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Coal desulfurization with sodium hypochlorite

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COAL DESULFURIZATION WITH SODIUM HYPOCHLORITE

Wei Li

Thesis
Submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements for the degree of

Master of Science in
Chemical Engineering

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Morgantown, West Virginia
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ABSTRACT

COAL DESULFURIZATION WITH SODIUM HYPOCHLORITE

Wei Li

Wet desulfurization of Pittsburgh No. 8 coal and Illinois No. 6 coal were conducted with sodium hypochlorite in the laboratory. Pittsburgh No. 8 coal was leached by hypochlorite at high pHs in one step only. The hypochlorite concentration varied from 0.2 to 0.6 molar; sodium hydroxide concentration, from 0.2 to 0.8 molar; and temperature was at the levels of 80 and 90°C. The desulfurization of Illinois No. 6 coal was conducted in three consecutive steps of pretreatment in concentrated ammonia at room temperature, leaching with hypochlorite at room temperature and hydrolysis in a sodium hydroxide solution at 90°C. In the leaching step, hypochlorite concentration varied from 0.2 to 0.8 molar.

The desulfurization method of Pittsburgh No. 8 coal was found to reduce mainly pyritic sulfur. More than 70% of pyritic sulfur removal was achieved at the optimum conditions of 0.4 molar hypochlorite, 0.4 molar sodium hydroxide and 90°C. The desulfurization method for Illinois No. 6 coal was capable of reducing significant amounts of organic sulfur. The removal of organic sulfur achieved a 37.8% reduction at the optimum operation of leaching at 0.4 molar hypochlorite and room temperature followed by hydrolysis at 0.3 molar sodium hydroxide and 90°C. The chlorine content in the coal produced by the chlorination during leaching was kept below the threshold value of 0.3% at the optimum conditions of the desulfurization method for each coal.

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CHAPTER 1

INTRODUCTION

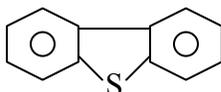
Coal is a very complex material and its chemical composition varies widely. Of all the elements found in coal, sulfur is the single most important one which impedes the utilization of coal as a clean fuel. Many U.S. steam coals contain high percentages of sulfur which must be reduced as air pollution regulations become increasingly more stringent. According to Clean Air Acts of 1976 and 1990, sulfur dioxide emission from coal-fired power plants should be limited to 1.2 lb/MBTU, which can be translated to a total sulfur content in normal coal below 0.8 wt%.

Coal has three sources of sulfur: pyritic, organic and sulfate sulfur. The distribution of these sulfur contents and the total sulfur vary much from coal to coal produced in the U.S.. The total sulfur varies in the range of 2-4wt% and the organic sulfur and pyritic sulfur contents are almost equally partitioned in many coals. The sulfate sulfur content is usually very small with its content being lower than 0.2%.

Pyritic sulfur refers to ferrous disulfide (FeS_2). Much of the pyritic sulfur can be removed by physical separation methods such as gravity separation and froth flotation processes. The froth flotation process can remove up to 50% pyritic sulfur. However, the limitation of physical cleaning methods is that very fine pyrite particles are disseminated in the coal particles and those that are not exposed to the surface and not liberated are not amenable to physical separation.

Organic sulfur is part of, and chemically bonded to the coal matrix and it cannot be removed unless the chemical bonds holding it are broken. Meyers (Meyers, 1977) summarized the structure of the organic sulfur in the coal to include mercaptans (RSH),

sulfides ($R - S - R'$), disulfides ($RS - S - R'$) and thiophenes where R and R' stand for hydrocarbon groups. For mercaptans, R stands for aliphatic groups. The structure of dibenzothiophene is characterized by:



It is reported that certain forms of organic sulfur are amenable to removal by hypochlorite (Brubaker and Stoicos, 1985).

Many chemical methods were developed in the past; however, none has been commercialized. The Meyers process (Meyers, 1977) uses ferric chloride solutions to remove pyritic sulfur. However, it requires rigorous operating conditions. It used six one-hour leachings with one-molar ferric chloride at 100°C to achieve more than 95% pyritic sulfur removal. Organic sulfur is generally much more difficult to remove than pyritic sulfur. A solvent of p-cresol was identified as a chemical to reduce organic sulfur (Meyers, 1977). It is reported that a leach with p-cresol for 3 hours at 200°C achieved the average organic sulfur reduction of 47 wt. % for Indiana No. 5 seam coal.

The Chlorinolysis process was developed by Hsu et al. (Hsu et al., 1977). Chlorine gas and methyl chloroform were utilized to leach pyritic and organic sulfur at 74°C . Methyl chloroform was used to solubilize bubbled chlorine gas. The coal matrix was chlorinated during the leaching. The chlorine content in the coal reached up to 25% in two hours. The coal was effectively dechlorinated by treating it with steam at a temperature of 500°C . This process could remove up to 70% of organic sulfur and 77% of pyritic sulfur, and 76% of total sulfur.

Cho (Cho, 1989) conducted a similar study in a system where Sewickley seam coal was leached in a 0.1-N hydrochloric acid solution through which chlorine gas was bubbled. The results showed that most of the pyritic sulfur and approximately 40% of the organic sulfur were removed at room temperature. It was observed that the chlorine content in the leach coal reached up to 31%.

A similar desulfurization scheme with sodium hypochlorite (Brubaker and Stoicos, 1985), was utilized to remove substantial amounts of organic sulfur but not much pyritic sulfur from Illinois No. 6 coal. Further treatment with sodium carbonate at 80°C (hydrolysis) reduced the organic sulfur additionally. The organic sulfur was reduced by 62% when different coals were leached and subsequently hydrolyzed for one hour each, and this treatment was repeated once more. The pyritic sulfur was reduced by only 23% under the same treatment. Another interesting result of this leaching scheme was that hypochlorite chlorinated the coal matrix only slightly, or much less severely, than aqueous chlorine. It was observed that the chlorine levels in the coal ranged between 2 and 2.7%.

The disadvantage of the use of aqueous chlorine in the Chlorinolysis process is that it chlorinates the coal matrix extensively and that treatment at a high temperature (500°C) is needed to restore the chlorinated coal. The cost of this treatment is high so that the entire desulfurization process with aqueous chlorine would not be feasible for commercialization. However, Brubaker and Stoicos (Brubaker and Stoicos, 1985) have proven that desulfurization with hypochlorite does not readily chlorinate the coal structure, while it can reduce the organic sulfur as well as the aqueous chlorine process.

The objectives of this study are:

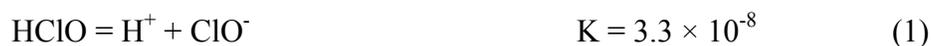
- (1) To explore a proper desulfurization method by which Pittsburgh No. 8 coal and Illinois No. 6 coal can be leached effectively with hypochlorite;
- (2) To determine the effects of parametric conditions such as hypochlorite concentration, pH and temperature on the desulfurization;
- (3) To determine the optimum operating conditions in consideration of the maximum sulfur reduction and minimum coal loss by hypochlorite oxidation;
- (4) To determine the technical feasibility for commercialization of this technology by considering the leaching conditions and sulfur reductions.

CHAPTER 2

THEORY

2.1 Chlorine Solution Chemistry

Sodium hypochlorite solution is not stable at low pHs due to the equilibrium reactions of chlorine (Garrels, 1965):



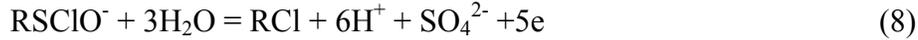
where K is the equilibrium constant at 25°C. At high pH (>10), hypochlorite ClO^- is predominant. Hypochlorous acid, HClO, will become dominant when pH decreases. At pH 7.5, the two species have the same concentration. Below 7.5, aqueous chlorine will form and escape as gaseous chlorine. So sodium hydroxide should be added to the hypochlorite solution to maintain high pH and stabilize the original hypochlorite concentration.

2.2 Hypochlorite Leaching

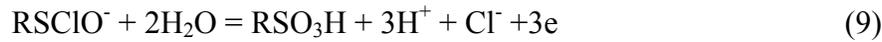
Some of the organic sulfur in coal may exist as carbon sulfide and disulfide. These sulfides react with hypochlorite to produce sulfonyl chloride (RSOCl^-) as shown (Hsu et al., 1977):



R and R' stand for the hydrocarbon groups and S refers to sulfur. The sulfonyl chloride is further oxidized to sulfonate or sulfate:



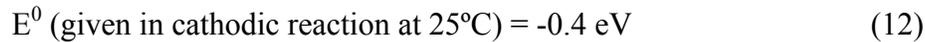
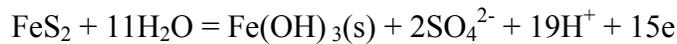
Reactions (7) and (8) are electrochemical reactions and their corresponding anodic reactions are:



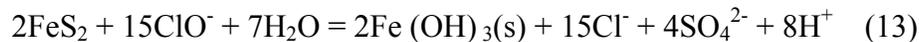
And the cathodic reaction is:



Pyritic sulfur also can be leached with hypochlorite. The anodic reaction is:



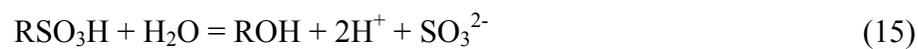
Then the overall reaction is:



$$\Delta G^\circ \text{ (at } 25^\circ\text{C)} = -1466.6 \text{ kcal/mole}$$

The magnitude of ΔG° suggests that the overall reaction is thermodynamically very spontaneous under normal conditions.

The second step of the desulfurization is the hydrolysis step in which further removal of the organic sulfur and dechlorination will take place. In this step, the leach coal will be treated in a solution containing sodium hydroxide around 90°C . The following reactions may take place in the hydrolysis step:



2.3 Coal Oxidation with Hypochlorite

It is known that coal is oxidized with hypochlorite, resulting in its weight loss. It is reported that sodium hypochlorite oxidizes Illinois No. 6 coal. The oxidation yields several products, depending on the pH and the kind of the coal (Mayo and Kirshen, 1979; Chakrabartty, 1978; Mayo, 1975). The products vary from black, high-molecular weight, bicarbonate-soluble acids to the benzene polycarboxylic acids and carbon dioxide. For example, at pH 13, 96% of the coal was dissolved and 80% of the carbon dissolved was found as the high-molecular-weight acids (Mayo and Kirshen, 1979). Between pH 9 and 11, the production of soluble acids was lower while that of CO₂ was higher. Below pH 9 more coal structure was destroyed — simple, oxidation-resistant benzene and aliphatic carboxylic acids were the principle organic products in the solution. According to Chakrabartty (Chakrabartty, 1978), Mayo and Kirshen studied the oxidation of Illinois No. 6 coal with hypochlorite. It was found that in one experiment, 80% loss of the original carbon was accounted for as follows: 13.6% in undissolved residue, 59.4% in colored acids soluble in aqueous bicarbonate, 7.1% in lighter colored acid readily soluble in water and 19.9% in carbon dioxide. The colored acids had an average molecular weight of 900 g and the water soluble acids had a molecular weight of about 200 g.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials

Pittsburgh No. 8 coal and Illinois No. 6 coal were used in this study. Pittsburgh No. 8 coal was obtained from the Fair Fax Mine #3, Anker Energy, Morgantown, WV. Illinois No. 6 coal (IBC 101) was obtained from the Illinois Geological Survey. A bulk Pittsburgh No. 8 coal sample was crushed and screened to produce a 65 × 150 mesh fraction. This fraction was floated by the conventional froth flotation techniques. The concentrate was dried and used in this study. Illinois No. 6 coal (IBC 101) sample was also crushed and screened to produce a 65 × 150 mesh fraction. This fraction was used for leaching experiments directly without further treatment by froth flotation because the coal had already low ash content. The analytical results of the cleaned 65 × 150 mesh fractions of Pittsburgh No. 8 coal and IBC 101 coal are presented in Table 1.

Table 1. Analytical Results of Untreated Coal

	Pittsburgh No. 8	IBC 101
Ash (%)	8.18	8.02
Pyritic sulfur (%)	0.82	0.33
Organic sulfur (%)	1.60	3.33
Sulfate sulfur (%)	0.02	0.10
Total sulfur (%)	2.44	3.76
Total acid (mmol/g)	0.47	3.14
Chlorine content (%)	0.06	0.03
Moisture content (%)	1.25	4.67

Hypochlorite solutions to be used for the leaching experiments were prepared by diluting the hypochlorite stock solution which was purchased from a chemical supplier. It

had about 2.14 molar hypochlorite concentration and pH 12.3~12.6. This stock solution was kept in a refrigerator to minimize the loss due to evaporation.

3.2 Experimental Apparatus

The leaching experiments for Pittsburgh No. 8 coal and the hydrolysis experiments for Illinois No. 6 coal were conducted in a one-liter reactor placed in a constant-temperature paraffin-oil bath (Figure 1). The reactor had four necks. The central neck was equipped with a stirrer connected to a variable-speed motor. The stirring speed was 500 rpm for all the experiments. One of the side necks was fitted with a reflux condenser which was used to prevent excessive evaporation at high temperatures. The next one was equipped with a thermometer which was used to measure the temperature of the solution. And the last one was used for charging the coal sample and/or pipetting solution to analyze its chlorine concentration.

3.3 Experimental Procedures

3.3.1. Pittsburgh No. 8 Coal:

A 500-ml hypochlorite solution at the desired concentration was charged into the reactor. When the leach solution reached the desired temperature, twenty grams of coal sample was added to the reactor. The leaching continued for 2 hours. After leaching, the coal slurry was filtered on Whatman No. 1 filter paper. The filtered coal was dried naturally in air for overnight, weighed and analyzed for total sulfur, pyritic sulfur, sulfate sulfur, chlorine content and ash content. Leaching conversions of pyritic sulfur and organic sulfur were determined using these data.

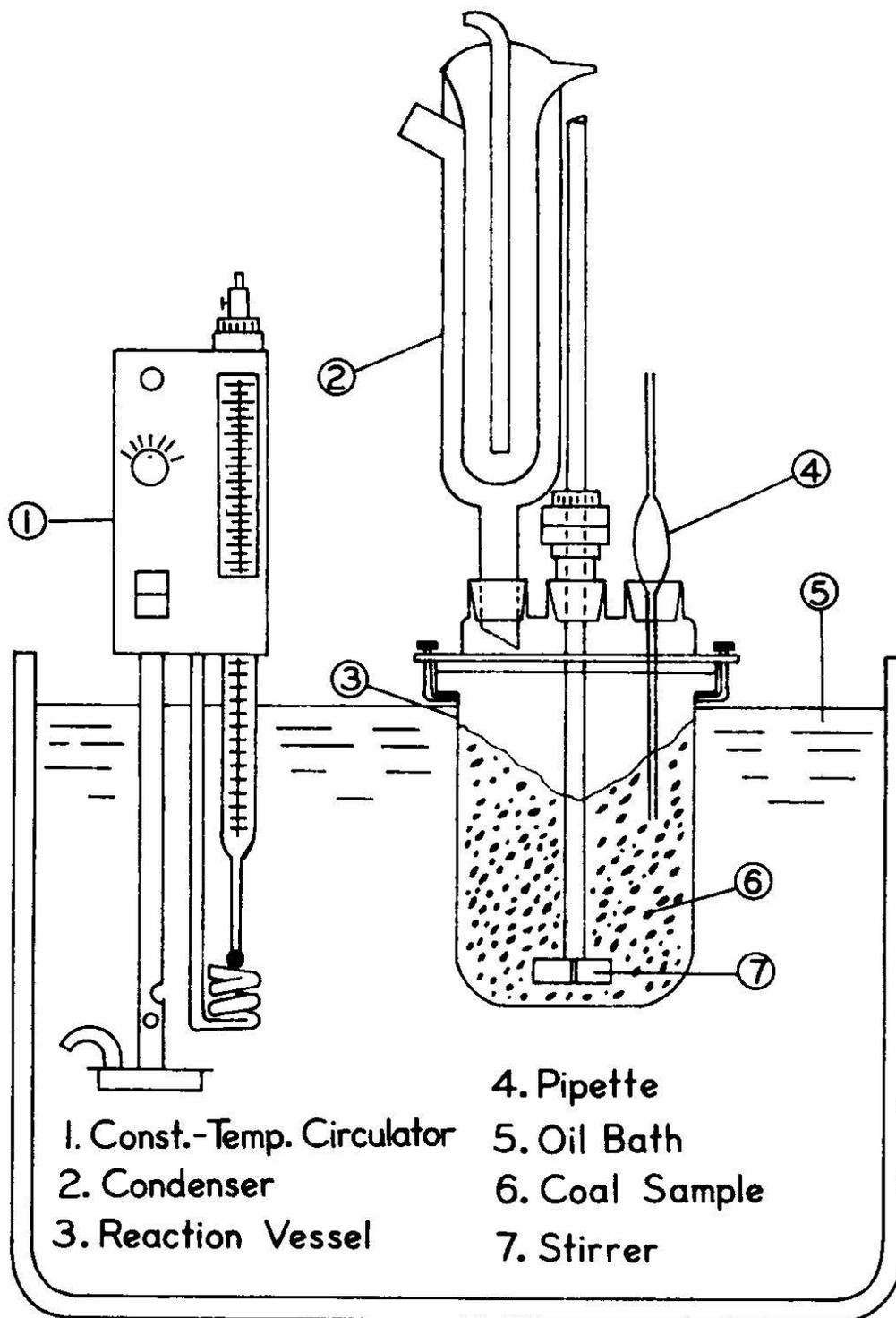


Figure 1. Schematic diagram of leaching apparatus

3.3.2. Illinois No. 6 Coal:

It was found that the procedures taken for the leaching of Pittsburgh No. 8 coal was not suitable for leaching Illinois No 6 coal, mainly due to the excessive loss of Illinois No. 6 coal during leaching. Thus, an alternate method was explored and adopted to leach this coal more effectively. More details will be given in the next chapter.

Twenty grams of coal was pretreated at room temperature with 50 ml of a concentrated ammonia hydroxide solution in a 250-ml beaker. The coal was stirred on a magnetic stirrer. The stirring speed was fast enough to keep the particles in suspension. The coal was stirred for one hour, filtered through Whatman No. 1 paper and dried under an infrared lamp. The dried coal was then leached at room temperature with a 100 ml hypochlorite solution in a 250-ml beaker. The coal was stirred in the same way as in the pretreatment. The coal was stirred for one hour, then filtered and dried in the same way as in the pretreatment. About 2 grams of the dried coal was taken for analyses for total sulfur, pyritic sulfur, chlorine content and ash content. And the rest was hydrolyzed.

The hydrolysis was conducted in the same reactor as shown in Figure 1. A 500 ml sodium hydroxide solution was charged to the reactor and when the temperature reached 90°C, the leach coal was added to start hydrolysis. After hydrolysis for one hour, the coal was filtered on Whatman No. 1 paper and dried in the same way as in the pretreatment. About 2 grams of the dried coal was taken to be analyzed for total sulfur, pyritic sulfur, chlorine content and ash content. This is the end of the first cycle. The second cycle was made by repeating the leaching and hydrolysis. The leaching was conducted with the dried coal which resulted from the hydrolysis step of the previous cycle. All the procedures were the same as in the first cycle.

3.4 Experimental Conditions

Table 2 encompasses the experimental conditions applied. The conditions were designed to determine their effects on the coal desulfurization.

Table 2. Experimental Conditions

	Pittsburgh No. 8	IBC 101
Leaching temperature, °C	50, 60, 70, 80, 90	Room temperature
Hypochlorite concentration in leaching solution, M	0.2, 0.3, 0.4, 0.6	0.2, 0.4, 0.6, 0.8
Sodium hydroxide concentration in leaching solution, M	0.2, 0.3, 0.4, 0.8	0, 0.1
Leaching time, hr	2	1
Sodium hydroxide concentration in hydrolysis, M	N/A	0.1, 0.3

3.5 Analyses

Total sulfur was analyzed according to ASTM method D3177-84, (Eschka Method). A weighed sample was well mixed with Eschka mixture and burned in a furnace at 800°C. All the sulfur transformed into sulfate and was dissolved into hot water. And the sulfate was precipitated as barium sulfate, which was filtered, burned in a furnace and weighed. Total sulfur was also analyzed by an elemental analyzer. The elemental analyzer was a Flash 1112 instrument, manufactured by ThermoQuest. Most of the Illinois No. 6 coal samples were analyzed by this method. Both methods were reliable in analyzing the total sulfur content. For example, the untreated Illinois No. 6 coal was analyzed for total sulfur by both methods at virtually the same level of 3.76%.

Pyritic sulfur was analyzed according to ASTM method D2492-84. Coal was leached with hydrochloric acid (2+3) solution (2 volumes of concentrated HCl and 3 volumes of water) to remove non-pyritic iron and the left-over pyrite was again leached with nitric acid (1+7) solution (1 volume of concentrated HNO₃ and 7 volumes of water). The solubilized iron was determined by Perkin-Elmer Atomic Absorption Spectroscopy, which was stoichiometrically converted to pyritic sulfur.

Sulfate sulfur was analyzed according to ASTM method D2492-84. Sulfate sulfur was extracted together with non-pyritic iron using hydrochloric acid (2+3) solution and was precipitated as barium sulfate. The precipitate was filtered, burned in a furnace and weighed.

Organic sulfur was calculated by subtracting the combination of pyritic sulfur and sulfate sulfur from the total sulfur.

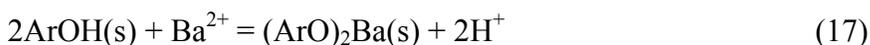
Ash content in coal was analyzed according to ASTM method D2795-85 and moisture content was analyzed according to ASTM method D3173-87.

Chlorine content in the coal was analyzed according to ASTM method D2361-85, (Eschka Method). A slight modification of the ASTM method was made. In this analytical method, nitrobenzene was not used but the precipitate of AgCl was filtered before Ag-containing solution was titrated with potassium thiocyanate. A 5-ml indicator solution of ferric ammonium sulfate was added to the filtrate instead of 8 to 10 drops suggested by the ASTM method. This modification was made for better detection of the color change at the end point.

Chlorine concentration of the hypochlorite solution was analyzed according to ASTM method D2022-64. Solid potassium iodide was added to the chlorine-containing

solution and dissolved. The solution was acidified by adding concentrated acetic acid. The aqueous chlorine oxidizes the iodide to iodine, which was titrated by sodium thiosulfate solution using starch as an indicator.

The concentration of the total acidic groups on the coal surface was analyzed in order to particularly explain the drastically different leaching behaviors between Pittsburgh No. 8 coal and Illinois No. 6 coal. The method adopted by Luo (Luo, 1994) was used for the determination of total acidic groups on the coal surface. The coal sample was contacted with barium ion in a solution. Then the barium ion exchanged with H⁺ in the carboxylic and phenolic groups to form precipitates on the coal surface. The H⁺ ions were produced. The following reactions were involved:



where the (s) denotes a solid species at the coal surface, RCOOH is carboxylic acid group and ArOH stands for phenolic group. The total acidic groups are taken as the combination of carboxylic and phenolic groups. The H⁺ ions produced according to reactions 16 and 17 were titrated with sodium hydroxide solution.

For determination of the total acidic group content on coal, one gram of as-received or oxidized coal sample was transferred into a 200 ml plastic bottle. Before transferring the sample, the bottle was purged with nitrogen, and while still purging, 100 ml of 0.3 N Ba(OH)₂ solution was pipetted into the bottle. The bottle was then sealed and agitated at room temperature on a shaker for 16 hours. The contents of each bottle with nitrogen purging was then vacuum-filtered using No. 1 Whatman filter paper. Immediately after this filtration step, 25 ml of the filtrate was pipetted into the titrator

cup, which already contained 30 ml of 0.3 N HCl and 10 ml of CO₂-free distilled water, and this solution was titrated with 0.2 N NaOH using m-cresol purple as the indicator. A blank titration was also performed so that the content of total acidic groups in the coal (in meq/g coal) could be calculated. These procedures determined the concentrations of Ba(OH)₂ in the blank test and the test with coal sample. The difference in concentrations of Ba(OH)₂ in these two tests determined the concentration of the total acidic groups.

CHAPTER 4

RESULTS AND DISCUSSION

In the early stages of the research, many preliminary experiments were conducted to find ways in which sulfur contents from Pittsburgh No. 8 and Illinois No. 6 could be leached effectively. It was found that Pittsburgh No. 8 coal could best be leached with one step of leaching at high temperatures. Pretreatment with ammonia solution or hydrolysis at high temperature and high pH was not found particularly effective. Thus, only the leaching step was applied to Pittsburgh No. 8 coal in this study. In the case of Illinois No. 6 coal, all the consecutive steps of pretreatment, leaching and hydrolysis were found to be necessary for effective reduction of sulfur content. Thus, all these steps were applied to the desulfurization of Illinois No. 6 coal in this study.

It was observed that the coal weight was reduced through leaching or hydrolysis particularly for Illinois No. 6 coal. Weighing the coal sample before and after treatment was not used to determine the weight loss because very fine particles produced from each step could not be recovered through filtration. This was because the filtration rate was so low that a part of the slurry solution was decanted in order to speed up the filtration. The loss of coal was determined by comparing the ash contents in the coal. The assumption was that coal ash was not dissolved through each step. Also, the weight loss of coal due to the sulfur reduction was considered to be negligible. The calculation was based on a proportionality relationship. The loss was extrapolated into a scale between 100% loss when the ash content is 100% and 0% when the ash content is the same as that of the untreated coal. For example, when the ash content of the leach coal is 10% and the ash content of the untreated coal is 8%, the weight loss would be:

$$\frac{100}{100-8} \times (10-8) = 2.17\%$$

4.1 Pittsburgh No. 8 Coal

Three series of experiments were conducted; namely, those for temperature effect, pH effect and concentration effect. It was found throughout all the experiments that the loss of coal due to oxidation with hypochlorite was negligible.

Hypochlorite leaching was conducted at 50, 60, 70, 80 and 90°C. No solid sodium hydroxide was added to the hypochlorite solution for this series of experiments. Table 3 presents the leaching results.

Table 3. Effect of Temperature on the Desulfurization of Pittsburgh No. 8 Coal

([OCl] = 0.49 molar, pH 12.6, 2 hours)*

Temperature, °C	50	60	70	80	90
TS, %	1.86(23.8)	1.78(27.0)	1.70(30.0)	1.66(32.0)	1.55(36.5)
PS, %	0.25(70.0)	0.24(70.7)	0.22(73.2)	0.22(73.2)	0.18(78.0)
OS, %	1.61(----)	1.54(3.8)	1.48(7.5)	1.44(10.0)	1.37(14.4)
Cl, %	0.71	0.72	0.79	1.30	1.35

*Values in parentheses are reduction percentages.

The reduction percentage values through the leaching which are given in the parentheses were calculated based on the amount of total sulfur, pyritic sulfur or organic sulfur in the untreated coal. Throughout all the leaching experiments for Pittsburgh No. 8 coal, sulfate sulfur content was found to be very small (less than 0.01%); thus, it was neglected in the calculation for the organic sulfur content. Table 3 shows that the reduction in total sulfur (TS), pyritic sulfur (PS) or organic sulfur (OS) increases as the temperature increases. The total sulfur was reduced by 36.5% at 90°C. This is the highest

reduction value in this series. The reduction values in total sulfur are mainly attributed to the reductions in pyritic sulfur not by those in organic sulfur. The pyritic sulfur content was reduced by 70% at 50°C and 78% at 90°C. However, very small amounts of organic sulfur were reduced. The organic sulfur was reduced from 1.6 to 1.37%, or by 14.4%, which was the maximum reduction in this series. Table 3 also shows that the chlorine content in the leach coal increases with increasing temperature. The chlorine content reaches 1.35% at 90°C. This is well above the threshold value. The threshold value is generally accepted as a level of 0.3% chlorine in coal (Wandless, 1957).

The temperature effect on the leaching rate of pyritic sulfur is generally very small, which suggests that the leaching may be limited by a diffusion process such as pore diffusion inside the coal particle. It seems that most of the organic sulfur (e.g., 80%) is not amenable to leaching by hypochlorite. This suggests that the organic sulfur structures in Pittsburgh No. 8 coal mainly are those which are intrinsically difficult to be leached out by hypochlorite.

Since the reduction in sulfur forms is at maximum at 90°C as shown in Table 3, this temperature was used for all the subsequent series of experiments for the Pittsburgh No. 8 coal. The next series was conducted particularly in order to reduce the chlorine content in the leach coal by adding various amounts of solid sodium hydroxide, i.e., by changing the pH of the hypochlorite solution. The results are given in Table 4.

Table 4. Effect of pH on the Desulfurization of Pittsburgh No. 8 Coal**(90°C, [OCl⁻] = 0.4 molar, 2 hours)***

pH	11.47	12.46	13.01	13.14	13.23
NaOH, M	0	0.035	0.2	0.4	0.8
TS, %	1.94 (20.5)	1.73 (29.1)	1.58 (35.2)	1.56 (36.1)	1.68 (31.1)
PS, %	0.53 (35.4)	0.34 (58.6)	0.24 (70.8)	0.24 (71.1)	0.30 (63.7)
OS, %	1.41 (11.8)	1.39 (13.1)	1.34 (16.2)	1.32 (17.3)	1.38 (13.6)
Cl, %	1.75	1.51	0.56	0.30	0.37

* Values in parentheses are reduction percentages.

The pH was varied from 11.47 to 13.23 as shown in Table 4. It is seen that the chlorine content decreases from 1.75 to 0.3% as pH increases from 11.47 to 13.14. However, further increase in pH from 13.14 to 13.23 increases the chlorine content from 0.30 to 0.37%. These results show that there is a minimum value of the chlorine content at pH 13.14, or at 0.4 molar sodium hydroxide solution. The data in Table 4 show that at pH 13.14, the reduction of TS, PS and OS is at a maximum. The minimum sulfur values are 1.56% total sulfur, 0.24% pyritic sulfur and 1.32% organic sulfur. This may be explained by two reaction mechanisms that take place simultaneously during the leaching process: one is the leaching reaction and the other is hydrolysis. The leaching rate of the sulfur forms would increase with decreasing pH because decreasing pH would increase the rate of the cathodic reaction of hypochlorite dissociation (Equation (11)). However, the hydrolysis (Equations (14) and (15)) increases as pH increases. This hydrolysis in turn increases the reduction in the sulfur forms and decreases chlorine content. The decrease in sulfur reductions as pH increases from 13.14 to 13.23 may be explained by a

mechanism in which the hydrolysis levels off above pH 13.14 but the leaching rate decreases as mentioned previously. However, the increase in chlorine content as pH increases from 13.14 to 13.23 cannot be explained by this mechanism and is not well understood at this time.

Using the optimum values of pH 13.14 and temperature 90°C previously determined, a series of experiments was conducted to determine the effect of hypochlorite concentration. The concentration was varied from 0.2 to 0.6 molar and the results are given in Table 5.

Table 5. Effect of Hypochlorite Concentration on the Desulfurization of Pittsburgh No. 8 Coal (90°C, pH 13.14, 2 hours)*

Concentration, M	0.2	0.3	0.4	0.6
TS, %	1.75 (28.3)	1.62 (33.6)	1.56 (36.1)	1.71 (29.9)
PS, %	0.29 (64.2)	0.31 (62.4)	0.24 (71.1)	0.22 (73.1)
OS, %	1.51 (5.8)	1.36 (14.9)	1.32 (17.3)	1.54 (3.8)
Cl, %	0.18	0.23	0.30	0.60

* Values in parentheses are reduction percentages.

The data given in Table 5 show the same trend as for the effect of pH as shown in Table 4. The sulfur reductions increase as the hypochlorite concentration increases from 0.2 to 0.4 molar, but decreases as it increases further. The reduction in pyritic sulfur is an exception. The deterioration of desulfurization with application of higher hypochlorite concentration (0.6 molar) may be due to the rigorous chlorination of coal at the high concentration level. The chlorine content with the 0.6 molar hypochlorite leaching rises to 0.6% which is twice as much as that at 0.4 molar hypochlorite.

The leaching behaviors of the sulfur forms in this series or as a whole may be explained by a mechanism in which hypochlorite ions are adsorbed on the coal surface, followed by sulfur reduction and chlorination of the coal matrix. The surface concentration of the adsorbed hypochlorite at 0.6 molar may be greater than that at 0.4 molar. This higher surface concentration of the species can chlorinate the coal structure more rigorously than that at 0.4 molar, as can be seen from the chlorine analysis. Thus, the remaining surface concentration of hypochlorite may be lower than that at 0.4 molar, leading to deterioration of the desulfurization.

4.2 Illinois No. 6 Coal

In the early stages of leaching of Illinois No. 6 coal, the coal was leached at 0.4 molar hypochlorite at room temperature without addition of solid sodium hydroxide. It was found that the temperature of the leach slurry went up significantly above room temperature, indicating that the coal was dissociated by oxidation during leaching. The filtrate was a black solution. According to literature (Mayo and Kirshen, 1979), the black solution contains oxidation-resistant benzene and aliphatic carboxylic acids as the principle organic products. Bubbles which were believed to be carbon dioxide were seen on top of the leach solution. Also the dried and filtered coal appeared to be much harder than before. Ash analysis showed that the ash content in the leach coal increased significantly, indicating that the coal was oxidized and lost its weight. For example, in one experiment, 20 grams of coal was leached in a 100 ml solution of 0.4 molar hypochlorite and the initial pH 11.41 at room temperature. Soon after adding the coal into the hypochlorite solution, the temperature went up continuously to 39°C in 30 minutes. Bubbles were produced violently in the beginning of the reaction. After one-hour

leaching, the coal was filtered and dried, and the pH of the filtrate was found to have decreased to 7.20. The ash content of the leach coal was analyzed to be 10.88%. This ash content was translated into the weight loss of 3.11% using the method mentioned previously.

Next, ammonia pretreatment was tested in an effort to reduce the oxidation of Illinois No. 6 coal with hypochlorite. Ammonia pretreatment was applied prior to leaching and hydrolysis by Brubaker and Stoicos (Brubaker and Stoicos, 1985). In one experiment of this study, 20 grams of coal was pretreated in a 50-ml concentrated ammonia hydroxide solution (14.8 molar) at room temperature for 1 hour. Then the coal was filtered and washed thoroughly with distilled water. This pretreated coal was leached in a 100-ml solution of 0.4 molar hypochlorite and initial pH 11.41. These conditions were the same as those of direct leaching without pretreatment which was mentioned previously. The temperature of the coal slurry during the leaching went up to 39°C in 30 minutes which was the same temperature rise as in the previous test. After one-hour leaching, the coal was filtered and dried, and the pH of the filtrate was found to decrease to 7.94 which was higher than that in the previous case. The ash content of the leach coal was analyzed to be 9.54%. This ash content was translated into the weight loss of 1.65% which was smaller than that in the previous test. The observation of the pH decrease and weight loss through the leaching of the two different treatment methods may lead one to believe that the ammonia pretreatment reduces the oxidation of Illinois No. 6 coal somewhat in the subsequent hypochlorite leaching step. However, as mentioned previously, the Pittsburgh No. 8 coal did not lose its weight through leaching with hypochlorite even at 90°C. The temperature of the leach slurry did not rise. No bubbles

were observed on top of the slurry and the color of the leach solution did not change.

Also, the ash content of the leach coal did not change from that of the untreated coal.

These data prove that the role of ammonia in the pretreatment was to reduce the weight loss of Illinois No. 6 coal in the subsequent leaching step with hypochlorite. However, the ammonia pretreatment was not necessary for Pittsburgh No. 8 coal because the coal did not lose its weight through leaching with hypochlorite. It is speculated that the acidic groups on the coal surface such as phenolic and carboxylic groups may play a role in coal oxidation. Comparison of the total acid concentrations between the two coal samples reveals that the Illinois No. 6 coal has much higher concentration than that of the Pittsburgh No. 8 coal as shown in Table 1. It is also speculated that the coal oxidation has much to do with the total acidic groups existing on the coal surface. However, the investigation over the coal oxidation with hypochlorite was beyond the scope of the present study. There was circumstantial evidence to reinforce this speculation. As mentioned previously, the Illinois No. 6 coal was less oxidized somewhat in the leach step with hypochlorite after the coal had been pretreated with ammonia. The concentration of the total acidic group on the Illinois No. 6 coal was found to be reduced from 3.14 to 2.74 mmol/g coal or by 12.7% through the ammonia pretreatment. Thus, the ammonia pretreatment was applied to all the subsequent experiments with Illinois No. 6 coal.

Unlike the desulfurization of Pittsburgh No. 8 coal, Illinois No. 6 coal was leached at room temperature and then hydrolyzed. This was due to the fact that Illinois No. 6 coal could not be leached at high temperature because of the problems connected with severe weight loss. Thus, Illinois No. 6 coal was leached at room temperature and

the leach coal was subsequently hydrolyzed at 90°C, and these two steps were repeated once in the second stage. Twenty grams of leach coal was produced each time by reacting it in 100 ml of 0.6 molar hypochlorite at room temperature at natural pH; that is, without addition of solid sodium hydroxide. Then three hydrolysis experiments were conducted using this leach coal to determine the optimum conditions especially in terms of the concentration of the hydrolysis reagents. The results are provided in Table 6.

**Table 6. Effect of Reagents on the Hydrolysis of Illinois No. 6 Coal
(90°C, 1 hour)**

Concentration, M	Na ₂ CO ₃ , 0.3	NaOH, 0.1	NaOH, 0.3
TS after leaching, %	3.15	3.15	3.15
Cl after leaching, %	1.58	1.58	1.58
TS after hydrolysis, %	3.14	2.97	2.68
Cl after hydrolysis, %	0.233	0	0.092
Ash after hydrolysis, %	15.58	10.98	15.43
Wt loss after hydrolysis, %	8.22	3.22	8.06

It can be seen that all the hydrolysis conditions reduce the chlorine content from 1.58% to below its threshold value. The hydrolysis with 0.3 molar sodium carbonate is not effective because it can not reduce the total sulfur content. Thus, this reagent hydrolysis was discarded. The hydrolysis at 0.3 molar sodium hydroxide seems more effective than that at 0.1 molar sodium hydroxide because the total sulfur content at the former condition is significantly lower than that at the latter condition. Thus, all the subsequent hydrolysis experiments were conducted using 0.3 molar sodium hydroxide.

This condition was particularly selected although the coal weight loss amounted to 8.06% as opposed to 3.22% at 0.1 molar sodium hydroxide. The underlying judgment was that this much coal weight loss should be tolerated for the additional reduction in total sulfur by 0.29%.

Table 7 presents data from two experiments conducted to determine the effect of sodium hydroxide concentration in the leach solution. One experiment was conducted at 0.6 molar hypochlorite without addition of solid sodium hydroxide and the other experiment was conducted at the same hypochlorite concentration and 0.1 molar sodium hydroxide.

Table 7. Effect of Sodium Hydroxide Concentration in the Leach Solution on the Leaching of Illinois No. 6 Coal

([OCl] = 0.6 molar, room temperature)

Sodium hydroxide concentration, M	0	0.1
pH of the leaching solution	11.63	12.59
TS, %	3.15	3.07
Cl, %	1.58	3.44
Ash, %	10.45	14.14
Weight loss, %	2.64	6.65

It is seen that the inclusion of solid sodium hydroxide in the leach solution at the level of 0.1 molar yields worse results in terms of chlorine content, ash content and weight loss. Thus, no solid sodium hydroxide was added to the leach solution for all the subsequent leaching experiments.

The next series of experiments was conducted to determine the effect of hypochlorite concentration in the leach solution. For each concentration, two cycles of experiments were conducted. Coal was leached and hydrolyzed in the first stage and the leach coal was leached and hydrolyzed again under the same conditions in the second stage. The results are given in Table 8 for the first stage.

Table 8. Effect of Hypochlorite Concentration on the Desulfurization of Illinois No. 6 Coal in the First Stage*

Concentration	TS, %	PS, %	OS, %	Cl, %	Ash, %	Wt loss, %
Leaching 0.2 M [ClO ⁻]	3.33 (11.4)	0.25 (24.2)	3.08 (7.5)	0.29	8.47	0.49
Hydrolysis 0.3 M [OH ⁻]	2.74 (27.1)	0.26 (21.2)	2.48 (25.5)	0	15.25	7.86
Leaching 0.4 M [ClO ⁻]	3.35 (10.9)	0.29 (12.1)	3.06 (8.1)	1.26	9.54	1.65
Hydrolysis 0.3 M [OH ⁻]	2.89 (23.1)	0.23 (30.3)	2.67 (19.8)	0	14.40	6.94
Leaching 0.6 M [ClO ⁻]	3.15 (16.2)	0.30 (9.1)	2.86 (14.1)	1.58	10.45	2.64
Hydrolysis 0.3 M [OH ⁻]	2.68 (28.7)	0.23 (30.3)	2.45 (26.4)	0.09	15.43	8.06
Leaching 0.8 M [ClO ⁻]	2.74 (27.1)	0.28 (15.2)	2.47 (25.8)	4.52	13.54	6.00
Hydrolysis 0.3 M [OH ⁻]	2.53 (32.7)	0.25 (24.2)	2.28 (31.5)	0.19	15.41	8.31

* Values in parentheses are reduction percentages.

It is seen that the reduction in total sulfur increases with increasing hypochlorite concentration in the leach solution. Throughout all the desulfurization experiments for Illinois No. 6 coal, sulfate sulfur content was found to be very small (less than 0.01%); thus, it was neglected in the calculation for the organic sulfur content. The reduction increases from 11.4% to 27.1% when the hypochlorite concentration increases from 0.2 to 0.8 molar. The total sulfur is reduced further through hydrolysis. It is reduced by

15.7% more by hydrolysis when the coal was leached at 0.2 molar hypochlorite and by 5.6% more when the coal was leached at 0.8 molar hypochlorite.

For the pyritic sulfur reduction, it seems that there is no effect from either changing hypochlorite concentration or hydrolysis. The pyritic sulfur reduction was by 21% on the average. On the other hand, the organic sulfur reduction seems to follow a pattern similar to that of the reduction of total sulfur reduction. The largest organic sulfur reduction occurred when the coal was leached at 0.8 molar hypochlorite and then hydrolyzed. The organic sulfur was reduced from 3.33% to 2.28% or by 31.5%, which is a significant reduction considering that organic sulfur is generally very difficult to be leached.

When it comes to chlorination of coal with hypochlorite, there seems to be no problem because leaching with hypochlorite raised the chlorine content to a high level up to 4.52%, but hydrolysis lowers the level far below the threshold value as can be seen in Table 8. The weight loss increases as the hypochlorite concentration increases in the leaching step. The weight loss was by 0.49% when the coal was leached at 0.2 molar hypochlorite, and increased to 6.00% when the coal was leached at 0.8 molar hypochlorite. However, additional weight loss is caused by the subsequent hydrolysis, and the weight loss seems to be at the same level around 7-8%, irrespective of hypochlorite concentration in the leaching.

Table 9 provides the data for the desulfurization results after the second-stage leach and hydrolysis. Comparison of the data for the total sulfur reduction between the first and the second stages (Tables 8 and 9) reveals that the desulfurization in the second stage is not as effective as that in the first stage. It is also seen that the total sulfur

reduction increases by increasing hypochlorite concentration from 0.2 to 0.4 molar, yields a maximum value of 39.6% at 0.4 molar, and then decreases as hypochlorite concentration increases further. This phenomenon was detected in the first stage; however, it was not as pronounced as in the second stage. This mechanism may be due to the more rigorous chlorinations at higher hypochlorite concentrations as explained previously for the leaching of Pittsburgh No.8 coal (see Table 5). Table 9 also shows that the pyritic sulfur was not additionally reduced by the second-stage desulfurization.

Table 9. Effect of Hypochlorite Concentration on the Desulfurization of Illinois No. 6 Coal in the Second Stage*

Concentration	TS, %	PS, %	OS, %	Cl, %	Ash, %	Wt loss, %
Leaching 0.2 M [ClO ⁻]	2.80 (25.5)	0.22 (33.3)	2.58 (22.5)	0.98	13.77	6.25
Hydrolysis 0.3 M [OH ⁻]	2.67 (29.0)	0.19 (42.4)	2.49 (25.2)	0	14.46	7.00
Leaching 0.4 M [ClO ⁻]	2.70 (28.2)	0.23 (30.3)	2.47 (25.8)	2.89	15.67	8.32
Hydrolysis 0.3 M [OH ⁻]	2.27 (39.6)	0.20 (39.4)	2.07 (37.8)	0.09	15.97	8.67
Leaching 0.6 M [ClO ⁻]	2.57 (31.6)	0.25 (24.2)	2.32 (30.3)	4.07	16.15	8.84
Hydrolysis 0.3 M [OH ⁻]	2.53 (32.7)	0.24 (27.3)	2.29 (31.2)	0	16.21	8.90
Leaching 0.8 M [ClO ⁻]	2.60 (30.9)	0.22 (33.3)	2.38 (28.5)	7.04	18.28	11.15
Hydrolysis 0.3 M [OCl ⁻]	2.48 (34.0)	0.23 (30.3)	2.26 (32.1)	0	18.41	11.30

* Values in parentheses are reduction percentages.

The organic sulfur reduction seems to follow the same pattern as that for the total sulfur reduction. The largest organic sulfur reduction occurred when the coal was leached at 0.4 molar hypochlorite and hydrolyzed. This is contrasted with the first stage because the largest organic sulfur reduction in the first stage comes at 0.8 molar hypochlorite. The

organic sulfur at 0.4 molar in the second stage is reduced from 3.33% to 2.07%, or by 37.8%. This reduction is a significant accomplishment since organic sulfur is considered to be a refractory sulfur source in coal. Table 9 shows the optimum hypochlorite concentration for the desulfurization of Illinois No. 6 coal. It is undoubtedly 0.4 molar hypochlorite because the maximum organic sulfur reduction is achieved at this concentration and the coal weight loss by 8.67% is not exorbitant for this desulfurization method using a strong oxidation reagent of hypochlorite.

CHAPTER 5

CONCLUSIONS

1. The desulfurization of Pittsburgh No. 8 coal with hypochlorite is effective with one step of leaching at 90°C while that of Illinois No. 6 coal requires three consecutive steps of pretreatment with ammonia at room temperature, leaching with hypochlorite at room temperature and hydrolysis at 90°C for effective leaching.
2. The desulfurization method with Pittsburgh No. 8 coal can reduce mainly pyritic sulfur from 0.82% to 0.24% or by 71.1% at the optimum condition of 0.4 molar hypochlorite and 0.4 molar sodium hydroxide in the leach solution.
3. The desulfurization method with Illinois No. 6 coal can reduce significant amounts of organic sulfur. Organic sulfur was reduced from 3.33% to 2.07% or by 37.8% reduction with the optimum operation of leaching at 0.4 molar hypochlorite at room temperature followed by hydrolysis in 0.3 molar sodium hydroxide at 90°C.
4. The chlorination of the coal structure was observed during the desulfurization of both coals. However, the chlorine content in the Pittsburgh No. 8 coal was controlled at the minimum level of 0.3% which is the threshold value. The chlorine content in the Illinois No. 6 coal was reduced far below the threshold value through hydrolysis at each stage.
5. Weight loss of Illinois No. 6 coal occurs when reacting with hypochlorite. The weight loss was by 8.67% at the optimum conditions of leaching and hydrolysis. However, no weight loss of Pittsburgh No. 8 coal was detected.

6. This desulfurization method has merits as a feasible technology for some special commercial processes. It has merits on Pittsburgh No. 8 coal because this one-step operation can emulate the Meyers Process which utilizes multiple stages of rigorous leaching. Also, this desulfurizing method has merits on Illinois No. 6 coal because it can achieve significant organic sulfur reduction at moderate conditions. However, more research work is necessary on a larger scale such as bench scale or pilot plant scale before this technology is implemented for a commercial process.

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