of high-sulfur coals (a) before chlorination and (b) after chlorination (chlorine flow rate = 200 mL/min; chlorination temperature = 350 °C; reaction time = 3 h; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%).

compounds not containing sulfur can also be chlorinated by the following reactions.

$$RH + Cl_2 = RCl + HCl \tag{7}$$

Some unsaturated organic compounds can react with chlorine by the following reaction.

$$\tag{8}$$

Thus, the chlorine content in coal can increase a lot after dry chlorination. This in turn caused a rise in coal weight after dry chlorination [15].

3.3. Effect of activated carbon

The sulfur in the high-sulfur coal existed not only on the surfaces of coal particles, but also in the cores of coal particles. In order to react with the sulfur in the cores of coal particles, the gaseous chlorine molecules must diffuse into the cores. Meanwhile, the gaseous
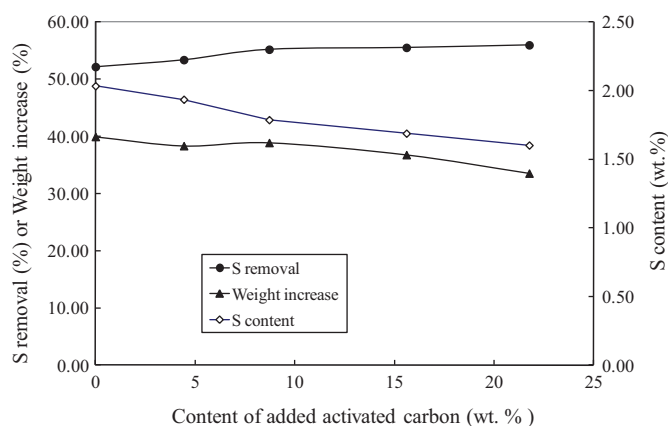
Fig. 3. Variation of sulfur content, removal percentage of sulfur and percentage of coal weight increase with content of added activated carbon (chlorine flow rate = 200 mL/min; chlorination temperature = 400 °C; reaction time = 2 h; particle size of coal = 49–75 μm; content of added NaCl = 7.13 wt.%).

Fig. 4. Variation of sulfur content, removal percentage of sulfur and percentage of coal weight increase with content of added NaCl (chlorine flow rate = 200 mL/min; chlorination temperature = 350 °C; reaction time = 2 h; particle size of coal = 49–75 μm; content of added activated carbon = 4.43 wt.%).

chlorinated products such as S_2Cl_2 must diffuse out of the cores to favor the removal of sulfur. However, coal surface was usually covered by some mineral oxides such as Fe_2O_3, As_2O_3, ZnO and MoO_3. Thus, these oxide solids are likely to obstruct the diffusions. These oxides such as Fe_2O_3 could be removed as volatile chlorides in the presence of $Cl_2 + C$ by the following reactions.

$$Fe_2O_3 + C + 3Cl_2(g) = 2FeCl_3(g) + 3CO(g) \quad (9)$$

$$Fe_2O_3 + 3CO + 3Cl_2(g) = 2FeCl_3(g) + 3CO_2(g) \quad (10)$$
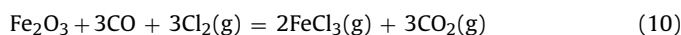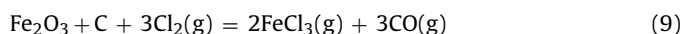
The sublimation temperature of solid $FeCl_3(s)$ was 315 °C. It implied that Fe_2O_3 could be removed in the form of gaseous $FeCl_3(g)$ by dry chlorination at about 315 °C. It was reported that the addition of CO may enhance the chlorination of Fe_2O_3 [24]. Thus, the effect of activated carbon on sulfur removal was investigated and the results were presented in Fig. 3.

The experimental results regarding the effect of activated carbon were presented in Fig. 3. The removal percentage of sulfur increased with increasing content of activated carbon (Fig. 3). Meanwhile, the percentage of weight increase of original coal and the sulfur content in chlorinated coal decreased with increasing content of activated carbon (Fig. 3). As mentioned previously, the introduction of chlorine to the matrix of original coal probably caused the increase of coal weight [15]. One of the possible species identified by XRD in the original coal was eta-Fe_2O_3 (Fig. 2(a)). After chlorination, the peaks representing above species almost disappeared (Fig. 2(b)). It implied that most of eta-Fe_2O_3 was removed by dry chlorination in the presence of activated carbon. In fact, apart from Fe_2O_3, some hazardous impurities from the coal such as As_2O_3, HgO, P_2O_5, V_2O_5 and MoO_3 were also probably removed by the reactions similar to Eqs. (9) and (10) at low chlorination temperatures since their chlorides were very volatile. The boiling points of $AsCl_3$, $HgCl_2$, PCl_3, $VOCl_3$ and $MoCl_5$ are 130 °C, 302 °C, 75 °C, 127 °C and 268 °C, respectively. The produced hazardous volatile chlorides during the coal chlorination went to the alkaline solutions from the gas adsorption bottles in Fig. 1. Thus most of hazardous pollutants such as S, As, and Hg from original coal were removed by dry chlorination at low temperature. The chlorinated coal thus obtained should be much cleaner than original one. The coal thus obtained can also be used in the production of other carbon materials such as activated carbon in addition to metallurgical coke if the hazardous pollutants in coal are removed to a reasonable level by dry chlorination.
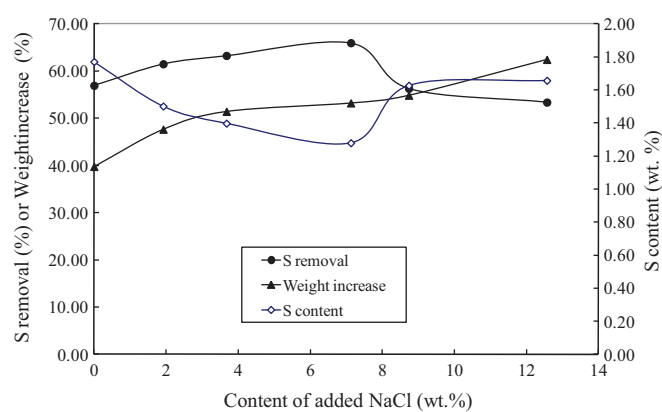
3.4. Effect of NaCl

The addition of NaCl can enhance the removal of FeO or Fe_2O_3 from chromite (FeO·Cr_2O_3) by carbochlorination [25,26]. Thus, the effect of NaCl on sulfur removal was investigated. The experiment was performed at 350 °C and the results were showed in Fig. 4. The sulfur content in chlorinated coal initially decreased with increasing NaCl content at content range of 0–7.13 wt.% and then increased at content range of 7.13–12.57 wt.% (Fig. 4). Conversely, the removal percentage of sulfur initially increased with increasing NaCl content at content range of 0–7.13 wt.% and then decreased at content range of 7.13–12.57 wt.% (Fig. 4). Thus the optimal NaCl content was 7.13 wt.%. The percentage of coal weight increase appreciably increased with increasing NaCl content (Fig. 4). The possible reasons for NaCl enhancing Fe_2O_3 removal from the coal were as follows. The m.p. and b.p. of $FeCl_3$ is 306 °C and 315 °C, respectively. At the optimal temperature of 350 °C, the $FeCl_3(g)$ or its gaseous dimer $Fe_2Cl_6(g)$ [27,28] or solid $FeCl_3(s)$ formed in the pore channels of coal particles reacted with NaCl to form eutectic mixtures $NaFeCl_4$ of lower melting point than solid $FeCl_3(s)$, which facilitating the diffusion of $FeCl_3$ or Fe_2Cl_6 in the pore channels and thereby improving the kinetics of Fe_2O_3 removal. NaCl is likely to react with $FeCl_3$ or Fe_2Cl_6 to form two eutectic mixtures with melting points of 157 °C (mole fraction $X_{NaCl} = 0.48$) and 162 °C (mole fraction $X_{NaCl} = 0.51$), respectively [28]. The probable reactions according to the literature [27] were as follows.

$$NaCl(s) + FeCl_3(s \text{ or } g) = NaFeCl_4(l) \quad (11)$$

$$2NaCl(s) + Fe_2Cl_6(g) = 2NaFeCl_4(l) \quad (12)$$
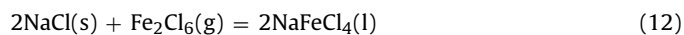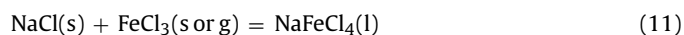
3.5. Effect of chlorination temperature

The experimental results regarding temperature effect was showed in Fig. 5. The maximum removal percentage of sulfur was obtained at 350 °C (Fig. 5). This was a very interesting phenomenon. This maximum value was confirmed by several times of repeated experiments. The percentage of coal weight increase were 54.0, 53.2, 33.5, 5.6, −8.1 and −22.2% at chlorination temperatures of 300 °C, 350 °C, 400 °C, 500 °C, 600 °C and 700 °C, respectively (Fig. 5). It indicated that the introduced chlorine began to be released at about 500 °C, since the weight increase of coal was mainly caused by the introduction of chlorine to coal. This dechlorination temperature was close to that reported by Cho [15]. The amount of released chlorine and other volatile matters increased with rising temperature (Fig. 5). The content of sulfur in chlorinated coal also attained a minimum at chlorination temperatures
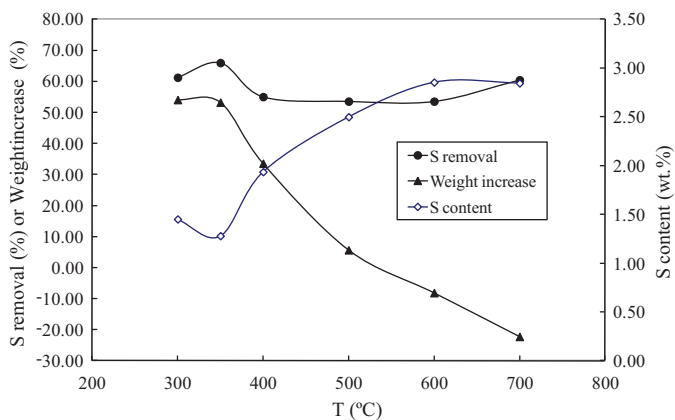
Fig. 5. Variation of sulfur content, removal percentage of sulfur and percentage coal weight increase with chlorination temperature (chlorine flow rate = 200 mL/min; reaction time = 2 h; particle size of coal = 49–75 μm; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%).

of 350 °C. Thus, the optimal chlorination temperature for sulfur removal was 350 °C. Many problems such as the effects of CaO and MgO in coal on the dry chlorinatrion process of coal by using fluidizing bed can be overcome at so low chlorination temperature. So the dry chlorination by using fluidizing bed has the potential to be used in coal desulfurization in industry considering so low optimal chlorination temperature. A portion of these inorganic chlorides such as $FeCl_3$ were removed by evaporation during the dry chlorination of coal, because the chlorination temperature used was 350 °C while the sublimation temperature of solid $FeCl_3$ was 315 °C. At higher temperatures than 350 °C, it was well known that coal structure began to be distorted around this temperature, which resulted in obstruction of the channels of coal particles. This in turn impeded the diffusion of Cl_2, S_2Cl_2 and $FeCl_3$ etc., which led to a decrease of the removal percentage of sulfur.

3.6. Effect of chlorination time

The experimental results concerning time effect were presented in Fig. 6. The contents of added NaCl and activated carbon were 7.13 and 4.43 wt.%, respectively. The removal percentage of sulfur generally increased with time (Fig. 6). The removal percentage of sulfur reached a maximum of 67.7% at 3 h. The contents of sulfur in chlorinated coal generally decreased with time (Fig. 6). The minimum content of sulfur of 1.12 wt.% was obtained at 3 h. The percentage
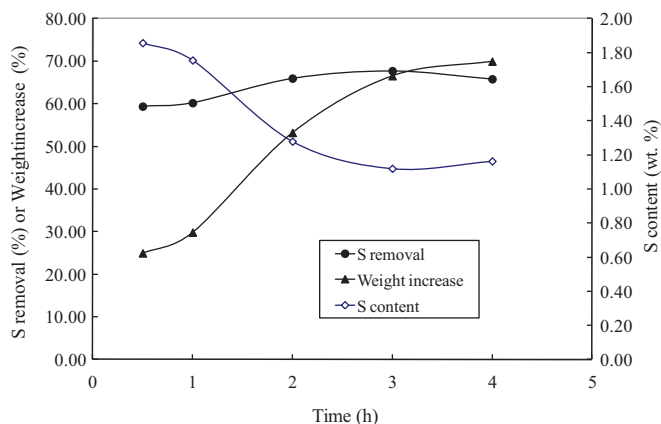

Fig. 6. Variation of sulfur content, removal percentage of sulfur and percentage of coal weight increase with reaction time (chlorine flow rate = 200 mL/min; chlorination temperature = 350 °C; particle size of coal = 49–75 μm; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%).
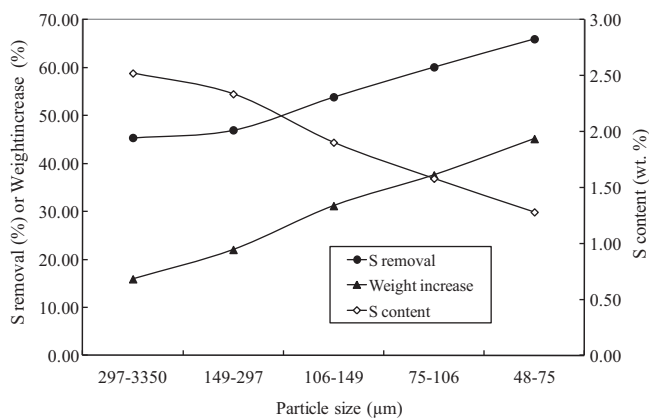
of coal weight increase rose significantly with time. The percentage of weight increase was 66.5% at 3 h.

3.7. Effect of particle size

The dry chlorination of coal is a gas–solid reaction. Internal diffusion was often a rate-controlling step in selective chlorination of iron oxides of chromite [26]. It implied that the chlorination rate of sulfur in the coal was probably related to particle size of coal. Thus the effect of particle size on sulfur removal was studied in this work. Both the removal percentage of sulfur and the percentage of coal weight increase increased remarkably with decreasing particle size (Fig. 7). The content of sulfur in chlorinated coal also decreased greatly with decreasing particle size (Fig. 7). Thus, particle size had a great influence on sulfur removal. It implied that internal diffusion was probably main rate-controlling step during the sulfur removal.

3.8. Effect of flow rate of chlorine

The effect of Cl_2 flow rate on sulfur removal was showed in Fig. 8. The removal percentage of sulfur increased appreciably with increasing flow rate at the range 50–150 mL/min and increased slightly with increasing flow rate at the range 150–250 mL/min.

Fig. 7. Variation of sulfur content, removal percentage of sulfur and percentage of coal weight increase with particle size (chlorine flow rate = 200 mL/min; chlorination temperature = 350 °C; reaction time = 2 h; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%).

Fig. 8. Variation of sulfur content, removal percentage of sulfur and percentage of coal weight increase with Cl_2 flow rate (chlorine time = 2 h; chlorination temperature = 350 °C; particle size of coal = 49–75 μm; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%).

Table 2
Removal percentages of three forms of sulfur after chlorination.

Parameters	Original coal	Chlorinated coal[a]	Removal %
Weight (g)	8.004	13.7276	
Pyritic sulfur (wt.%)	1.08	0.04	93.0
Sulfate sulfur (wt.%)	0.66	0.13	65.6
Organic sulfur (wt.%)	4.22	0.96	61.6
Total sulfur (wt.%)	5.95	1.12	67.7

[a] Chlorine flow rate = 200 mL/min; chlorination temperature = 350 °C; particle size of coal = 49–75 μm; chlorination time = 3 h; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%.

Table 3
Variation of physical–chemical properties of high-sulfur coal before and after chlorination.

Parameters	Original coal	Chlorinated coal[a]	Increase (%)
Weight (g)	8.004	13.7276	
Moisture (wt.%)	1.15	2.35	
Ash (wt.%)	16.48	7.34	−23.6
Volatile matter	12.33	46.76	550.4
Cl⁻ content (wt.%)	0.01	1.85	31629
Fixed C (wt.%)	70.04	43.55	6.6

[a] Chlorine flow rate = 200 mL/min; chlorination temperature = 350 °C; particle size of coal = 49–75 μm; chlorination time = 3 h; content of added NaCl = 7.13 wt.%; content of added activated carbon = 4.43 wt.%.

In contrast, the content of sulfur in chlorinated coal decreased appreciably with increasing flow rate at the range 50–150 mL/min and decreased slightly with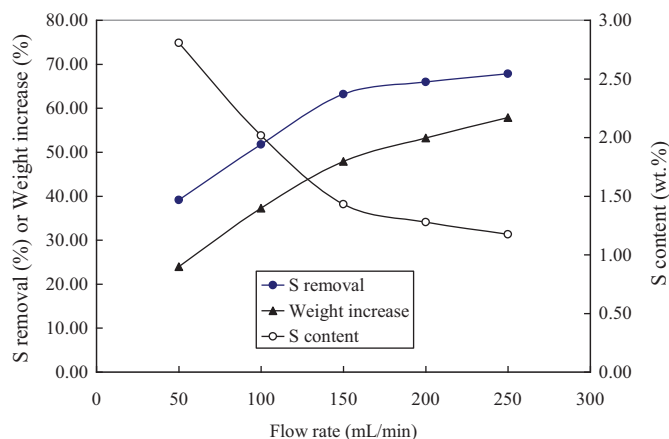 increasing flow rate at the range 150–250 mL/min. The percentage of coal weight increase always increased with increasing flow rate. The effect of external diffusion of on sulfur removal can be eliminated when the Cl_2 flow rate was more than 150 mL/min. Industrial pyro-chlorination was usually carried out in the reactors such as a fluidizing bed for the reasons of economy and efficiency. In those cases, a sufficient contact of fluidizing coal powder and gaseous chlorine can be realized. The optimal chlorine consumption for economical utilization of Cl_2 can be evaluated using the reactor. The present lab apparatus (Fig. 1) cannot be used for this purpose, because the coal powder was stationary in this case.

3.9. Removal of three forms of sulfur

Sulfur in coal exists mainly in three forms, i.e. disulfides, sulfate sulfur and organic sulfur. Under optimal conditions, the removals of these three forms of sulfur in the high-sulfur coal by dry chlorination were investigated and the results were listed in Table 2. This experiment was performed at 350 °C with chlorine flow rate of 200 mL/min. The chlorination time was 3 h. The particle size of coal ranged from 45 to 75 μm. The contents of added NaCl and activated carbon were 7.13 and 4.43 wt.%, respectively. The weights of original coal and chlorinated coal were 8.004 g and 13.7276 g, respectively. The possible species of inorganic sulfur identified by XRD in the original coal was FeS_2 (Fig. 2(a)). After chlorination, all peaks representing above species almost disappeared (Fig. 2(b)). It indicated that most of these inorganic sulfurs were removed by dry chlorination. The quantitative analysis of three forms of sulfur presented in original and chlorinated coal was showed in Table 2. About 93.0% of pyritic sulfur was removed by dry chlorination (Table 2). The removal percentage of pyritic sulfur in current work was slightly higher than the value of 90% reported in the case with aqueous chlorination [15]. The removal percentage of organic sulfur in current work was 61% (Table 2), which was much higher than the value of 40% reported in the case with aqueous chlorination [15]. Normally, the diffusion rate of gas in solid is faster than that of liquid in solid mainly due to a higher reaction temperature involved in gas–solid reaction. Probably for this reason, the removal percentage of organic sulfur with dry chlorination in this work showed a higher value.

3.10. Variation of physical–chemical properties of the high-sulfur coal

Under the same experimental conditions as described in section 3.7., the variations of physical–chemical properties of the high-sulfur coal before and after chlorination were studied and the results were presented in Table 3. The variation of ash amount was

denoted as "Ash increase" and its value was calculated based on the following equation.

$$\text{Ash increase} = \frac{W_R[\text{Ash}]_R - W_O[\text{Ash}]_O}{W_O[\text{Ash}]_O} \times 100\% \qquad (13)$$

where $[\text{Ash}]_O$ and $[\text{Ash}]_R$ were the ash contents from original coal and chlorinated coal (wt.%), respectively.

The values of $[\text{Ash}]_O$ and $[\text{Ash}]_R$ were 16.48 and 7.34 wt.%, respectively (Table 3). The values of W_O and W_R were 8.004 g and 13.7276 g, respectively (Table 3). The value of "Ash increase" calculated based on Eq. (13) was −23% (Table 3). This implied that the content of inorganic minerals in original coal reduced a lot after dry chlorination. These minerals such as Fe_2O_3 were probably removed by some chlorination reactions similar to reactions (8) and (9). A portion of these inorganic chlorides such as $FeCl_3$ were probably removed by evaporation during the coal chlorination, because the chlorination temperature used in this case was 350 °C while the sublimation temperature of solid $FeCl_3$ was 315 °C. Some $FeCl_3$ were also washed out from the chlorinated coal during the water washing step. Although a lot of inorganic minerals were removed, the weight of original coal still increased greatly after dry chlorination (Figs. 3–7). The variation of Cl element amount was denoted as "Cl increase" and its value was calculated based on the following equation.

$$\text{Cl increase} = \frac{W_R[\text{Cl}]_R - W_O[\text{Cl}]_O}{W_O[\text{Cl}]_O} \times 100\% \qquad (14)$$

where $[\text{Cl}]_O$ and $[\text{Cl}]_R$ were the Cl element contents from original coal and chlorinated coal (wt.%), respectively. The values of $[\text{Cl}]_O$ and $[\text{Cl}]_R$ were 0.01 and 1.85 wt.%, respectively (Table 3). The value of "Cl increase" calculated based on Eq. (14) was 31629%. It indicated that substantial Cl element combined with organic matrix by chlorination reactions represented by Eqs. (5)–(7), which resulted in weight increase of original coal. This conclusion was consistent with the findings of Chao [15]. The variation of amount of volatile matters was denoted as "Volatile increase" and its value was calculated based on the following equation.

$$\text{Volatile increase} = \frac{W_R[\text{volatile}]_R - W_O[\text{volatile}]_O}{W_O[\text{volatile}]_O} \times 100\% \qquad (15)$$

where $[\text{volatile}]_O$ and $[\text{volatile}]_R$ were the contents of volatile matters from original coal and chlorinated coal (wt.%), respectively. The values of $[\text{volatile}]_O$ and $[\text{volatile}]_R$ were 12.33 and 46.76 wt.%, respectively (Table 3). The value of "Volatile increase" calculated based on Eq. (15) was 550.4% (Table 3). It implied that some volatile matters were composed of organic chlorides and inorganic chlorides. These chlorides were much more volatile than corresponding not chlorinated organic compounds or inorganic oxides such as Fe_2O_3 in coal, which resulted in a significant increase in the content of volatile matters after chlorination. The variation of amount

of fixed carbon was denoted as "C increase" and its value was calculated based on the following equation.

$$C\ increase = \frac{W_R[C]_R - W_O[C]_O}{W_O[C]_O} \times 100\% \qquad (16)$$

where $[C]_O$ and $[C]_R$ were the contents of fixed carbon from original coal and chlorinated coal (% (w/w)), respectively. The values of $[C]_O$ and $[C]_R$ were 70.04 wt.% and 43.55 wt.%, respectively (Table 3). The value of "C increase" calculated based on Eq. (16) was 6.6% (Table 3). It implied that dry chlorination of coal did not result in an appreciable loss of fixed carbon in coal. The increase of fixed carbon was probably caused by the added activated carbon. Considering low loss of fixed carbon at 350 °C, we speculated that the removal of organic sulfur from the high-sulfur coal proceeded mainly based on the previous reaction (5).

4. Conclusions

Desulfurization of a high-sulfur coal prior to use by dry chlorination under various conditions was investigated. It was found that the removal percentage of sulfur increased with decreasing particle size or chlorination time or increasing content of added activated carbon or sodium chloride. The chlorination temperature and particle size had a great influence on sulfur removal. The optimal chlorination temperature and particle size was 350 °C and 48–75 μm. Under optimal conditions, sulfur content in the chlorinated coal was 1.12 wt.% and removal percentages of total sulfur, pyritic sulfur, sulfate and organic sulfur were 67.7, 93.0, 65.6 and 61.6%, respectively. Meanwhile, the amount of coal weight, ash, volatile matters, chlorine content and fixed carbon increased by 66.5, −23.6, 550.4, 31629 and 6.6%, respectively.

Acknowledgements

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