

CHEMICAL COAL BENEFICIATION WITH AQUEOUS HYDROGEN
 PEROXIDE/SULFURIC ACID SOLUTIONS

By

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INTRODUCTION

There is a pressing need for significant improvement in the effectiveness and the economics of coal desulfurization, especially in the light of the latest, strict air-quality standards set by EPA for coal-fired power plants. The challenge is particularly crucial for the future of chemical (or precombustion) desulfurization of coal, where specific reagents are used to attack selectively and to remove both the inorganic and the organic sulfur from coal before combustion. Current chemical desulfurization processes are faced with a serious dilemma: either operate under severe process conditions (high temperatures and pressures, strong- and thus nonselective- desulfurizing media) promoting high sulfur removal from coal but at the expense of higher capital and operating costs and/or severe degradation of the coal material, or utilize mild reaction schemes not affecting the integrity of the coal matrix during processing but displaying low efficiency of sulfur-reduction (especially organic-sulfur reduction) in coal. A low-cost, technically simple, coal-treatment process that removes the organic as well as inorganic sulfur in coal effectively without having to destroy the carbon matrix would be a major breakthrough in coal utilization.

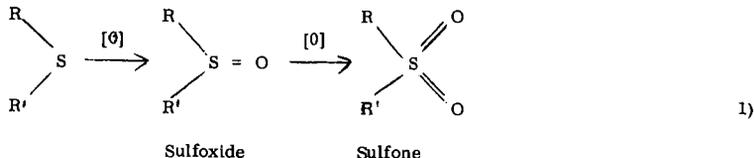
All the chemical desulfurization processes that are presently in an advanced development stage (TRW Meyers, Battelli Hydrothermal, KVB, DOE Oxydesulfurization, and JPL Chlorinolysis processes) employ either oxidizing reagents or basic media to reduce the sulfur content in coal. Oddly enough, little consideration has been given so far in the coal desulfurization literature to the potential benefits from acid systems. Inherent advantages exist in coal treatment by acid systems over alkaline ones, namely:

- Acid systems can extract sodium from the organic phase of the coal, thereby improving the slagging characteristics of the coal during combustion; alkaline systems add alkali.

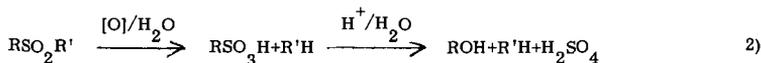
- Acid systems can attack apatite/phosphorite in the coal as well as pyrite (1) and, thus, can free ash and trace elements (including radioactives) from their original association; alkaline systems do not attack the phosphate minerals and tend to immobilize trace elements in the form of hydroxides, etc.

- Acid systems have a potential for extracting nitrogenous substances such as aniline and pyridine from the coal; alkaline systems can only extract phenols and organic acids, thus, removing fuel value without improving NO_x emissions.

Oxidizing systems, on the other hand, can in principle remove both the pyritic and organic sulfur from coal in the form of sulfates, but oxidizing systems suffer from the serious drawback of being unselective, resulting in large losses in heating value of the treated coal. The high cost and scarcity of feed stock the severe conditions required and the lack of effectiveness on organic sulfur of current chemical desulfurization processes has stimulated renewed interest in selective oxidation under mild conditions as a method for removing sulfur from coal and residual oil. The basic scheme consists of selectively oxidizing the organosulfur compounds to the corresponding sulfones, thus destabilizing the carbon-sulfur bond (2):



The sulfones are then oxidized further to sulfonic acids which can, in turn, be hydrolyzed to yield sulfuric acid and completely desulfurized hydrocarbon products (3):



The first step in the sequence, i. e. the oxidation of sulfur compounds to sulfones, is extensively documented in the literature. Numerous oxidants have been reported which can effect the conversion of even the most stable organosulfur compounds (thiophenes) to the corresponding sulfones, including NO_2 (4), $\text{Cl}_2/\text{H}_2\text{O}$ (5), $\text{H}_2\text{O}_2/\text{acetic acid}$ and hydroperoxides (6).

The oxidation of sulfur beyond the sulfone stage (Reaction 2) has not been studied to any significant extent and there are very few references in the literature on the desulfurizing effects of extended oxidation of organosulfur compounds. Vasilakos (7) has reported the complete desulfurization of aliphatic sulfides by oxidative chlorination in aqueous systems at low temperatures (60°C) and atmospheric pressure.

The key to an economically feasible desulfurization process based on oxidation is, of course, selectivity. Concurrent oxidation of the remainder of the coal matrix by the sulfur-oxidizing agent should be minimized to prevent excessive loss of the heat content of the coal. A comparison of half-wave potentials for oxidation of organic substrates of the type found in coal (8) shows that organosulfur compounds as well as alcohols and amines are vastly more susceptible to oxidation than are ether and benzene derivatives. Thus, given a mild oxidizing agent, it may be possible to oxidize the organic sulfur compounds, amines and alcohols without destroying the hydrocarbon portion of the coal molecule.

One of the most promising oxidants in this direction is hydrogen peroxide, particularly in acid solutions, where it has a standard oxidation potential approximately 1.4 V more positive than that of pyrite and about 1.6 V more positive than the SO_2/S couple (9). Thus, H_2O_2 is an oxidizing agent capable of oxidizing effectively the pyritic sulfur to the sulfate form.

Mukai et al. (10) studied the treatment of several Japanese bituminous coals with 3 wt % aqueous hydrogen peroxide. This treatment was claimed to give nearly quantitative removal of pyritic sulfur without changing the caking properties of the coal. No data on organic-sulfur reduction were given. Nalwalk and coworkers (11) also reported that decomposition of coal with 30 wt % H_2O_2 slowly oxidized pyrite to sulfate.

Smith (12) investigated the desulfurization of U. S. coals with 10-15 wt % H_2O_2 , 0.1-0.3 N H_2SO_4 , aqueous solutions. Treatment of several coals at ambient temperature with H_2O_2 alone had a noticeable effect in removing pyritic sulfur, but the reaction was significantly enhanced when a small amount of sulfuric acid was added to the peroxide solutions. Although pyritic sulfur and ash were effectively removed in this way, organic sulfur remained unaffected. Minimal attack on the organic constituents of the coal matrix was observed. The reaction mechanism was postulated to involve the intermediate formation of peroxysulfuric acid, H_2SO_5 (catalyzed by metal ions and sulfates present in coal), followed by oxidation of the pyrite, with competing peroxide decomposition by metal ions.

The apparent resistance of the organic sulfur in coal to oxidative desulfurization in this case does not necessarily imply that organic sulfur functionalities are not affected by the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treatment. As we will show in the section on model compounds, all the basic organosulfur structures present in coal can be readily converted to the sulfone form under the conditions of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ attack. In most cases, however, the oxidation does not proceed beyond the sulfone stage, and the additional desulfurization steps necessary to free the organic sulfur from the coal matrix (Equation 2) do not take place.

In a recent study (13), Kralik has reported that a hot aq. Na_2CO_3 wash of coal pretreated with a mild oxidizing agent results in significant organic-sulfur reduction, mainly by splitting off relatively low-molecular-weight, oxidized sulfur compounds from the hydrocarbon matrix. It is feasible that the high selectivity of the peroxide treatment of coal towards sulfur oxidation could be combined with a subsequent alkaline hydrolysis step to leach out a significant portion of the oxidized organosulfur compounds, thus affecting not only pyritic, but also organic-sulfur removal from coal.

EXPERIMENTAL

Chemical beneficiation experiments were carried out in batch mode at ambient temperature and pressure with a Redstone high-volatile A, bituminous coal. The ultimate analysis and sulfur forms for this coal, designated as PSOC-715, are included in Table I. In each run, approximately 20 grams of the dried and sized (200x325 mesh) coal was slurred in a 500-ml Pyrex Erlenmeyer flask with 300 ml of a 15 wt % H_2O_2 solution of the desired H_2SO_4 concentration. At the end of the reaction period the slurry was vacuum-filtered through a fine-porosity fritted glass funnel and the coal was washed several times with water for analytical purposes. Treated coal samples were dried for 24 hours under vacuum at 110°C and then analyzed for proximate and ultimate composition and heating value. A portion of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treated coal was further subjected to an extended

leaching cycle with a hot (80°C) 0.1 molar Na_2CO_3 solution, then washed with water and dried as before. Both the Eschka and the Fisher methods for total-sulfur content and the ASTM-D-2492 wet method for forms of sulfur were employed in the analysis of the raw and treated coals. The wet method was modified to eliminate any ash interference in the determination of the pyritic and, thus, the organic sulfur (14). In this modified method, the pyritic-sulfur content of the coal is determined by oxidation of the pyrite to ferric sulfate and subsequent gravimetric analysis of barium sulfate precipitate, rather than by atomic absorption determination of the iron as described in the ASTM method.

TABLE I

ULTIMATE ANALYSES AND SULFUR FORMS OF COAL SAMPLES TREATED WITH A 15 WT % H_2O_2 , 1N H_2SO_4 AQUEOUS SOLUTION AT 25°C FOR VARIOUS LENGTHS OF TIME^a

Reaction Time ^b (min)	Carbon	Hydrogen	Oxygen	Nitrogen	Ash	Total Sulfur	
						Eschka	Fisher
0 (Raw Coal PSOC 715)	73.6	4.73	11.2	1.08	7.02	2.46	-
15	78.0	5.50	8.24	1.16	5.14	2.04	-
	77.7	5.45	8.78	1.18	5.00	1.85	1.94
30	78.6	5.20	7.99	1.15	5.07	2.01	-
	78.3	5.47	8.47	1.18	4.76	1.80	1.83
60	74.4	4.98	13.3	1.17	4.41	1.71	-
	74.5	4.84	13.5	1.19	4.44	1.55	1.37
90	74.6	4.90	13.6	1.10	4.18	1.58	-
	74.9	4.91	13.3	1.18	4.26	1.47	1.29
120	78.2	5.27	9.46	1.15	4.38	1.57	-
	78.2	5.35	8.75	1.24	5.08	1.38	1.48
180	77.4	5.21	10.8	1.06	4.16	1.35	-
	77.5	5.22	10.8	1.24	3.96	1.26	1.23
240	77.5	4.99	11.4	1.14	3.76	1.23	-
	77.2	5.21	11.7	1.03	3.72	1.12	1.17

Reaction Time ^b (min)	Sulfate Sulfur	Pyritic Sulfur	Organic Sulfur ^c	Heating Value (Btu/lb)
0 (Raw Coal PSOC 715)	0.39	1.31	0.76	12869
15	<0.05	1.11	0.93	13805
	<0.05	0.96	0.89	13811
30	<0.05	1.04	0.97	13877
	<0.05	0.91	0.89	13693
60	<0.05	0.89	0.82	12915
	<0.05	0.80	0.75	12969
90	<0.05	0.70	0.88	12921
	<0.05	0.60	0.87	12885
120	0.07	0.65	0.86	13743
	<0.05	0.47	0.91	13895
180	<0.05	0.50	0.85	13587
	<0.05	0.37	0.89	13592
240	0.09	0.35	0.79	13530
	<0.05	0.20	0.92	13526

- All reported values are wt % (on a dry basis), unless otherwise noted.
- For each reaction time, the first row of data corresponds to a single-step, $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treatment. The second row of data corresponds to the same $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treatment followed by an aqueous wash of the treated coal with a hot (80°C) 0.1M Na_2CO_3 solution.
- Determined by difference using the Eschka total-sulfur value.

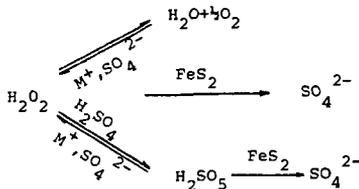
RESULTS AND DISCUSSION

Tables I and II summarize our data on the treatment of the PSOC-715 coal with a 15 wt % aqueous H_2O_2 solution of various H_2SO_4 concentrations, at 25°C and for various lengths of time. Total sulfur and pyrite and ash removal from coal are depicted in Figures 1 and 2, respectively, as functions of the reaction time. Figure 3 shows the effect of the H_2SO_4 concentration of the peroxide solution on pyritic sulfur removal.

The results indicate that there is a very significant reduction in total sulfur content for the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treated coal under the given experimental conditions. This reduction ($\sim 55\%$ in 4 hours) comes entirely from the almost complete elimination of pyrite and sulfates from coal. While sulfate sulfur (and ash) is leached out at the very early stages of the peroxide treatment, pyritic sulfur removal continues at a reasonable rate even after 4 hours of reaction. The results confirm earlier observations about the high selectivity of the peroxide reactions towards sulfur, the rest of the organic coal matrix being affected to a minimal extent. Carbon, hydrogen, nitrogen and oxygen contents of the treated coal remain at approximately the raw coal levels. No organic sulfur is removed in these room temperature experiments. On the other hand, pyritic sulfur reduction is accompanied by a significant reduction in the ash content of the coal ($\sim 47\%$ in 4 hours), and by a slight but noticeable increase in its heating value. This increase of about 5% is most probably due to the removal of low-heat-content inorganic matter from coal.

Subsequent wash of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treated coal with a sodium carbonate solution does not result in additional ash reduction, or, as was expected, in any organic sulfur removal. However, a small but consistent decrease in the total sulfur content is observed in all cases, due to further removal of pyritic sulfur from the coal. The exact mechanism of this alkaline pyrite desulfurization is not clear at this point.

Pyritic sulfur removal also displays an interesting dependence on the H_2SO_4 concentration of the peroxide solution. The data in Table II show that aqueous hydrogen peroxide alone is quite efficient in removing a substantial portion of the pyrite and the ash from coal. At the other extreme, treatment of the coal with a 1N sulfuric acid solution has absolutely no effect on pyritic sulfur, although some ash is actually removed. The combination of H_2O_2 and H_2SO_4 in aqueous solution results in a synergistic effect, where pyrite and ash reduction in coal significantly exceed the corresponding reduction brought about by each reagent alone. The effect is pronounced at low acid concentrations, but above a concentration of approximately 0.2N H_2SO_4 the trend is reversed. Concentrated sulfuric acid seems to have an adverse effect on the oxidation of pyrite by hydrogen peroxide, so that, for example, the level of pyritic sulfur removal for a 2N H_2SO_4 peroxide solution falls below even that for pure hydrogen peroxide. As Smith (12) has pointed out, the H_2SO_4 -assisted oxidation of iron pyrite by hydrogen peroxide involves a complex system of parallel and consecutive reactions that may be strongly catalyzed by metal ions and sulfates present in coal. A simplified reaction mechanism can be schematically represented as follows:



The concentration of sulfuric acid in the peroxide solution may affect the kinetics and/or the equilibrium of any of these reactions (14), but the extent of the specific contribution of each step to the overall concentration effect that was observed experimentally is very difficult to estimate.

Model Compound Studies

To investigate the effect of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treatment on organic sulfur under more controlled conditions, a series of kinetic experiments was carried out with three organosulfur compounds modeling possible sulfur functionalities in coal, namely dibenzothiophene, phenyl sulfide and *t*-butyl sulfide.

In each run with phenyl sulfide or dibenzothiophene, an aqueous phase consisting of 5ml 30 wt % H_2O_2 and 3.3 ml 36N H_2SO_4 was emulsified under intense stirring with 100 ml of a hexane phase containing 0.006 moles of the sulfide. The sulfide/peroxide-acid proportion corresponds to a 2.5 fold excess of the oxidant (assumed to be the intermediate peroxy-sulfuric acid) over the stoichiometric requirement for complete conversion (oxidation) of the sulfidic sulfur to sulfate

(Equations 1 and 2). All the reactions were carried out at 25°C. Samples of the hexane phase were withdrawn every 15 minutes and analyzed quantitatively on a Tracor 565 capillary-column gas chromatograph equipped with a Hall Electrolytic Conductivity Detector set at the sulfur detection mode. The corresponding sulfone was found to be the only final product of oxidation of phenyl sulfide and dibenzothiophene, with small amounts of the sulfoxide formed intermediately. Due to the very low solubility of the sulfoxides and the sulfones in hexane, these products were obtained mostly as solid crystals separating from the reaction mixture. The crystals were filtered, dissolved in tetrahydrofuran and analyzed on the gas chromatograph. Under the given reaction conditions, a 25% conversion of phenyl sulfide to the sulfone was obtained in 8 hours and 75% in 24 hours. For dibenzothiophene, the 24-hour conversion level was 42%. The oxidation rate was strongly dependent on the concentration of the sulfuric acid and complete conversion of the sulfide to sulfone could be achieved in a few minutes of reaction with a much higher excess of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ oxidant.

In the t-butyl sulfide runs, 14 ml of the (liquid) sulfide was directly dispersed under intense stirring in an aqueous phase consisting of 140 ml 30 wt % H_2O_2 and 96 ml 36N H_2SO_4 (= 5 fold excess of oxidant). The oxidation reaction was carried out at 25°C for various lengths of time. At the end of each run, the reaction mixture was exhaustively extracted with hexane. The aqueous phase was separated and analyzed for total SO_4^{2-} content by the $\text{BaCl}_2 \rightarrow \text{BaSO}_4$ precipitation method. The difference in sulfate contents between this phase and the initial aqueous phase (before reaction) was used to determine the SO_4^{2-} yield of the sulfide oxidation reaction. The hexane phase was analyzed for sulfur species on the gas chromatograph. After 8 hours of reaction, the t-butyl sulfide had been completely converted, t-butyl sulfone and SO_4^{2-} being the only reaction products that were detected. The sulfone yield (based on the sulfide) was approximately 20%, the remaining 80% appeared as sulfate.

The results with t-butyl sulfide are very encouraging, because they demonstrate the ability of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ system to promote complete oxidative desulfurization of aliphatic sulfide structures under ambient reaction conditions. The fact that no organic sulfur removal was observed under similar conditions with the PSOC-715 coal may simply be an indication that most of the organic sulfur in this coal is in stable phenyl and thiophenic forms that can survive the oxidative peroxide attack. Vasilakos (7) has reported a similar case in his studies of the selective desulfurization of two bituminous coals with aqueous chlorine solutions. The coals displayed completely different organic-sulfur-reduction characteristics despite the almost identical extent and pattern of the chlorinolysis reactions.

The effect was attributed to the different distribution of the organic sulfur in the two coals in aliphatic and aromatic structures. We are currently conducting a series of $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ experiments with two high organic-sulfur coals, a Texas Darco lignite and an Illinois #5 bituminous coal, to test this hypothesis and to study further the removal of sulfur functionalities from the coal matrix.

SUMMARY

The removal of sulfur and ash from coal treated with aqueous hydrogen peroxide/sulfuric acid solutions at ambient temperature was studied under a variety of experimental conditions. Almost complete elimination of the sulfate and the pyritic sulfur was observed in most cases, as well as substantial reduction in the ash content. The rest of the organic coal matrix was not affected to any significant extent, indicating a high selectivity of the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ system towards sulfur oxidation. An optimal H_2SO_4 concentration level was established, beyond which sulfuric acid was found to have an adverse effect on the oxidation of pyrite by hydrogen peroxide. The oxidative desulfurization of model organosulfur compounds, such as t-butyl sulfide, phenyl sulfide and dibenzothiophene, by the $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ system was also investigated.

ACKNOWLEDGMENTS

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TABLE II

ULTIMATE ANALYSES AND SULFUR FORMS OF COAL SAMPLES TREATED WITH A 15 WT % H_2O_2 SOLUTION (OF VARYING H_2SO_4 CONCENTRATION) AT 25°C FOR TWO HOURS^a

H_2SO_4 Concentration ^b , (N)	Carbon	Hydrogen	Oxygen	Nitrogen	Ash	Total Sulfur	
						Eschka	Fisher ^a
Raw Coal (PSOC 715)	73.6	4.73	11.2	1.08	7.02	2.46	-
0	77.7	5.29	9.53	1.19	4.73	1.50	-
(H ₂ O ₂ only)							
0.1	80.3	5.63	7.93	1.22	3.88	1.08	-
	79.1	5.38	9.47	1.24	3.71	1.05	1.06
0.3	78.2	5.40	10.2	1.15	3.80	1.27	-
	78.3	5.36	9.98	1.25	3.92	1.18	1.16
0.5	78.0	5.31	10.1	1.21	4.04	1.33	-
	77.8	5.29	10.4	1.20	4.05	1.23	1.21
2.0	77.3	5.15	10.8	1.11	4.15	1.47	-
	77.5	5.09	10.8	1.24	4.02	1.31	1.35
5.0	78.1	5.26	9.78	1.10	4.23	1.48	-
	77.6	5.16	10.6	1.24	4.13	1.30	1.40
10.0	77.9	5.19	10.4	1.12	4.04	1.33	-
	77.6	5.19	10.9	1.15	3.93	1.25	1.32
1N H ₂ SO ₄	76.6	5.17	9.43	1.04	5.46	2.24	-
(No H ₂ O ₂)	76.0	4.95	10.6	1.22	5.13	2.10	2.19

H_2SO_4 Concentration ^b , (N)	Sulfate Sulfur	Pyritic Sulfur	Organic Sulfur ^c	Heating Value (Btu/lb)
Raw Coal (PSOC 715)	0.39	1.31	0.76	12869
0	<0.05	0.54	0.96	13282
(H ₂ O ₂ only)				
0.1	<0.05	0.13	0.95	14064
	<0.05	0.13	0.92	14014
0.3	<0.05	0.32	0.95	13800
	<0.05	0.26	0.92	13762
0.5	<0.05	0.47	0.86	13735
	<0.05	0.34	0.89	13648
2.0	<0.05	0.55	0.92	13600
	<0.05	0.42	0.89	13595
5.0	<0.05	0.54	0.94	13568
	<0.05	0.40	0.90	13599
10.0	0.11	0.37	0.85	13552
	<0.05	0.37	0.88	13559
1N H ₂ SO ₄	<0.05	1.30	0.94	13563
(No H ₂ O ₂)	<0.05	1.22	0.88	13368

a. All reported values are wt % (on a dry basis), unless otherwise noted.

b. For each concentration, the first row of data corresponds to a single-step, $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treatment. The second row of data corresponds to the same $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ treatment followed by an aqueous wash of the treated coal with a hot (80°C) 0.1M Na_2CO_3 solution.

c. Determined by difference using the Eschka total-sulfur value.

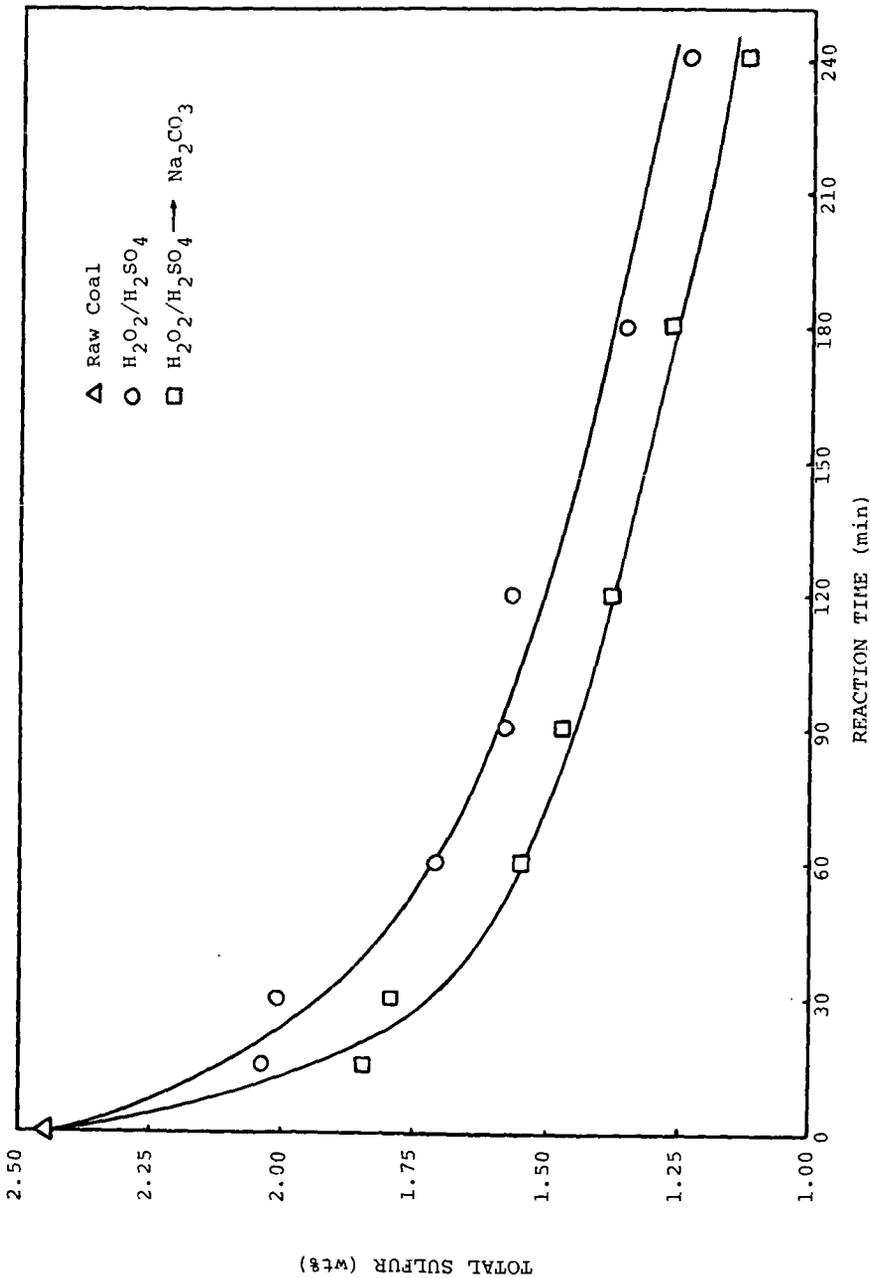


Figure 1: Total-sulfur dependence on reaction time (coal treated with a 15 wt% H_2O_2 , 1N H_2SO_4 aqueous solution at 25°C)

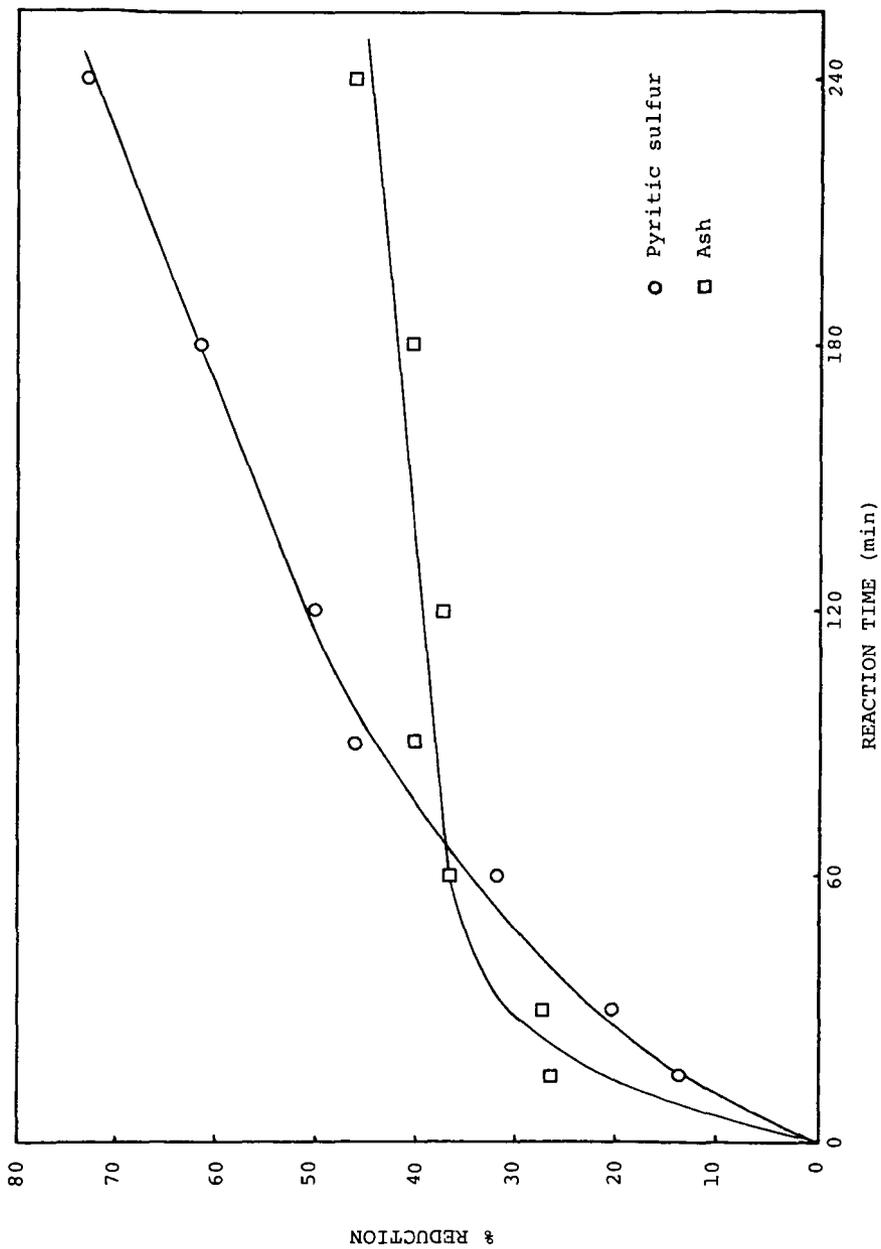


Figure 2: Pyritic-sulfur and ash reduction versus reaction time (coal treated with a 15 wt% H_2O_2 , 1N H_2SO_4 aqueous solution at 25°C)

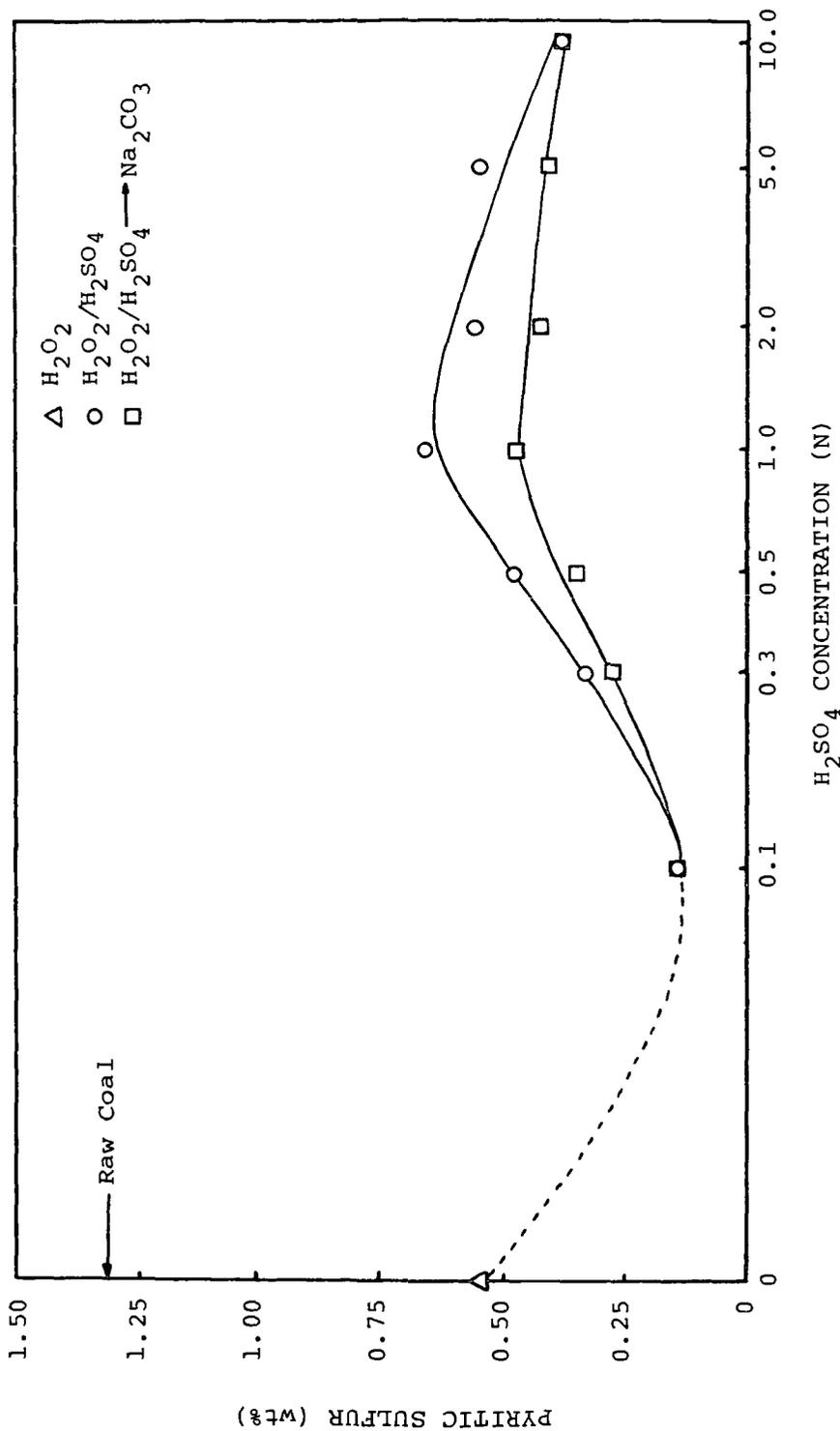


Figure 3: Effect of the acid concentration of the peroxide solution on pyritic sulfur (coal treated for 2 hours at 25°C)

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