

## Thermal and Chemical Desulfurization of Low Sulfur Coals

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**Abstract**—This paper describes desulfurization characteristics of low sulfur coals prior to combustion and optimum conditions of three different desulfurization processes. These processes include two thermal treatment processes (mild pyrolysis and air oxidation) and an H<sub>2</sub>O<sub>2</sub> leaching process. Dual processes composed of thermal and leaching processes were also evaluated. Low sulfur coals employed were two imported bituminous coals and two domestic anthracite coals. The optimum reaction temperatures and times of the thermal processes were 500-550 °C and 15-20 minutes, respectively. The optimum condition for the leaching process was obtained when the experiment carried out for 60 min at 90 °C using 30% H<sub>2</sub>O<sub>2</sub>. The dual process showed the best sulfur removal efficiency as expected among the evaluated processes.

Key words: Desulfurization, Low Sulfur Coal, Mild Pyrolysis, Air Oxidation, Leaching

### INTRODUCTION

One major source of SO<sub>2</sub> emission is the combustion of coal in power plants. The various techniques to control SO<sub>2</sub> emissions can be classified as before-, during- and after-combustion techniques [Eliot et al., 1978; Song et al., 2000]. As an after-combustion technique the flue gas desulfurization (FGD) process is widely used to meet the emission standard of SO<sub>2</sub> in coal fired power plants. However, the cost of the FGD process is known to be expensive (20-60 billion won/500 MW). Hence, the idea of processing of coal at one site and delivering the processed char to every power plant has been drawing attention recently. Before combustion, coal desulfurization can be achieved by physical, microbial, thermal, and chemical methods. While physical treatment is effective for coal with high inorganic sulfur contents, microbial treatment can eliminate most of the inorganic and some organic sulfur [Eliot et al., 1978; Ryu et al., 1993; Juszczak et al., 1995; Moran et al., 1997]. Unfortunately, however, this method has the principal disadvantage of requiring quite a long period of treatment.

On the other hand, mild pyrolysis and chemical process are believed to be promising desulfurization techniques among before-combustion techniques. With mild pyrolysis, high sulfur removal efficiency can be obtained with less loss of heating value of coal, since destruction of sulfur containing bonds occurs more easily than devolatilization reaction at temperatures below 600 °C [Ibarra et al., 1989; Lolja et al., 1995; Sydorovych et al., 1996; Lin et al., 1997]. Chemical cleaning processes are reported to have several advantages over the other methods. It has been shown that aqueous hydrogen peroxide is an effective oxidizing agent for coal desulfurization [Ali et al., 1992; Karaca et al., 1997; Borah et al., 2001].

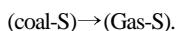
According to desulfurization studies using high sulfur coals (3-8%), sulfur removal efficiency was in the range of 60-80% [Fried-

man et al., 1977; Wheelock et al., 1977; Eliot et al., 1978]. It is believed that to drop final sulfur content of char below 1% is very difficult. In Korea, power plants use imported bituminous coal with sulfur content below 0.5%. Combustion of these coals without the FGD process cannot meet the emission standard of SO<sub>2</sub>. In order to enhance the efficiency of the FGD process or to install a smaller scale FGD plant to a newly constructed power plant, systematic desulfurization studies of low sulfur coal are required.

In this paper, desulfurization characteristics of two imported low sulfur coals and two domestic anthracite coals are studied with three different desulfurization processes: mild pyrolysis, air oxidation and H<sub>2</sub>O<sub>2</sub> leaching. Optimization studies were also performed. In pursuit of maximizing desulfurization efficiency, experiments employing dual processes composed with the thermal and the leaching process were also investigated.

### DESULFURIZATION KINETICS

The study of the behaviour of sulfur in coals during desulfurization processes is complicated by a number of interrelated factors, making it difficult to isolate individual effects. If coal is pyrolyzed in an inert atmosphere, the sulfur release is influenced by the formation of H<sub>2</sub> during devolatilization. A single reaction model for sulfur evolution in the gas phase could thus be written as



The production rate of gaseous sulfur species could be modeled by assuming a first order model [Garcia-Labiano et al., 1995; Lin et al., 1997].

$$-\frac{dC_s}{dt} = kC_s \quad (1)$$

where C<sub>s</sub> is sulfur concentration of char (wt%/g), and k is a rate constant. Integration of Eq. (1) yields the Eq. (2).

$$\frac{C_s}{C_{so}} = \exp(-kt) \quad (2)$$

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<sup>‡</sup>This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

**Table 1.** The proximate analysis and the elemental analysis of coals

Coal	Proximate analysis (wt%, dry basis)			Heating value (cal/g, dry basis)	Elements (wt%, dry and ash free basis)				
	Fixed carbon	Volatile matter	Ash		C	H	N	S	O (diff)
Australian	65.2	28.7	6.1	6115	85.02	4.70	2.79	0.63	11.56
South African	58.4	35.3	6.2	5858	84.79	4.72	2.25	0.63	7.61
Dogye	65.7	8.1	26.2	4822	93.04	1.49	0.80	1.43	4.04
Jangseong	64.3	6.1	29.6	4247	91.72	2.23	1.79	0.74	3.52

where  $C_{so}$  is sulfur concentration of coal (wt%/g). Introducing total sulfur conversion  $X_s$ , Eq. (2) changes to as follows.

$$\ln\left(\frac{1}{1-X_s}\right) = kt \quad (3)$$

In the air oxidation process,  $O_2$  adsorbs chemically and irreversibly on coal surface. Adsorbed  $O_2$  reacts with reactive C or S chemical species and then releases to gas phase. If oxygen is supplied in excess, oxygen concentration is maintained constant during the reaction. Then the sulfur release rate can be expressed as follows [Borah et al., 2001],

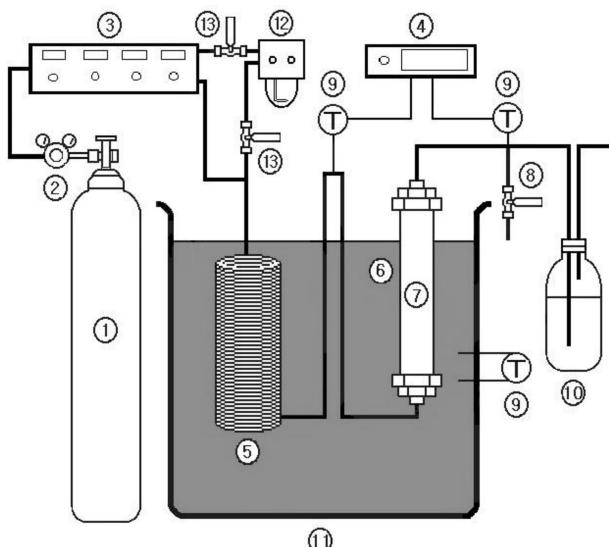
$$-r_s = kC_s C_{O_2} \approx k'C_s \quad (C_s \ll C_{O_2}) \quad (4)$$

where  $k'$  is pseudo 1st-order rate constant. When introducing sulfur conversion  $x_s$ , Eq. (4) yields the expression same as Eq. (3).

## EXPERIMENTAL

### 1. Coal Sample

Two imported bituminous coals (Australian and South African)

**Fig. 1.** Experimental setup for thermal treatment processes.

1. $N_2$ or air	8. Gas sampling port
2. Pressure gauge	9. Thermocouple
3. Mass flow controller	10. $CaO$
4. Thermocouple indicator	11. Fluidized sandbath
5. Pre-heater	12. Vapor generator
6. Alumina	13. On/off valve
7. Reactor	

and two domestic anthracite coals (Dogye and Jangseong) were used in this study. The results of proximate and elemental analysis of sample coals are tabulated in Table 1.

### 2. Mild Pyrolysis and Air Oxidation

Experimental setup for thermal treatment process is shown in Fig. 1. The reactor was made of stainless steel with total volume of  $8.0\text{ cm}^3$ . Preheating section and reactor were placed in the fluidized sandbath (SBL-2, Techne) equipped with temperature controller (TC-8D, controller/C, Techne). Nitrogen (mild pyrolysis) and air (air oxidation) were supplied through MFC (Unit co.) to reactor system with a flow rate of  $100\text{ mL/min}$ . In the air oxidation experiment, steam from vapor generator (Micromeritics) at  $105\text{ }^\circ\text{C}$  was supplied to reactor system with the flow rate of  $30, 60, 100\text{ mL/min}$ , respectively. Coal loaded on the reactor was  $2.5\text{ g}$ . Thermal treatment was performed in the temperature range of  $300\text{--}550\text{ }^\circ\text{C}$ .

### 3. Hydrogen Peroxide Leaching

About  $1\text{ g}$  coal was treated with  $10\text{ mL}$   $H_2O_2$  solution (Junsei chemical) in a  $35\text{ mL}$  test tube placed in a water bath (MC-11, Jeio Tech). Reaction temperature was varied from  $30\text{ }^\circ\text{C}$  to  $90\text{ }^\circ\text{C}$ . The solid materials were filtered with GF/C (47 mmΦ, Whatman), washed several times with distilled water and dried at  $105\text{ }^\circ\text{C}$  for 6 hours. The dried sample was stored in a desiccator. The leachate was stored in the refrigerator at  $4\text{ }^\circ\text{C}$ .

### 4. Analysis

Total sulfur contents of coals and chars were measured by element analyzer (EA 1112, Thermoquest) three times and then averaged. Inorganic sulfur (sulfate and pyritic sulfur) was measured by IS 1350 method [Karr et al., 1978]. Heating values of coal and char were measured by bomb calorimeter (bomb calorimeter 1261, Parr).

Desulfurization yield and sulfur removal efficiency ( $X_s$ ) were calculated by dry basis, and defined as follows:

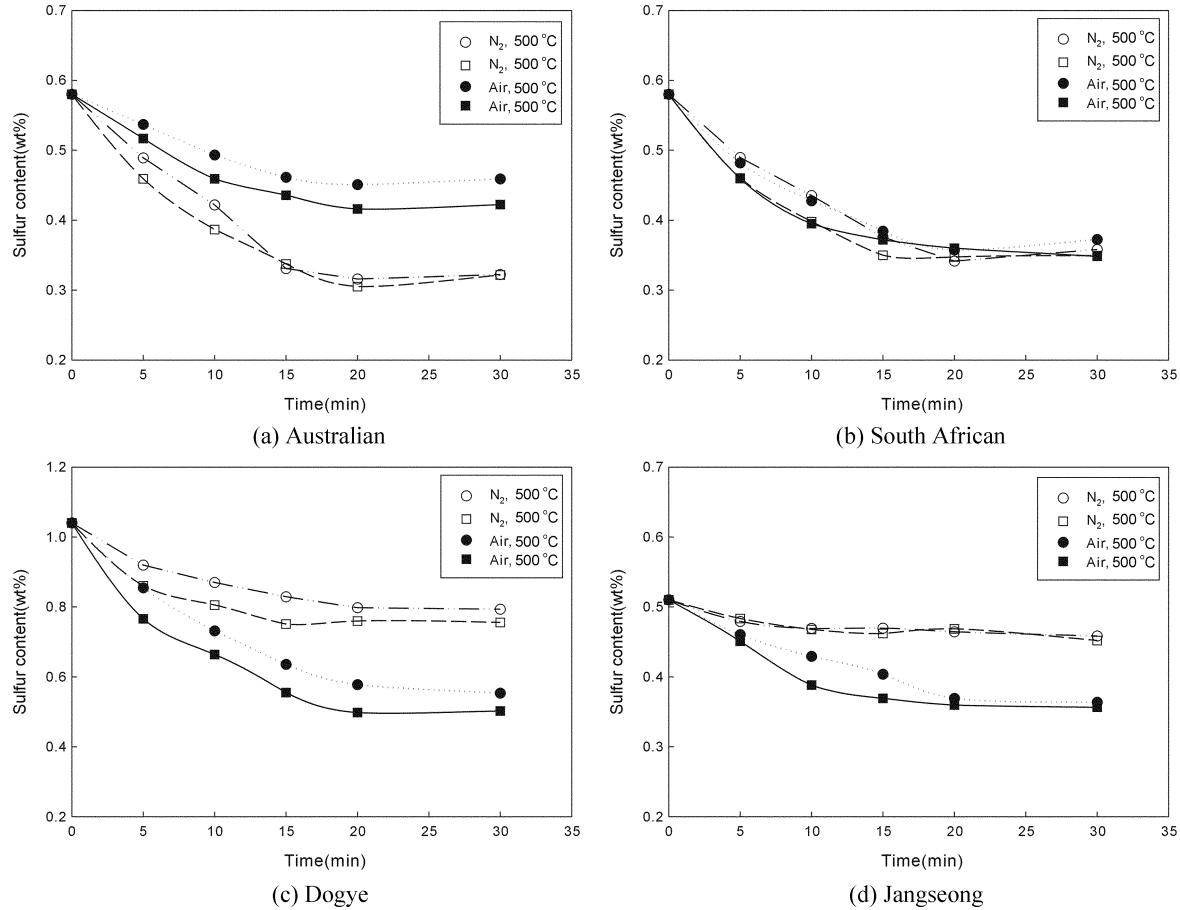
$$\text{Yield} = \frac{\text{weight of char}}{\text{weight of coal}} \quad (5)$$

$$X_s = \frac{S\% \text{ in coal} - \text{Yield} \times S\% \text{ in char}}{S\% \text{ in coal}} \quad (6)$$

## RESULT AND DISCUSSION

### 1. Effect of Reaction Time and Temperature

Total sulfur contents of char treated by mild pyrolysis ( $N_2$  atmosphere) and air oxidation (air atmosphere) at  $500$  and  $550\text{ }^\circ\text{C}$  are compared in Fig. 2. Regardless of the coal type and source, the sulfur contents of char decreased for first 15-20 minutes of reaction and remained almost constant afterwards. Thus, the optimum time for thermal treatment process was determined to be 15-20 min. Among the domestic coals, mild pyrolysis seemed to have no effect for Jang-

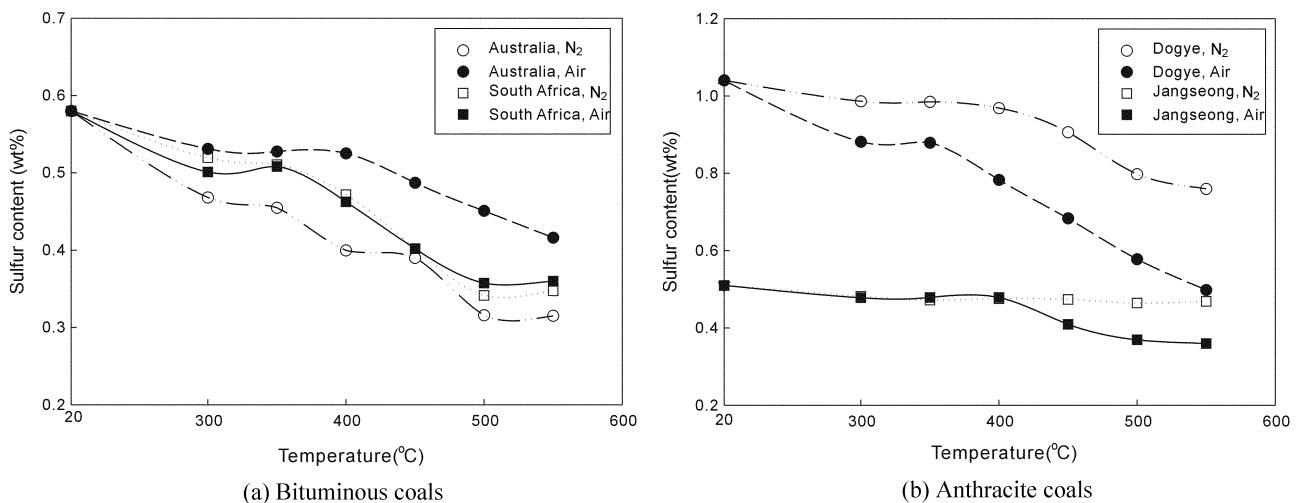


**Fig. 2. Effect of reaction time on sulfur content of coals after thermal treatment processes.**

seong coals.

Air oxidation was more effective than mild pyrolysis for the domestic anthracite coals. It can be seen more distinctively for Jangseong coal. For air oxidation process, the combined effect of thermal release of sulfur and oxidative removal by oxygen was believed to give higher sulfur removal efficiency. Unexpectedly, however,

mild pyrolysis acted more effectively than air oxidation for Australian coal. There was severe weight loss at 500 and 550 °C for bituminous coals when carrying out the thermal methods [Park, 2003]. When oxygen was supplied, the weight loss was more severe. We believe that this weight loss difference between the two treatment methods consequently altered sulfur removal efficiency. Both re-



**Fig. 3. Effect of reaction temperature on sulfur content of coals after thermal treatment processes.**

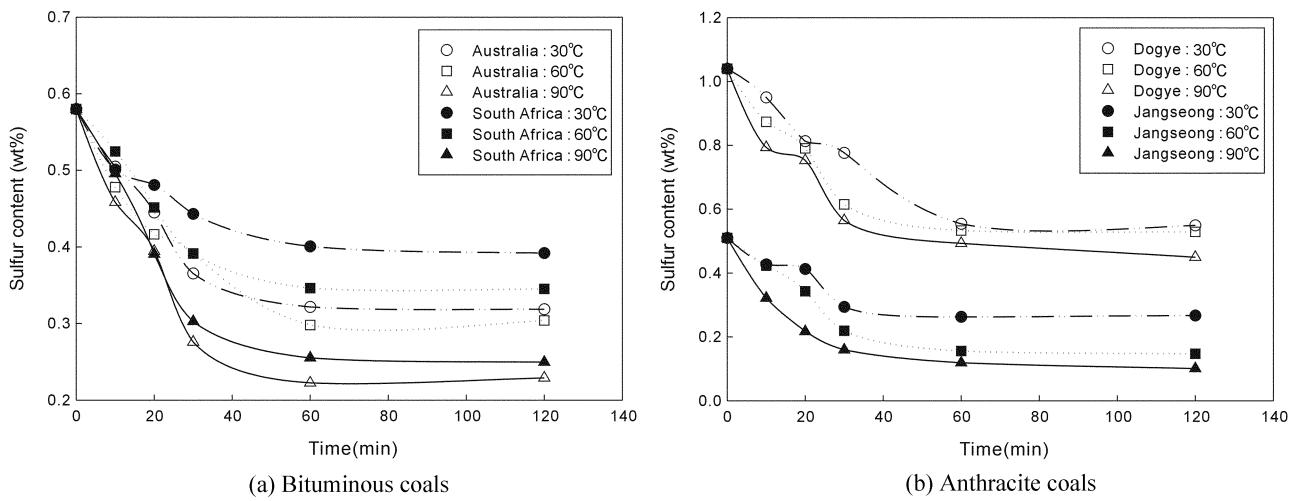


Fig. 4. Effect of reaction time on sulfur content of coals after leaching processes.

removal methods were almost equally effective for South African coal.

The effect of reaction temperature on sulfur content of char after 20 min is shown in Fig. 3. Mild pyrolysis showed better desulfurization effect than air oxidation for Australian coal, while that of South African coal showed small difference between treatment methods. Sulfur content of Australian coal decreased continuously with increasing temperature for air oxidation process. Minimum sulfur content of char was observed between 500 and 550 °C for bituminous coals processed by mild pyrolysis. When pyrolysis temperatures were higher than 600 °C, the pore structure of coal reportedly collapsed, changing the coal matrix structure which inhibited further release of sulfur [Wen et al., 1978; Lin et al., 1997]. Considering the report and our results for the bituminous coals, the optimum temperature in mild pyrolysis turned out to be in the range of 500–550 °C. On the other hand, for the domestic anthracite coals, maximum sulfur removal was observed at 550 °C when air oxidation technique was applied. Thermal treatment was not effective below 400 °C for Jangseong coals.

Effects of reaction time and temperature on sulfur contents of

coals treated by 30%  $H_2O_2$  solution are shown in Fig. 4. We believe that regardless of coal types, leaching of sulfur was almost completed in 60 min. Sulfur contents of the bituminous coals decreased almost linearly for 30 minutes of leaching. Increasing temperature resulted in enhanced sulfur removal efficiency. At 90 °C, the final sulfur contents of Australian and South African coals were 0.23% and 0.25%, respectively. Compared to the thermal processes, the leaching process was more effective in general. On the other hand, increasing reaction temperature caused increase in weight loss. Changes in sulfur contents of anthracite coals showed similar trends with bituminous coals. However, the differences in sulfur reductions when increasing the leaching temperature from 60 °C to 90 °C were not large compared to bituminous coals. The leaching process was much more effective than thermal processes for Jangseong coals. The optimum condition for the leaching process was obtained when the experiment was carried out for 60 min at 90 °C using 30%  $H_2O_2$ .

## 2. Desulfurization Kinetics

The kinetics of desulfurization was investigated graphically by using Eq. (3) and Eq. (5). Fig. 5 shows that total sulfur removal for

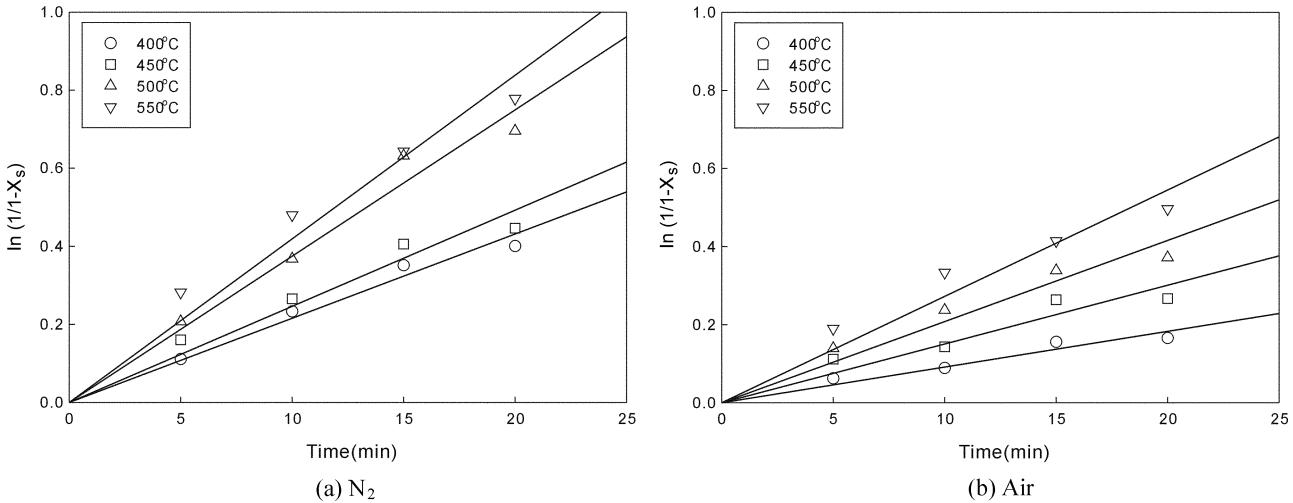


Fig. 5. Comparison of measured thermal treatment desulfurization data of Australian coal with first-order reaction kinetics.

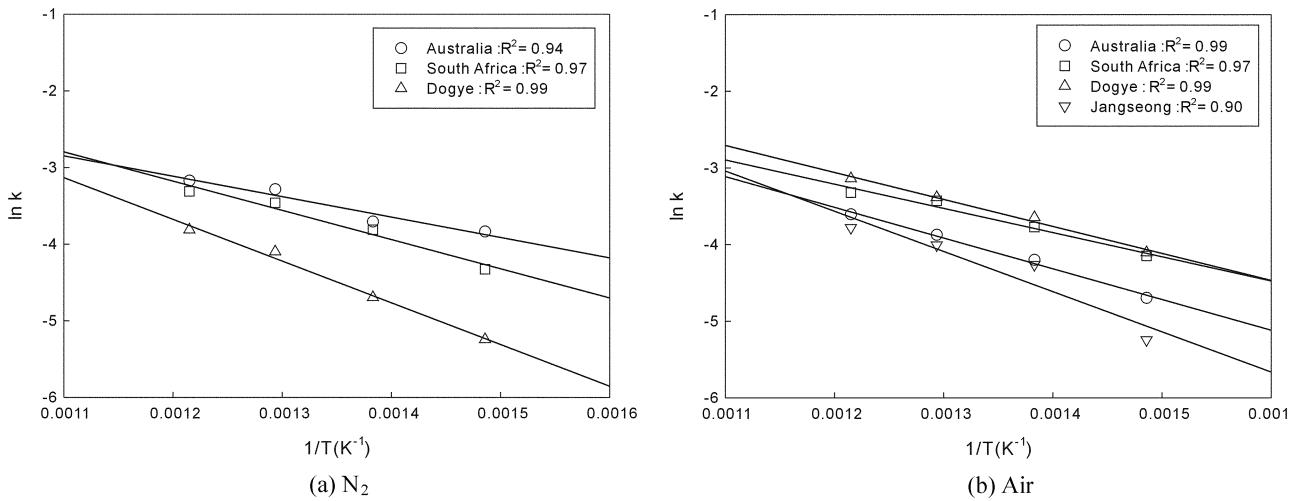


Fig. 6. Arrhenius plot for thermal treatment process.

Table 2. Activation energy and frequency factor for three desulfurization processes

Processes	Unit	Australian	South African	Dogye	Jangseong
Pyrolysis	DSE (kJ/mol)	22.1	31.7	45.2	-
	$k_0 (\times 10^2, \text{s}^{-1})$	1.6	6.4	28.8	-
	$k (\times 10^4, \text{s}^{-1})$	5.2	4.6	2.5	-
Air oxidation	DSE (kJ/mol)	33.3	26.2	29.3	43.6
	$k_0 (\times 10^2, \text{s}^{-1})$	6.1	3.0	5.3	25.6
	$k' (\times 10^4, \text{s}^{-1})$	3.4	5.0	5.6	2.9
$\text{H}_2\text{O}_2$ leaching	DSE (kJ/mol)	7.9	12.7	6.2	12.1
	$k_0 (\times 10^2, \text{s}^{-1})$	0.5	2.0	0.2	3.1
	$k' (\times 10^4, \text{s}^{-1})$	3.4	2.9	3.0	5.6

$k_0$ : frequency factor,  $k$  : rate constant at 500 °C.

$k'$ : pseudo rate constant at 500 °C for air oxidation or 90 °C for  $\text{H}_2\text{O}_2$  leaching.

Australian coal had a first-order kinetics in both mild pyrolysis and air oxidation processes. Due to the highly heterogeneous nature of coal samples, relatively small discrepancies were observed between measured data and first-order kinetics. Relations between  $\ln k$  and  $1/T$  for all coals under investigation are shown in Fig. 6, from which activation energies (DSE) were calculated. Most of regression coefficients in regression analysis were better than 0.94. Values of DSE and frequency factors of thermal treatment processes are listed in Table 2.

The reported value of DSE for mild pyrolysis using Ohio #8 coals [Lin et al., 1997] were 78.8 kJ/mol for the overall desulfurization reaction. This value was three times higher than that of Australian coal. The coal pyrolysis reaction seemed to depend on the types of coal since the sulfur release began after the swelling of coal particles due to the rearrangement of the physical coal matrix.

DSE value of the air oxidation for Australian coal increased 50% compared to mild pyrolysis. For South African and Dogye coals the DSE values decreased 17% and 35%, respectively, compared to mild pyrolysis. Comparing first-order rate constants at 500 °C, desulfurization reaction for Australian coal proceeded faster in mild pyrolysis than in air oxidation. However, desulfurization proceeded faster in air oxidation than in mild pyrolysis for South African and Dogye coals.

$\text{H}_2\text{O}_2$  leaching for total sulfur has not been reported yet, but the kinetics for organic and inorganic sulfur release were studied. Karaca and Ceylan [1997] reported that a second-order model was found to be the best with the highest correlation coefficient for desulfurization of pyritic sulfur by  $\text{H}_2\text{O}_2$  leaching for two kinds of Turkish lignites. To determine the reaction order of total sulfur desulfurization, the least square method was applied. Contrary to the second-order model by Karaca and Ceylan, a first-order model fitted better in our desulfurization study. Although some discrepancies appeared, results of a first-order model for Australian coals are shown in Fig. 7. An Arrhenius plot of  $\text{H}_2\text{O}_2$  leaching for four kinds of coal is shown in Fig. 8. Values of DSE and the frequency factor of the  $\text{H}_2\text{O}_2$  leaching process are collected in Table 2. DSE values were 6.2-12.7 kJ/mol which were much smaller than 53.4 kJ/mol reported by Yaman et al. [1996] who studied organic sulfur leaching by  $\text{Na}_2\text{CO}_3$  for Turkish coals.

DSE values of the  $\text{H}_2\text{O}_2$  leaching process were smallest among those of the processes tested, which implies that total sulfur is easily released by the  $\text{H}_2\text{O}_2$  leaching. Comparing the rate constant for the thermal process at 500 °C and rate constant for  $\text{H}_2\text{O}_2$  leaching at 90 °C for various coals, the highest values were obtained in pyrolysis for Australian coal, in air oxidation for South African and Dogye coals, and in  $\text{H}_2\text{O}_2$  leaching for Jangseong coal, respectively.

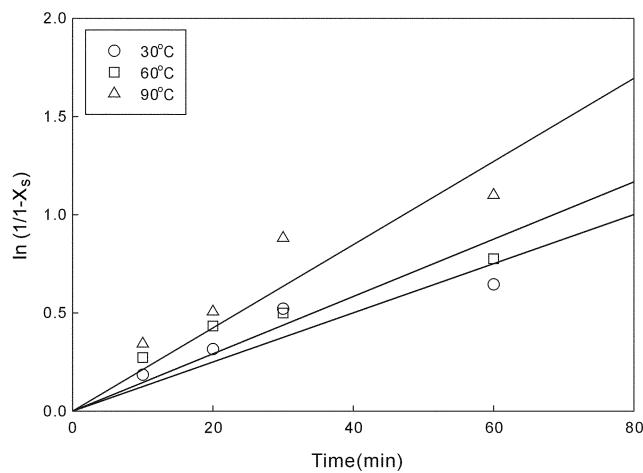


Fig. 7. Comparison of measured  $\text{H}_2\text{O}_2$  leaching desulfurization data of Australian coal with first-order reaction kinetics.

These results suggest that the appropriate process must be chosen according to coal characteristics.

### 3. Inorganic Sulfur and Organic Sulfur

The effect of reaction temperature on organic and inorganic sulfur removal for the thermal treatment processes is shown in Fig. 9. Sulfur removal efficiencies were calculated from Eq. (6) by using chars treated for 20 minutes. Organic sulfur removal efficiency for South African coal in mild pyrolysis increased with increasing temperature for the range 350-500 °C. Organic sulfur removal efficiency was better than that of inorganic sulfur. In air oxidation, however, inorganic sulfur removal efficiency was higher than that of organic sulfur. The same tendency was observed for Australian coals. For South African coal, organic sulfur removal efficiency dropped at 550 °C compared to that obtained at 500 °C. We believe that, as Chen et al. [2000] reported, some  $\text{H}_2\text{S}$  was not released to the outer of the coal particle and adsorbed to ash component of coal and then reacted with coal matrix to form organic sulfur again. Decreasing

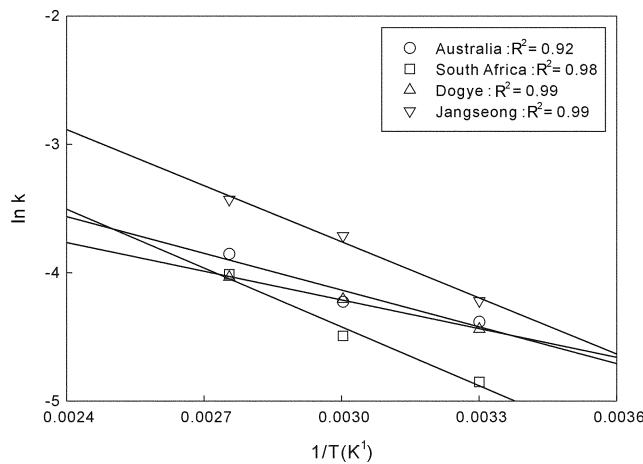


Fig. 8. Arrhenius plot for  $\text{H}_2\text{O}_2$  leaching process.

of organic sulfur removal efficiency at 550 °C was also observed for Australian coal. Inorganic sulfur was removed efficiently by air oxidation for both kind of coals at 550 °C. However, the organic sulfur removal efficiency at this temperature was higher in the mild pyrolysis than in air oxidation. It was believed that mild pyrolysis was effective for organic sulfur removal while the air oxidation was more effective for inorganic sulfur removal.

Changes of inorganic and organic sulfur contents during  $\text{H}_2\text{O}_2$  leaching process by 30%  $\text{H}_2\text{O}_2$  solution at 90 °C are summarized in Table 3. Inorganic sulfur removal efficiency for South African coal was above 85% and organic sulfur removal efficiency was about 55% after 1 hour of treatment. Inorganic sulfur was removed completely after 12 hours of leaching. For Dogye coal, inorganic sulfur removal efficiency was above 95% and organic sulfur removal efficiency was approximately 45% after 1 hour of treatment. As was the case for South African coal, inorganic sulfur was removed completely after 12 hours of leaching. The  $\text{H}_2\text{O}_2$  leaching process was very effective for inorganic sulfur removal. The organic sulfur re-

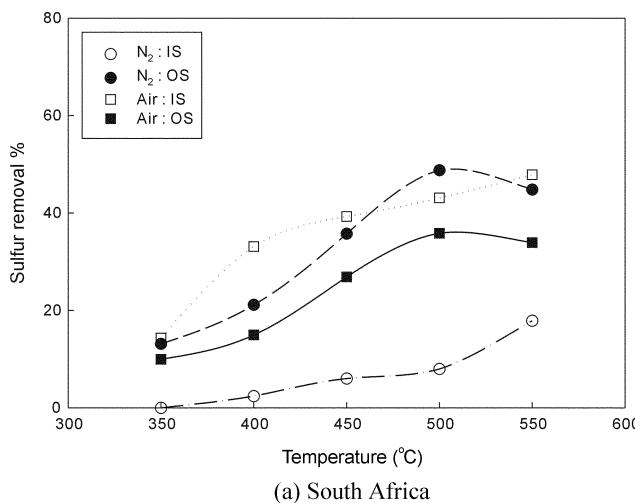


Fig. 9. Effect of organic and inorganic sulfur removal of South Africa coal and Dogye coal after thermal treatment processes (reaction time : 20 min).

IS : Inorganic Sulfur, OS : Organic Sulfur

**Table 3. Results of sulfur form of south african coal and dogye coal after 30%  $H_2O_2$ leaching at 90 °C**

unit: wt%, dry basis

Coal	Time (min)	Total sulfur	Inorganic sulfur				Organic sulfur	
			Pyrite	Sulfate	Sum	SR%	OS	SR%
South African	0	0.58	0.12	0.01	0.13	-	0.45	-
	60	0.25	0.02	0.00	0.02	86.3	0.23	55.4
	720	0.22	0.00	0.00	0.00	100.0	0.22	57.8
Dogye	0	1.04	0.29	0.03	0.32	-	0.72	-
	60	0.49	0.02	0.00	0.02	94.6	0.47	43.4
	720	0.45	0.00	0.00	0.00	100.0	0.45	47.0

removal efficiency was higher in the  $H_2O_2$  leaching process than in the thermal treatment methods. It was believed that some metal components leached during the  $H_2O_2$  leaching process enhanced the sulfur removal by catalytic action [Borah et al., 2001]. Total sulfur removal efficiencies in the  $H_2O_2$  leaching process at 90 °C by 30%  $H_2O_2$  solution after 1 hour were about 67% for Australian coal, 61% for South African coal, 59% for Dogye coal, and 80% for Jangseong coal, respectively.

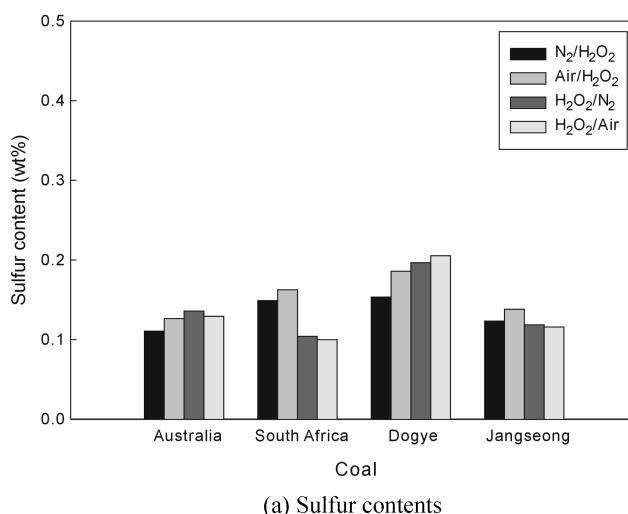
#### 4. Dual Processes

As described above, we could not get satisfactory results to prepare coals which would meet the emission standard without FDG process by single treatment method. Dual processes combined with the thermal treatment and the  $H_2O_2$  leaching were introduced. Among the possible combinations,  $H_2O_2$  leaching after thermal treatment (thermal/leaching) and thermal treatment after  $H_2O_2$  leaching process (leaching/thermal) were evaluated. Individual processes were operated by their optimum conditions resulting from the experiments. Total sulfur contents and sulfur removal efficiencies are shown in Fig. 10. Overall, the dual processes resulted in better desulfurization efficiencies except for Jangseong coal. Total sulfur contents after thermal/leaching process for Australian and South African coals were 0.12% and 0.16%, respectively. Sulfur contents were 0.13% and 0.10% after leaching/thermal process for Australian and South African coals, respectively. Accounting the analysis error ( $\pm 0.02\%$ ),

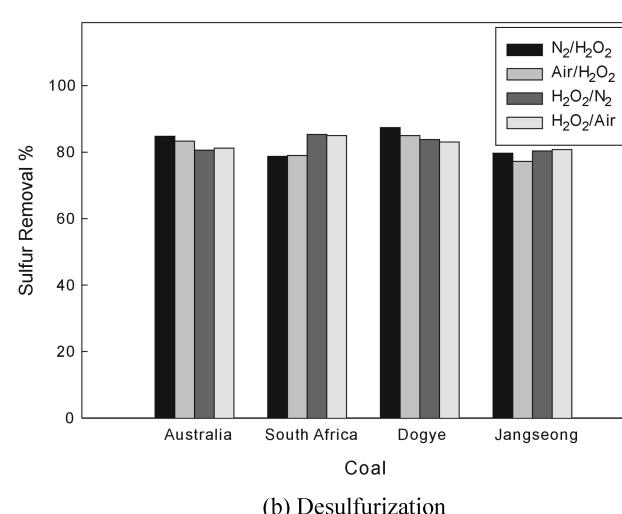
sulfur contents of Australian coal did not change by operation order of individual process. However, sulfur content was lower in leaching/thermal process than in thermal/leaching process for South African coal. Total sulfur contents after thermal/leaching process for Dogye and Jangseong coals were 0.17% and 0.13%, respectively. Sulfur contents were 0.20% and 0.12% after leaching/thermal process for Dogye and Jangseong coals, respectively. The effect of the operation order was insignificant for Dogye coal. However, sulfur content was lower in leaching/thermal process than that in thermal/leaching process for Jangseong coal. From the results above, the leaching/thermal process was somewhat more effective than the thermal/leaching process.

Total sulfur did not remove under 0.1% even with dual processes. The remaining sulfur species seemed difficult to remove due to their strong bonding to coal matrix. Total sulfur removal efficiencies exceeded 80%, 20% higher than  $H_2O_2$  leaching process alone except for Jangseong coal. Jangseong coal showed low sulfur removal in the thermal treatment, resulting in similar removal efficiency compared to the leaching process alone.

In the thermal treatment process, swelling of coal particles occurred as the reaction temperature increased. Swelling caused reconstruction of coal matrix and formed metaplast by depolymerization of organic species in coal [Wen et al., 1979]. The effect of swelling on leaching has not been studied before. From this study, leaching



(a) Sulfur contents

**Fig. 10. Sulfur contents and desulfurization efficiency after dual processes (thermal treatment processes at 500 °C for 15 min, 30%  $H_2O_2$  leaching at 90 °C for 60 °Cmin).**

of swelled coal turned out to cause 4-7% more weight loss than leaching/thermal process due to weakened coal matrix after thermal treatment. Changes of heating value of bituminous coals after dual process, as described elsewhere [Park, 2003], showed that the loss was 5% smaller for the leaching/thermal process.

## CONCLUSIONS

Desulfurization characteristics of low sulfur coals prior to combustion were studied and the following conclusions were obtained.

1. The optimum reaction temperatures and times of the thermal processes were 500-550 and 15-20 minutes, respectively. The optimum condition for the leaching process was obtained when the experiment was carried out for 60 min at 90 °C using 30% H<sub>2</sub>O<sub>2</sub>.

2. It is believed that mild pyrolysis is effective for organic sulfur removal while the air oxidation is more effective for inorganic sulfur removal. H<sub>2</sub>O<sub>2</sub> leaching process was very effective for inorganic sulfur removal. The organic sulfur removal efficiency was higher in the H<sub>2</sub>O<sub>2</sub> leaching process than in the thermal treatment methods.

3. The dual process showed the best sulfur removal efficiency as expected among the evaluated processes. The effect of swelling on leaching has not been studied before. In this study, leaching of swelled coal turned out to cause more weight loss than the leaching/thermal process due to weakened coal matrix after thermal treatment. Changes of heating value of bituminous coals after dual process showed that the loss was smaller for the leaching/thermal process.

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## NOMENCLATURE

C <sub>s</sub>	: sulfur concentration of char [wt%/g]
k	: rate constant [s <sup>-1</sup> ]
C <sub>so</sub>	: sulfur concentration of coal [wt%/g]
x <sub>s</sub>	: total sulfur conversion defined by Eq. (6)
k'	: pseudo 1st-order rate constant [s <sup>-1</sup> ]

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