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REVIEW ARTICLE
A REVIEW OF COAL DESULFURIZATION

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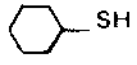
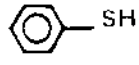
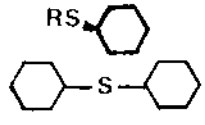
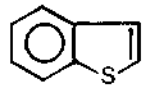
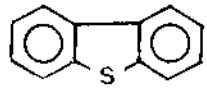
A REVIEW OF COAL DESULFURIZATION

INTRODUCTION

Sulfur in coal is present in both organic and inorganic forms and ranges from 0.5 to 8% by weight in a coal seam (Greer, 1977). Inorganic sulfur is primarily in the form of pyrite (FeS_2), but small amounts of sulfite also are present. Meyers (1977) had listed a Table of coals (20 coals) from all the major producing regions of the world and reported a range of sulfur from 0.38% to a high of 5.32%. The pyritic sulfur in these selected coals ranged from 0.09% to a high of 3.97%.

Organic sulfur is found in coal in different functional groups and Given (1961) was the first to publish an extensive list of organic functional groups associated with coal. These are shown in the following Table 1.

Table 1. Organic Sulfur Species in Coal

Thiols	
a) alkyl	RSH
b) cyclic	
c) aromatic	
Sulfides	
a) alkyl	RSH
b) alkyl-cycloalkyl	
c) cyclic	
Disulfides	RS-SR
Thiophene	
Benzothiophene	
Dibenzothiophene	

Several years later Hayatsu *et al.* (1975) confirmed the benzothiophene and dibenzothiophene structures in coal by oxidation with dichromate where they isolated several aromatic acids of benzothiophene and dibenzothiophene.

In the desulfurization of coal, the most difficult form of sulfur to remove is the organic sulfur. The organic sulfur is partially removed by grinding the coal and washing it thoroughly with solvents.

This review of the desulfurization of coal will focus on the attempts that have been made to remove both inorganic and organic sulfur forms. Most of these methods have used an oxidation procedure, but later attempts have used elevated temperatures with alkali in organic solvents.

DESULFURIZATION VIA OXIDATION PROCEDURES

Weathering

Chakrabarti *et al.* (1982) was the first to report the organic desulfurization of coal by weathering or auto-desulfuration. He reported a decrease in organic sulfur from 2.29% to 1.87% (18% decrease) over a 4-year period. This same coal when ground (<63 um) continued to lose organic sulfur content and after an additional 228 days had dropped to 1.40%. The pyritic sulfur decreased 93% during the 4 years, but remained constant for the remaining 228 days.

The PETC Process

The PETC process (Pittsburgh Energy Technology Center) is one of the oldest desulfurization processes that was elevated to pilot plant scale at the TRW San Capistrano, CA location (Morrison, 1981a). This "oxydsculfurization" process utilizes air pressure at elevated temperatures with a wet coal slurry. A majority of the pyritic sulfur is removed along with a small percentage of organic sulfur. Pyritic sulfur is oxidized to iron oxide and sulfuric acid which is neutralized by lime

$$4FeS_2 + 15O_2 + 8H_2O \text{----} > 2Fe_2O_3 + 8H_2SO_4$$

Unfortunately, due to a cutback in DOE funds in 1980, this project was discontinued. Over 20 different coal were oxydesulfurized at PETC. As mentioned previously, almost all of the pyritic sulfur can be removed by the PETC process, but it has limited success with organic sulfur removal. Table 2 illustrates the reduction in organic sulfur for the 24 coal samples.

Table 2. Organic Sulfur Removal by the PETC Process

No. of Coals	Before		After	
	Range of % S	Ave. & Ave. Dev., % S	Range of % S	Ave. & Ave. Dev., % S
10 coals	0.39 – 0.78	0.61 ± 11	0.36 – 0.79	0.55 ± 0.14
7 coals	0.82 – 1.14	1.07 + 15	0.76 0.84	0.83 ± 0.05
7 coals	1.53 – 2.33	2.05 ± 17	1.22 – 2.03	1.78 ± 0.26

Temperatures were varied in the PETC process from 150° C to one reaction which was run at 250° C. All other reactions were run at 200° or lower. As expected, the oxygen uptake by the coal parallels the heating value loss, and the heating value loss reached a maximum value of 34%. The heating value loss is shown in Table 3, and the reactions are grouped according to the batch temperature. The PETC process does an excellent job of removing the pyritic sulfur, but the organic sulfur removal is hampered by a parallel loss in heating value for the coal.

Table 3. Heating Value Loss in the PETC Process

Temperature	No. of Coal Samples	Percent Heating Loss
150°	9	7.82 ± 4.1
160°	2	3.53 ± 2.7
180°	8	12.7 ± 2.5
200°	4	12.7 ± 1.9
250°	1	18.2

The Ledgemont Oxygen Process

A patent was issued to the Chemical Construction Corp. in 1974 for the desulfurization of coal with air and water (Thomas *et al.* 1974) and a year later Agarval *et al.* (1975) had treated coal with oxygen and water in an attempt to desulfurize the coal. His work was done at the Ledgemont Laboratory of Kennecott Copper Corporation. This Ledgemont oxygen process is similar to the PETC process except they have used oxygen in place of air, and their leaching solution was 0.2 M in Na_2CO_3. The success in removing sulfur with this process is shown in Table 4.

Table 4. Ledgemont Oxygen Leaching Desulfurization Process[a]

Temp	% Pyritic Sulfur Loss	% Organic Sulfur Loss	% Heating Value Loss
200°	56.7%	14.3%	17.4%
220°	70.2%	10.9%	19.2%
240°	54.0%	19.7%	22.6%

[a]Each coal was leached 1h. at 100° with 0.34 MPa O_2 and 0.2 M Na_2CO_3. A second process at the indicated temperature was done with 0.2 Na_2CO_3 in a nitrogen atmosphere for 1 h.

Again, the greatest success with the Ledgemont process was done with the pyritic sulfur content, and the organic sulfur reduction was at the expense of the heating value of the coal.

Sareen Ammonia — Oxygen Desulfurization

As a modification to the Ledgemont process, Sareen (1977) attempted to remove the sulfur from coal with an ammonia/oxygen/water system. With a reaction time of 2 hours, this process removed 90% of the pyritic sulfur and up to 25% of the organic sulfur.

Sareen's process used an Illinois #6 coal (Total sulfur 4.99%, pyritic sulfur 2.06% and organic sulfur 2.28%) which was ground in a closed-circuit wet ball mill to − 100 mesh. The coal slurry was treated at 130° C in an oxygen-sparged leach reactor at an oxygen pressure of 300 psi.

The chemical equation for the oxidation of pyritic sulfur with an ammonical solution is given below:

$$FeS_2 + 4NH_3 + 7/2\ H_2O + 15/4O_2 \text{-----> } 4NH_4^{\cdot} + 2SO_4^{\cdot} + Fe(OH)_3$$

The sulfide sulfur is converted to soluble sulfate and can be easily removed from the coal matrix via aqueous solutions. Stoichiometrically, the molar ratio of FeS_2/NH_3 is 4, and the experimental runs were always higher than 6.5. The ammonia concentration was varied from 0.5 M to 5.01 M; and the pyritic sulfur removal was found to be independent of the ammonia concentration. However, the organic sulfur removal increased with increase in ammonia concentration from a low of 15% to a high of 23% removal.

No mention was made of the ammonia retention by the coal, but a detailed study of the oxygen consumption was done. Three sources were identified as removing oxygen; 1) oxygen reacting with pyrite 2) oxygen uptake by the coal and 3) oxygen reacting with coal to form carbon dioxide. All three processes were found to be nearly equivalent in oxygen consumption. A fourth area for oxygen consumption could be through the organic sulfur oxidation, but there was no way to measure this oxygen consumption.

The total oxygen consumption by this method, which also allows for a 20% increase for organic sulfur removal, is the same quantity required by the oxygen/water system which is 1000 tons/day of oxygen for a plant size of 8000 tons/day of coal with sulfur content of 4% (50% pyritic and 50% organic sulfur).

A third area Sareen studied was the overall thermal efficiency. Unfortunately the ammonia/oxygen system lost 13% of the thermal efficiency compared to only 8% for the oxygen/water process. They contributed this additional loss to the formation of water soluble carbon acids formed under the basic conditions.

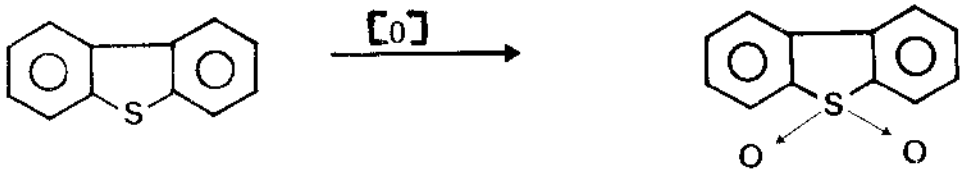
A Table which illustrates the success of this ammonia leaching process as a function of the ammonia concentration is shown below.

Table 5. Pyritic and Organic Sulfur Removal via Air/Ammonia Leaching

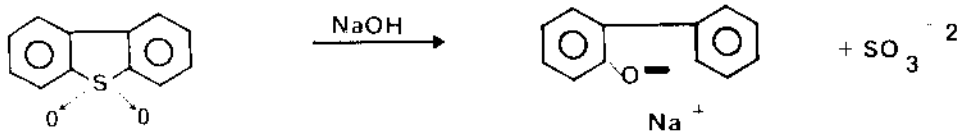
Ammonia Concentration	Reaction Time	Pyritic Sulfur Removal	Organic Sulfur Removal
0.5M	30 min	67%	12%
	120 min	70%	18%
	200 min	82%	30%
1.04M	30 min	48%	17%
	120 min	80%	28%
	200 min	87%	39%
1.94M	30 min	68%	35%
	120 min	86%	—
	200 min	86%	41%
2.95M	30 min	52%	26%
	120 min	81%	35%
	200 min	92%	44%
5.01M	30 min	—	—
	120 min	—	48%
	200 min	—	—

Friedman Air-Nitrogen Dioxide Desulfurization

The most detailed study of oxidative desulfurization of coal was reported by Friedman *et al.* (1977). He attacked the organic sulfur content of coal, specifically, substituted thiophene, with an oxidizing agent which converted the organic sulfide to a sulfone:



Subsequent basic hydrolysis of the sulfone would remove the sulfur as sulfur dioxide:



The oxidative systems they explored in their studies were nitrogen dioxide and air nitrogen dioxide are known to convert sulfides to sulfone, however, when the coal was treated with nitrogen dioxide, the coal consumed the nitrogen dioxide through the nitration of the coal matrix and, consequently, consumed too much nitrogen dioxide to make this system economically feasible.

The experiments with air were more fruitful, and they were successful in removing 95% of the pyritic sulfur and 40% of the organic sulfur. The pyritic sulfur was removed satisfactorily at temperatures as low as 150° C at reaction times of 1 hr. However, if the air pressure was 200 psi or lower, the reaction is much slower, and improves rapidly above 500 psi.

They reported an upper limit for organic sulfur removal between 40 and 50%. Higher values of organic sulfur can be accomplished with temperatures higher than 200° C, but the heating values of the coal residue is reduced considerably. If the temperature was kept below 200° C, 90% of the heating value could be recovered.

In their oxydesulfurization reaction, no sludge formation was found and the undesirable by-product was the sulfate ion which could be removed as a precipitate with calcium ion ($CaSO_4$). The results of this oxydesulfurization process are shown in the following Table 6.

Ames Oxydesulfurization

Wheelock *et al.* (1983) of Ames Laboratory, have done extensive oxidative experimentation with air and molecular oxygen under acidic and alkaline conditions over the past decade. In their chemical oxydesulfurization process, they have found much better results under alkaline conditions, moreso than under acidic conditions.

The basic conditions used in the Ames' process was 0.2M Na_2CO_3, and both air and oxygen were run at 150° C. Whether air or oxygen were used, the partial pressure of oxygen was always kept at 3.4 atm. Under these conditions the organic sulfur content decreased very little, but pyritic sulfur was decreased over 79%. Reaction times were 1 hr. (See Table 7)

Table 6. Friedman Oxydesulfurization

Temperature	Coal Seam Sample	Pyritic Sulfur Removal	Organic Sulfur Removal
150°	Ill. No. 5	88.9%	
	Minshall (IN)	95.2%	
	Lovilia No. 4, (IO)	92.2%	
	Bevier (KA)		20%
	Mammoth (MO)	—	20%
	Wym. No. 9	—	27.3%
160°	Pittsburgh (OH)	92.8%	
	Lower Freeport (PA)	95.8%	
180°	Brookville (PA)	96.8%	—
	Pittsburgh (OH)	—	46.7%
	Lower Freeport (PA)	—	20.0%
200°	Ill. No. 6		43.4%
	Minshall (IN)	—	20.0%

Table 7. Leaching Coal with Alkali and Air or Oxygen[a]

Coal	Molarity Na_2CO_3	Gas	% Reduction Pyritic Sulfur	% Reduction Organic Sulfur	% Loss Heating Value
Pittsburgh No. 8	0	Air	58%	2%	0.7%
	0.2	Air	77%	7%	4.2%
	0	O_2	58%	0%	0.4%
	0.2	O_2	81%	4%	7.8%
Ill. No. 5	0	Air	67%	+4%[b]	1.1%
	0.2	Air	70%	+7%	8.7%
	0	O_2	67%	+4%	2.1%
	0.2	O_2	74%	+7%	11.7%
Lower Kittanning Coal	0	Air	91%	+116%	1.7%
	0.2	Air	81%	+10%	2.9%
	0	O_2	96%	+110%	0.7%
	0.2	O_2	79%	+5%	2.5%

[a]Reactions were leached for 1 hr at 150° C with 3.4 atm of oxygen partial pressure.
[b](+) indicates an increase in sulfur.

By increasing the partial pressure of oxygen to 6.8 atm, a decrease in organic sulfur of 13% was realized while pyritic sulfur decreased the same as with 3.4 atm of oxygen. Effects of temperature also were studied and maximum sulfur removal occurred between 120° and 150° C for 3.4 atm and 140°-160° C at 13.6 atm oxygen partial pressure. Heating values fell off rapidly with increasing temperatures and higher oxygen partial pressure, and at 200° C the heating value recovery had dropped to 35%.

Wheeler also studied the effects of organic sulfur removal after precleaning the coal. When using precleaned coal, the pyritic sulfur decreased 73% and the organic sulfur increased from 3.60% to 4.04%. In general, the organic sulfur removal increased with increase in oxygen partial pressure, reaction time and temperature, but the heating value loss increased dramatically with an oxygen partial pressure increase.

In summary, with the Ames chemical oxydesulfurization process, high sulfur bituminous coals can be effectively desulfurized with hot dilute alkaline solutions containing dissolved oxygen. Sodium carbonate or bicarbonate solutions at concentrations of 0.2 M to 0.4 M are the most effective. Higher concentrations promote sulfur removal, but at the sacrifice of the heating value loss. At 150° C the optium removal is obtained because at higher temperatures heating value loss is too great. These results are depicted in Table 7.

Desulfurization via Chlorinolysis

Chlorinolysis of coal to promote desulfurization was introduced by the Jet Propulsion Laboratory (JPL) in California in 1977 (Hsu *et al.*, 1977). Their process was a slurry-phase chlorination at ambient temperature of a ground, moist coal in an organic solvent. They attempted to dechlorinate the coal after hydrolyzing the coal at 60°. The dechlorination was done at 350°-550° with steam. Unfortunately, the chlorine content remained too high to make this a feasible process.

Corcoran *et al.* (1983), extended the study of chlorinolysis to different solvents near ambient temperatures and different reaction times. The solvents chosen for their study were water, methanol, carbon tetrachloride and a mixture of methanol and carbon tetrachloride (50/50 vol/vol). As expected, the pyritic sulfur reduction was high, 90% or greater, in most cases. However, the organic sulfur reduction was negligible except for the carbon tetrachloride/methanol mixed solvent where it reached 30.8% reduction for the Ill. No. 6 (hvC). Surprisingly, however, with an Ohio No. 8 (hvA), the reduction of organic sulfur varied from 11.8% to a high of 87% with methanol at 120° C. Unfortunately, the heating value lose and uptake of the chlorine in the coal matrix are two serious disadvantages of this method. (See Table 8)

Table 8. Desulfurization of Coal via Chlorinolysis

Coal	Reaction Temp.	Solvent	Chlorine Uptake	Reduction Pyritic Sulfur	Reduction Organic Sulfur	Heating Value Loss
Ohio No. 8 (hvA)	30°[a]	H_2O	0.396	98%	8.8%	—
	60°[a]	H_2O	0.376	97.5%	0%	—
	80°[a]	H_2O	0.295	95.9%	0%	—
Illinois No. 6 (hvC)	50°[b]	H_2O	0.070	13.4%	11.8%	0.3%
	50°[c]	H_2O	0.216	38.6%	24.6%	+0.9%[e]
	50°[d]	H_2O	0.351	65.9%	31.3%	0.4%
	50°[a]	H_2O	0.396	76.2%	27.4%	4.8%
Ohio No. 8 (hvA)	60°[a]	CCl_4	0.295	95.9%	0%	—
Illinois No. 6 (hvC)	50°[a]	CCl_4	0.413	32.9%	17.1%	+0.7%[e]
Ohio No. 8 (hvA)	50°[a]	CCl_4/MeOH	0.310	98.3%	30.8%	—
Illinois No. 6 (hvC)	50°[a]	CCl_4/MeOH	0.298	85.1%	44.0%	20.1%
Illinois No. 6 (hvC)	50°[a]	H_2O/MeOH	0.348	75.9%	28.9%	+3.2%[e]
Illinois No. 6 (hvC)	50°[a]	MeOH	0.339	87.3%	35.8%	32.8%

[a]- reaction time 120 min.
[b]- reaction time 8 min.
[c]- reaction time 20 min.
[d]- reaction time 45 min.
[e]- increase in heating value

Desulfurization via Bromination

Bromination also has been used by the Ames Laboratory group, (Venier *et al.*, (1984) and they reacted molecular bromine with a well stirred mixture of coal, water and methylene chloride. After collecting the brominated coal and washing it, the coal was fused at 380° C with potassium hydroxide. The percentage of sulfur removal by this method was 94%. If the coal sample was treated with potassium hydroxide before bromination, the desulfurization was only 65% effective. Unfortunately, the coal sample still retained bromine (1 Br/1000C) at the expense of losing hydrogen (approximately 25% hydrogen loss).

Desulfurization via Hydrogen Peroxide

Hydrogen peroxide was used to desulfurize coal, and Taylor *et al.*, (1981) reported limited success with organic sulfur, but complete removal of pyritic sulfur after 100 h. He treated his coal (<200 Tyler mesh) with 30% hydrogen peroxide for up to 16 days at temperatures below 40° C, but could only reduce the organic sulfur content from 2.4% to 2.2%.

Meyers' Ferric Sulfate Desulfurization Process

Milder oxidation methods have been used, and Meyers (1972) used an aqueous solution of ferric sulfate to remove pyritic sulfur. He was successful in removing 90-95% of pyritic sulfur, but little or no organic sulfur was removed.

Meyers initial process investigated 35 major coals with an average total sulfur content of 3.05% and an average pyritic sulfur content of 2.02%. The pyritic sulfur was converted to iron sulfate and elemental sulfur according to the following equation:

$$4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O + FeS_2 \text{-----} > 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8S$$

In this process the iron sulfates are removed by washing the coal, and sulfur is removed by vaporiztion or solvent extraction with toluene, acetone or kerosene. The ferric sulfate leach solution can be regenerated from the ferrous sulfate by oxidizing the aqueous ferrous sulfate with air under acidic conditions.

$$4\ FeSO_4 + 2\ H_2SO_4 + O_2 \text{-----} > 2\ Fe_2(SO_4)_3 + 2\ H_2O$$

Excess sulfates and acids are removed by treating the solution with lime (CaO) to restore the concentration of ferric sulfate to its original concentration for recycling.

Meyers compared his chemical cleaning method to a conventional coal washing process (based on the 1.4 mm, 1.90 float fraction of a float sink analysis). The summary of Meyers results and the conventional float sink method are shown in Table 9.

Table 9. Meyers Chemical Cleaning [$Fe_2(SO_4)_3$] and a Conventional Float Sink Process[a]

No. of	Initial		Meyers Process		Float Sink Process	
Coals	% S(ave)	Range of % S	% S(ave)	Range of % S	% S(ave)	Range of % S
11	1.36%	0.8-1.8%	0.61%	0.4-0.8%	1.11%	0.8-1.7%
9	3.04%	2.0-3.8%	1.15%	0.8-1.7%	2.16%	0.8-3.6%
12	4.92%	4.1-6.6%	1.81%	0.5-2.7%	3.32%	2.0-4.6%

[a]100 g of coal refluxed with 2000 ml of 1 N $Fe_2(SO_4)_3$ solutions from 4 to 6 hrs. Coal was filtered and refluxed an additional 4 to 20 hrs with fresh $Fe_2(SO_4)_3$ solution. Coal was filtered, washed with 0.2 N H_2SO_4 and water washed to remove soluble sulfates. Coal was extracted with 400 ml of toluene to remove sulfur.

For all of these coals treated by the Meyers chemical cleaning process, the average and average deviation for pyritic sulfur removal was 92.4 ± 1.49% while the total sulfur removal was 50.5 ± 9.47%.

Meyers chemical desulfurization process was converted to a process test plant which was built at TRW's Capistrano Test site in California. The plant processed 8-metric tons of coal per day and was operational for several years. However, today no further expansion is planned for the Meyers' process which is contributed mainly to the inability of the process to remove organic sulfur. (Morrison, 1981c)

Desulfurization via Cupric-Ions

Lompa-Krzymien (1982) was successful in removing 100% of the pyritic sulfur as well as the organic sulfur. The oxidizing agent in his reaction was aqueous solutions of cupric ions which oxidize the pyritic sulfur to sulfuric acid as follows:

$$FeS_2 + 14\ CuCl_2 + 8\ H_2O \text{ -----> } 14\ CuCl + FeCl_2 + 2\ H_2SO_4 + 12\ HCl$$

The mechanism for the oxidation of organic sulfur was not investigated, however, Lompa-Krzymien speculated that the sulfur atom was oxidized to sulfoxide or sulfone and carbon-sulfur bonds were cleaved to form sulfuric acid and carbonyl functional groups.

These reactions were carried out at 200° C for 1 hr with 5% or 10% cupric chloride solutions. At 150° C, the success in reaching 100% removal of total sulfur was not accomplished until after 2 days. Unfortunately, no mention was made of the amount of residue that was recovered. consequently, it would not be an effective method of sulfur removal if the recovery of the coal was very poor.

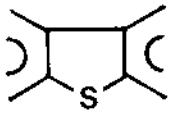
Gravi-Float — Gravi-Melt Process

The Gravi-Float and Gravi-Melt process are oxydesulfurization processes, but are used in conjunction with the Meyers process of desulfurization. (Meyers, 1979) The Gravi-Float process separates the coal into two fractions based on their specific gravity. The process uses a ferric sulfate leach solution (specific gravity 1.3-1.5) to float out a coal fraction that is exceptionally low in pyritic sulfur, ash and metal contaminants. The float fraction still contains the organic sulfur, and must be processed further if the sulfur content is too high.

The Gravi-Melt process is a desulfurization process which removes the organic sulfur content. Consequently, it could be used efficiently with the float fraction from the Gravi-Float separation or with the Meyers' process which has effectively removed the pyritic sulfur.

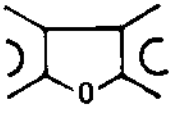
In the Gravi-Melt process the organic sulfur is removed at elevated temperatures with sulfur at atmospheric pressure. The coal is mixed with a dry caustic which impregnates the coal at elevated temperatures to remove the organic sulfur. This process in conjunction with the Gravi-Float process was demonstrated to remove 88% of the sulfur in an Appalachian coal and 92% from a Kentucky coal.

In the Gravi-Melt process the coal is mixed with potassium hydroxide and sodium hydroxide (50/50) at 370° for 1/2 hr. and, subsequently, water washed. (Morrison, 1981c) A suggested reaction pathway for organic sulfur and pyritic sulfur removal is shown below:



coal

$$+\ 2KOH \text{ -----> } K_2S +$$



coal residue

$$8\ FeS_2 + 30\ KOH \text{-----}> 4\ Fe_2O_3 + 14\ K_2S + K_2S_2O_3 + 15\ H_2O$$

Arco Desulfurization Process

The ARCO desulfurization process (A) is similar to the Ledgemont and PETC processes, but is different in the fact that it incorporates a complexing agent for metals, sodium oxalate. The batch tests were run at 120° C for 1 hour at 2.14 atm and the pyritic sulfur removal varied between 88% and 98%. The complexing agent, sodium oxalate, was successful in removing between 78% and 94% of the iron in the five bituminous coals studied.

A second process with a proprietory agent was applied to the coals under more severe conditions after their initial treatment, and 97% to 99% of the pyritic sulfur was removed with 19% - 31% of the organic sulfur removed. Heating value recoveries for the ARCO process were reported to be better than 95% regardless of whether the one step or two step processes were used.

DESULFURIZATION WITH ALKALI METALS AND ALKALI AT ELEVATED TEMPERATURES

Hydrothermal Battelle Process

The hydrothermal treatment of coal by Battelle was begun in 1969 where the ground coal was treated with a caustic solution of 2 to 3% by weight of calcium hydroxide and 10% by weight of sodium hydroxide (Morrison, 1981e). This mixture was heated from 1/6 to 1/2 h. between 250° - 350° C at pressures ranging from 0.79 atm - 3.29 atm. The final treatment was filtration, washing with lime water and drying.

Battelle has adapted this process to continuous flow on a bench scale of 10 kg/h of coal. The continuous flow process was successful in removing 90 to 99% pyritic sulfur and 20 to 70% organic sulfur from several bituminous coals in the Midwestern and Eastern states.

The Battelle process has two distinct advantages in addition to desulfurization, and these are 1) the heating value loss is only 5% to 10% and 2) the trace metals are reduced considerably, e.g. beryllium 70% as a low to potassium 96% as a high.

This hydrothermal process has not gone from bench scale to the pilot plant stage because of the severe corrosion that occurs at elevated temperatures with alkali, and these problems will have to be solved prior to any pilot plant construction.

The success of the Battelle hydrothermal treatment is shown in Table 10 (Slambaugh, 1977)

Desulfurization of Subbituminous Coals with Sodium Hydroxide Solutions.

Droguette *et al.* (1981) made a study of subbituminous coals from LaUnion, Chile. They studied the effects of hydrolysis time, temperature, sodium hydroxide concentration and particle size on the solubilization, ash removal and sulfur reduction. They studied these reactions at two temperatures, 50° C and 80° C with a sodium hydroxide concentration varying from 5 g/dm^3 to 120 g/dm^3. The maximum solubility of the coal occurred at a sodium hydroxide concentration of 50 g/dm^3 where the solubility reached 25.2 wt % at 80° C and only 10.6 wt % for 50° C.

Table 10. Battelle Hydrothermal Process[a]

Coal Seam	S (before)[b]	S (after)[b]
Pittsburgh 8	4.6	0.9
Ohio 6	3.9	1.2
Pittsburgh	3.4	0.7
Upper Freeport	2.4	0.9
Lower Kittanning	2.2	0.9
Lignite	1.5	1.2
Western	1.0	0.3

[a]- laboratory scale
[b]- SO_2 equivalent (lb/mm BTU)

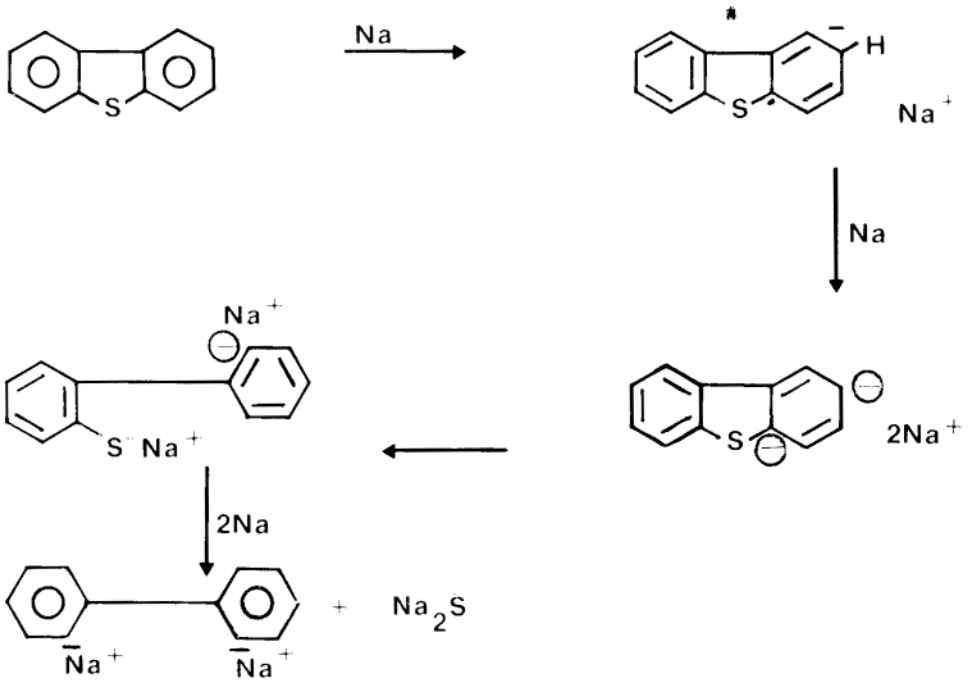
The hydrolysis times for these reactions varied from 1 hr. to 16 hrs., however, the greatest degree of hydrolysis occurred between the first and second hour. Ash content as well as sulfur content was decreased during this time, and their decrease is illustrated in Table 11.

Table 11. Sulfur and Ash Reduction

Temp.	NaOH conc. (g/dm^3)	Decrease % S (wt %)	Decrease Ash (wt %)
50°	5.0	23.8 ± 0.7	2%
50°	100.0	29.8 ± 0.9	3%
80°	5.0	24.6 ± 0.7	22%
80°	100.0	30.7 ± 0.9	28%

Desulfurization of Bituminous and Lignite Coals with Alkali Metals.

Alkali metals will react with organic sulfur compounds to convert the sulfur to sodium sulfide. Sternberg *et al.* (1974) reacted sodium metal with dibenzothiophene in decahydronaphthalene at 350° C under nitrogen, and converted dibenzothiophene to biphenyl, sodium sulfide and an insoluble layer. He explained the reaction with a mechanism patterned after Eisch (1963). The mechanism is illustrated below.



Sternberg did not perform his experiments on coal, but reacted the sodium with petroleum residuum containing 1.65% S. He ran his reactions in a hydrogen atmosphere, but noticed a decrease in sulfur with nitrogen as well. The results of his study are shown in the following Table 12.

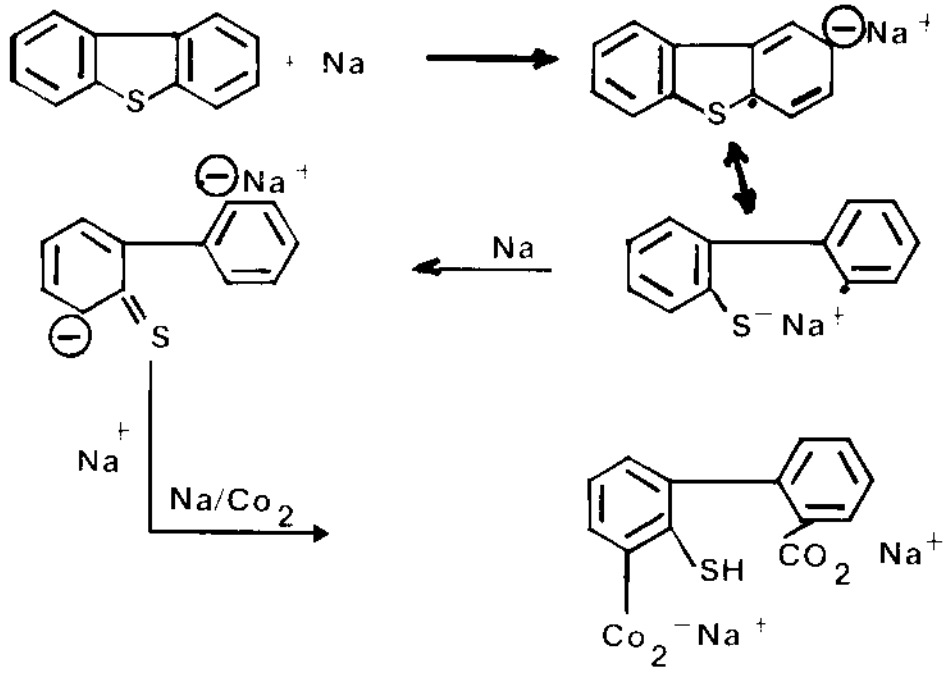
Table 12. Desulfurization of Petroleum Residuum with Sodium Metal[a] Containing 1.65 % S

Sodium per 100 g of Residuum	Na/S Mole Ratio	Gas Pressure (cold) psi	Time hr.	% S Decrease
3.7	3.1	1200	0.5	32%
3.7	3.1	200	0.5	57%
3.7	3.1	200[b]	6	67%
3.7	3.1	200	6	77%
3.7	3.1	200	18	78%
5.7	4.8	200	2	91%
7.1	6.0	200	6	95%
None	—	200	6	13%

[a]Reactions were run at 350° C
[b]All reactions were run with hydrogen except this one which was nitrogen

The weight percent recovery of this residuum was quite high for the eight runs in Table 12, and the average and average deviation for the percent recovery was 92 ± 7.6%. It also is interesting to note that the reaction with no sodium added removed only 13% of the sulfur.

In this laboratory we have been working with alkali metals and their reactions with bituminous and lignite coals. Duty *et al.* (1981) reacted sodium metal with an Illinois bituminous coal in the presence of a carbon dioxide atmosphere in the aprotic solvent tetrahydrofuran. The purpose of adding carbon dioxide was to carboxylate the anionic sites generated by the alkali metal. As suggested previously by Sternberg (1974), sodium will attack polynuclear aromatic sites, and if carbon dioxide is present, this site could be carboxylated to form water soluble acids. Organic sulfur is known to exist in coal as benzo and dibenzothiophene structures, consequently, it would be reasonable to suggest that carbon dioxide could carboxylate these organic sulfur sites as follows.



We studied this reaction from 150° to 350°, and at 350° we ran the reaction with and without the presence of carbon dioxide. The results of these experiments are shown in Table 13 below.

Table 13. Sulfur Reduction with Sodium Metal in Tetrahydrofuran

Temp.	% S Reduction Residue[a]	% S Reduction Residue (dmmf)[b]	% Recovery of Coal
150°	45%	35%	91%
200°	77%	65%	33%[d]
250°	75%	57%	29%[d]
300°	73%	56%	99%
350°	56%	28%	79%
250°	87%	73%	55%

[a]- Residue was material collected from a basic aqueous reflux.
[b]- Demineralization of the residue was done with 1 N HCl.
[c]- This reaction was run with no CO_2.
[d]- These percentages represent an increase in weight gained.

In these reactions 10 g of coal was reacted with 10 g of sodium for 48 hrs. in tetrahydrofuran, the reaction was cooled, vented, and repressurized with carbon dioxide. It was again heated to the reaction temperature for 48 hrs.

The percent reduction in sulfur for the demineralized residues are not as high as the residues because the material that is lost by treating the residues with 1N HCl undoubtedly removes a lot of the sodium atoms and other metals, but very little of the sulfur, e.g. weight is lost in the demineralization step, but little or no sulfur is lost.

If one compares these results with Sternberg's sodium reaction at 350° C (See Table 12) the reduction in sulfur with coal is not as efficient as it is with petroleum residuum. One reason that may account for this is the solubility difference between coal in tetrahydrofuran compared to petroleum residuum in decahydronaphthalene.

Chiri and Duty (1981) also conducted a study with potassium metal with Illinois coal, but the aprotic solvent used in their case was toluene instead of tetrahydrofuran. The experimental conditions were the same with the sodium reactions where 10 g of coal were reacted with 10 g of potassium for 48 hrs and, consequently, reacted with carbon dioxide for 48 hrs. In these reactions with potassium, an electron transfer agent, biphenyl, was added to the toluene solution along with the coal. Hoijtink *et al.* (1956) demonstrated that biphenyl radical would rapidly transfer an electron to the neutral polyaromatic pyrene molecule. Consequently, it was reasonable to assume that biphenyl would transfer the electron readily to the aromatic structure of coal. Unfortunately, the insoluble residue retained some of the biphenyl because 100% recovery was not realized for biphenyl when the residue was refluxed with a mixture of benzene and ether.

The sulfur reduction in these experiments paralleled the sodium metal reactions and are shown in Table 14.

Table 14. Percent Sulfur Reduction in Illinois Coal with Potassium Metal in Toluene

Temp.	% Sulfur Reduction	% Recovery
100°[a]	68%	---
100°	22%	89%
200°	75%	69%
200°	20%	70%
300°	83%	(64%)[b]
300°	91%	(14%)[b]

[a]- This reaction was run in tetrahydrofuran as solvent.
[b]- These represent an increase in the weight of coal recovered.

The increase in weight for 300° reaction can be contributed to two sources; the biphenyl used as the election transfer agent and the toluene becoming incorporated into the coal matrix. Wachowska (1979) reported that anions of the aromatic clusters in coal could react with solvent and electron transfer agents and become incorporated into the reaction products.

The 300° reactions reflect a large decrease in sulfur, however, the decrease is not as large as lower temperatures since the residue weights have increased due to solvent and biphenyl incorporation in the residues.

The potassium metal reactions were run also by Foster and Duty (1983) with a North Dakota lignite that contained 0.89% sulfur. They tried three solvents and varied the conditions as shown in Table 15.

Table 15. Autoclave Reactions

Solvent	Temperature	Gas(es) Employed
Tetrahydrofuran	100° C	N_2 (5 days) CO_2 (5 days)
Naphthalene	200° C	N_2 (5 days) CO_2 (2 days)
Toluene	100° C	CO_2 (5 days)
Toluene	100° C	CO_2 (5 days)
Toluene	100° C	CO_2 (5 days)

Again, the electron transfer agent, biphenyl, was added except for the naphthalene solvent which would act as its own electron-transfer agent. The effectiveness of sulfur removal is shown in Table 16.

Table 16. Sulfur Removal from North Dakota Lignite

Temp.	Solvent	% S Reduction	% Recovery
100°	tetrahydrofuran	68%	42%
200°	naphthalene	63%	32%
100°	toluene	76%	61%
100°	toluene	36%	51%
100°	toluene	46%	55%

Percent recovery is much lower in the case of lignite compared to bituminous coal, but the percent reduction in sulfur is comparable.

Lavin and Duty (1982) also investigated the removal of sulfur from North Dakota lignite at elevated temperatures in the aprotic solvent toluene. They also incorporated biphenyl as the electron transfer agent in all of their reactions. Again, the sulfur reduction was based on the sulfur content of North Dakota lignite (mf) and the recovered residue (dmmf). These results are shown in Table 17.

Table 17. Sulfur Reduction in North Dakota Lignite with Potassium Metal in Toluene[a]

Temp.	% S Reduction	% Recovery
100° C	26%	55%
100° C	89%	58%
200° C	89%	40%
200° C	85%	33%
300° C	84%	82%
300° C	80%	64%

[a]Reactions were run for 5 days under nitrogen, cooled and repressurized under carbon dioxide for 2 days. All reactions were run with 10 g. of coal, 10 g. of potassium and 10 g. of biphenyl.

Again, the percent recovery in these reactions with North Dakota lignite is not very large until the higher temperature is reached (300° C). Unfortunately, the incorporation of solvent and electron transfer agent probably contributes to these high recovery values.

The sulfur reductions are fairly uniform and exceptionally good. Unfortunately, the duplicate run at 100° C does not bear this out, however; where a ridiculously low value of 26% was found.

Desulfurization of Bituminous Coal with Alkali and Carbon Dioxide

Ouchi *et al.* (1978) reported that ethyl alcohol and alkali at elevated temperatures (350°-400° C) solubilized coal (less than 82% C) almost completely in pyridine. He attributed these results to the formation of hydrogen from ethanol at these high temperatures as follows:

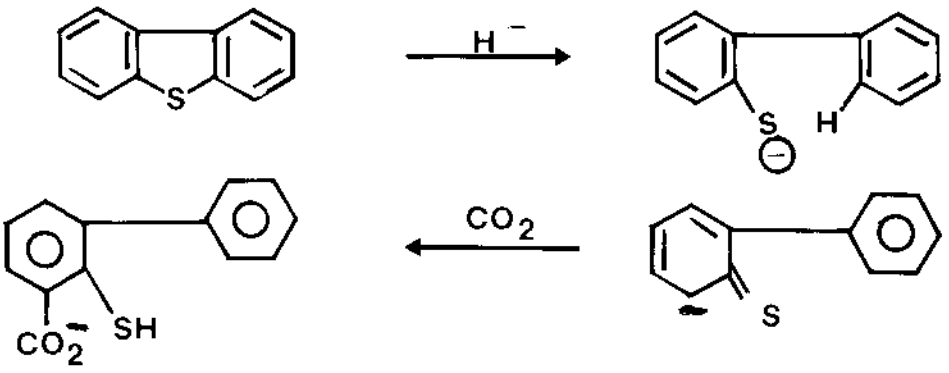
$$CH_3CH_2OH + OH^- \xrightarrow[-H_2O]{} CH_3\overset{O}{\overset{\|}{C}}O^- + 2H$$

Ross *et al.* (1977) had earlier reported the same results with isopropyl alcohol and alkali, and Ouchi (1978) suggested Ross's results could be attributed to the oxidation of isopropyl alcohol with alkali:

$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[-H_2O]{OH} CH_3-\overset{H}{\overset{|}{C}}-O \xrightarrow{} CH_3-C=O + H$$
$$\qquad\qquad\qquad\qquad\qquad\quad CH_3 \qquad\qquad\quad CH_3$$

Ouchi and Makabe (1978) also reported the results of the reaction of methanol with coal and alkali. Their results were similar to ethanol, and the coal was solubilized to 96% and 99% in pyridine with sodium hydroxide and potassium hydroxide, respectively, between 350°-400° C.

With this background information, this laboratory began a study of sulfur removal from Illinois bituminous coal with alkali with protic solvents, ethanol and isopropyl alcohol, and an aprotic solvent triethylamine. The reaction scheme was to react the coal with alkali at different temperatures for 24 hrs, under nitrogen, and then cool and repressurize with carbon dioxide. After pressurizing with carbon dioxide, the temperature again was raised to the reaction temperature for 24 hrs. If Ouchi's supposition was correct, the hydride ion (as well as nascent hydrogen) could initiate the precursors for carboxylation of the coal aromatic structure. This is illustrated as follows for dibenzothiophene.



The preliminary results of this study by Duty *et al.* (1983) was presented at the 39th annual Southwest Regional Meeting of ACS at Tulsa.

After the reaction with carbon dioxide, the solvent was rotary evaporated to remove solvent and the residue was refluxed with 5% (w/w) of potassium hydroxide to remove the carboxylic acids. The residue was demineralized with 1 N HCl, dried and total sulfur was determined. The acids were precipitated from the filtrate with concentrated hydrochloric acid, centrifuged, washed free of chloride ion and dried. The results of these reactions are shown in the following Table 18.

Table 18. Desulfurization of Illinois Bituminous Coal with Alkali and Carbon Dioxide

Temp.	Solvent	Wt. of Acids(g)	% Sulfur[a]	% Recovery (Residue)
100°	Triethylamine	0.12 g	2.37%	90%
100°	Triethylamine	0.09 g	2.06%	89%
100°	2-Propanol	0.13 g	1.36%	94%
100°	2-Propanol	0.20 g	2.42%	88%
100°	Ethanol	0.20 g	2.70%	83%
100°	Ethanol	0.40 g	2.62%	88%
200°	Triethylamine	0.07 g	1.96%	95%
200°	Triethylamine	0.36 g	2.68%	76%
200°	2-Propanol	0.28 g	2.25%	81%
200°	2-Propanol	0.26 g	2.11%	81%
200°	Ethanol	4.7 g	2.17%	84%
200°	Ethanol	3.2 g	2.30%	84%
200°	Triethylamine	0.18 g	1.69%	91%
300°	Triethylamine	0.44 g	1.53%	86%
300°	2-Propanol	0.56 g	1.06%	76%
300°	2-Propanol	0.57 g	1.49%	88%
300°	Ethanol	2.1 g	1.41%	53%
300°	Ethanol	2.7 g	1.45%	67%

[a]Illinois Bituminous #6 coal contained 4.42% sulfur and the dmmf Illinois Bituminous #6 coal contained 3.42% sulfur.

When this project was begun, the goals of the project were to reduce the sulfur content to less than 1% and recover 90% of the coal residue. Our greatest success was accomplished at 300° C with isopropyl alcohol where the percent sulfur was

reduced to 1.06%. Unfortunately, the lowest percent recovery occurred at this temperature with isopropyl alcohol where only 76% recovery was realized.

In the 300° reactions with isopropyl alcohol, the residue contained a highly viscous liquid which presented problems in centrifuging the residue. Consequently, we elected to extract the residue with a benzene/ether (3/1 v/v) reflux prior to extracting the residue with the 5% KOH reflux. The benzene/ether extract produced a neutral fraction which weighed 8.7 g and was predominately aliphatic in nature according to its infrared spectrum (3000-2800 cm^{-1}).

A material balance was determined for the sulfur, and the percent sulfur for each fraction is given in Table 19.

Table 19. Material Balance for Sulfur

Temp.	Solvent	% S Residue	% S Acids	% S Neutral	% S H_2O
300°	2-propanol	18.4%	1.19%	4.32%	76.0%

As was expected, the majority of the sulfur was lost in the water layer, with the smallest amount found in the acids.

The residue was analyzed for pyritc sulfur and organic sulfur for the 300° reaction, and the analyses revealed that the residue contained 1.01% pyritic sulfur and only 0.05% organic sulfur. This analysis was done according to the procedure of Chakrabarti (1978) for pyritic sulfur. The organic sulfur was assumed to be the difference between the total sulfur (1.06%) and the pyritic sulfur.

Since these reactions were all run with carbon dioxide, we elected to determine the BTU/lb value for some of these reactions. Since the carbon dioxide could add to the aromatic structures it seemed reasonable to expect the BTU/lb values to increase for the insoluble coal residues. In Table 20 are found these values for residues from different solvents and temperatures. The bomb calorimeter used was a Parr 1241 adiabatic bomb calorimeter which was standardized with pure benzoic acid which gave an energy equivalent of 2416 ± 1 for three determinations.

Table 20. BTU/lb for Insoluble Coal Residues (dmmf)

Solvent	Rx Temp.	BTU/lb[a]
TEA[b]	100°	11,448 ± 197
TEA	100°	11,616 ± 169
TEA	200°	11,596 ± 148
TEA	200°	12,406 ± 84
TEA	300°	13,167 ± 23
TEA	300°	14,638 ± 951
IPA[b]	100°	11,793 ± 230
IPA	200°	13,092 ± 75
IPA	300°	11,626 ± 48
IPA	300°	9,120 ± 153
Ill. #6 Bituminous Coal (dmmf)		9,891 ± 19

[a]duplicate runs
[b]TEA — triethylamine; IPA — isopropyl alcohol

As expected, the BTU/lb values were all higher than the starting coal except for one run at 300° C. Excluding this 300° value, the average increase over the starting coal was 20.0%.

MISCELLANEOUS PROCESSES FOR DESULFURIZATION OF COAL

Magnetic Process

Magnetic desulfurization of coal is not a new process and was first reported in the literature through a German patent by Siddiqui (1957). A year later Yurovsky *et al.* (1958) reported reductions of sulfur in coal to as high as 85% for pyrite. His process was an air-stream process which increased the magnetic properties of the pyrite. Kester (1965) reported better results without air-stream treatment by pulverizing the coal to a coarse 48/200 mesh fraction and subjecting it to a high-intensity magnetic separation. Since coal is diamagnetic and pyrite is paramagnetic, crushing the coal to liberate the pyrite from the coal matrix should and does prove beneficial for the magnetic separation of pyrite from coal.

Murray (1977) utilized the high extraction magnetic filtration technique for coal which had been used successfully for processing kaoline. His tests were run with coal that would pass through a 200 mesh screen. He ran tests on the solid meshed coal, and also on the 30% solids in water for the wet magnetic tests. For the separations he used Frantz screens with thin sharp ribbons of 430 magnetic stainless steel, and made several passes through these screens that lasted from 30 to 120 seconds. Table 21 shows the reduction achieved by the wet and dry coal samples that were -200 mesh.

Table 21. Desulfurization by Magnetic Filtration

Coal	Total S	Inorganic S	% S Removed	% Inorganic S Removed
IN #5[a]	4.63	2.45	35%	67%
IN #5[b]	4.63	2.47	29%	55%
IN #5[c]	4.63	2.12	18%	25%
IN #6[a]	4.17	0.66	45%	85%
IN #6[b]	4.17	1.14	31%	78%
IN #6[c]	4.17	1.66	31%	39%
IL #5[a]	3.59	2.37	46%	65%
IL #5[b]	3.59	2.41	39%	59%
IL #5[c]	3.59	2.38	20%	30%
IL #6[a]	1.98	1.00	42%	79%
IL #6[b]	1.98	1.03	35%	69%
IL #6[c]	1.98	1.02	21%	40%

[a]Wet coal — three passes
[b]120 — see retention
[c]dry — three passes

Microwave Process

The microwave treatment of coal was begun in 1977 by the General Electric Company (Morrison, 1977f). The microwave treatment of coal has never gone beyond the bench scale size, and the success of the process has been demonstrated for pyrite as well as for organic sulfur.

Dry powered coal has been subjected to microwave energy for 20 to 60 sec., and the microwave energy heats the pyrite and converts it to a related mineral of pyrite, pyrrhotite. Pyrrhotite has a higher magnetic susceptiblity than pyrite, and can be separated more easily than pyrite with a magnetic separator.

Microwave energy has been used in conjunction with sodium hydroxide to remove both pyrite and organic sulfur. (Morrison, 1981g) The advantage of this process is that the sodium hydroxide and sulfur species can be heated more effectively than the coal itself. Consequently, the pyritic and organic sulfur in coal react with the sodium hydroxide and convert then to soluble sulfides. This process has been successful on a bench scale to remove 90% of the pyritic sulfur and 50 to 70% of the organic sulfur providing the coal is washed and the sodium hydroxide pretreatment and microwave treatment are repeated a second time.

The advantage of the microwave process is that it causes very little coal structure degradation and, consequently, very little heating loss in the coal. Disadvantages would include the sodium retention in the coal and the high cost for microwave energy.

Chemical Comminution Process

Chemical comminution provides a convenient way to crush coal for extensive mineral matter removal. Chemical comminution is accomplished with solvents where methanol and ammonia have found the greatest success. Other solvents such as n-propylamine, pyridine and isopropyl alcohol have been tried (Datta, 1977; Yan, 1984).

Chemicals with a non-bonding electrons have been found to comminuate better, and their method of breakage appears to be along the bedding planes, maceral boundaries. Consequently, the comminution process has its greatest advantage in removing pyrite and ash content of coals. Unfortunately, different coals react differently to chemicals used in chemical comminution, and no process has been found which will work uniformily on all coals.

Yan (1984) discovered that isopropyl alcohol showed synergism with sodium hydroxide in coal comminution with concentrations of less than 0.1 N sodium hydroxide in 90% isopropyl alcohol/water. Very little sodium hydroxide was consumed in this process, and the isopropyl alcohol was recovered quantatively.

Used separately, isopropyl alcohol and sodium hydroxide do not have high levels of comminution, e.g. sodium hydroxide by itself would have to reach 6.2 wt% consumption before it would reach the same level of comminution as with 0.1 N sodium hydroxide and 90% isopropyl alcohol/water system. The consumption of sodium hydroxide was only 2.6 wt% for extensive comminution with isopropyl alcohol.

Yan (1984) found the following trend for solvents as an effective comminution medium.

$$\text{isopropylalcohol} > \text{methyl alcohol} >> \text{water}$$

He suggested the reactivity of the hydroxide ion might be enhanced by the solvation of the sodium ion by the isopropyl alcohol or methanol.

SUMMARY

Coal desulfurization has come a long way in the past 15 years, and chemical desulfurization has been at the fore-front of this progression. Unfortunately, unless some new technique is developed, the chemical desulfurization processes appears to be at a stalemate. A proliferous number of chemicals has been tried, and their greatest success has been in removing the inorganic sulfur, but their success with organic sulfur has been minimal.

Organic sulfur is incorporated into the carbon structure of the coal molecules, and as the present processes have shown, to remove the sulfur from the carbon structures, success is achieved at the heating value loss of the coal.

Chemical comminution is an interesting phenonunium, but it greatest success, also, has been in removing the pyritic sulfur which is not chemically bound to the coal structure as the organic sulfur atoms are. Microwave treatment and magnetic desulfurization have demonstrated, also, success with pyritic sulfur and limited success with the organic sulfur.

At the present time, desulfurization can be accomplished whereby the pyritic sulfur can be almost completely removed with several processes; Meyers ferric sulfate process, Ames air oxidation process under alkaline conditions, and the Arco complexing agents for metals to name a few. Unfortunately, a process has not been developed which successfully removes the organic sulfur from coal, consequently, to successfully remove the total sulfur from a coal burning establishment, a chemical desulfurization process would have to be the precursor to a stack gas scrubbing process as the final stage in removing sulfur.

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