

SULFUR REMOVAL FROM COALS: AMMONIA/OXYGEN SYSTEM

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INTRODUCTION

The emergence of chemical desulfurization of coal as a viable alternative to stack gas scrubbing(1) has prompted researchers in this field to consider a variety of chemical systems which remove pyritic sulfur or both the pyritic and part of the organic sulfur (2,3,4,5,6). A review of the more prominent chemical desulfurization schemes is presented in a recent article(6). Because chemical desulfurization is cost competitive with stack gas scrubbing(1), utilities are beginning to show an interest in the development of this technology which could provide them with a source of clean fuel to meet the rigorous EPA standards for sulfur emissions.

This paper discusses the sulfur removal from coals using an ammonia/oxygen system which removes almost all of the pyritic sulfur and up to 25% of the organic sulfur in about 2 hours. Because organic sulfur removal necessarily implies coal carbon losses, a balance must be struck between the amount of organic sulfur removed and the thermal losses than can be economically tolerated from the coals being cleaned.

Although no effort has been made to optimize the system reported here, the results of BTU loss, oxygen consumption, retention time, etc. are fairly consistent with the oxygen/water system for pyrite removal from coals(2). The carbon losses, as might be expected, are somewhat higher. Furthermore, the data presented here can be used to construct an optimization scheme for future development work.

PROCESS DESCRIPTION

In this desulfurization scheme, run-of-mine coal is treated in a conventional preparation plant, where the coal is crushed and washed to remove rock and clay material. The coarsely crushed coal is then fed into close-circuited wet ball mills where it is further ground to -100 mesh. The ground slurry is pumped into oxygen sparged leach reactors which operate at about 130°C and 300 psi oxygen pressure. All of the pyritic sulfur and up to 25% of the organic sulfur is removed in about two hours. The desulfurized slurry now goes through a solid/liquid separation operation where the coal and liquid are separated. Because of the formation of sulfates and the absorption of some of the CO₂ (from coal oxidation) into the ammonia solution, this mixed sulfate/ carbonate stream must be regenerated to recycle the ammonia back into the process. The ammonia regeneration may be accomplished by calcining and/or steam stripping.

A discussion of the sulfur removal from coals as a function of ammonia concentration and retention time is presented below.

EXPERIMENTAL CONDITIONS

All of the experiments reported here were carried out in a batch mode in high pressure autoclaves. The autoclaves were equipped with baffles, and the speed of agitation controlled with the help of a tachometer and verified at frequent intervals with a stroboscope. The system was heated with a jacketed electric heater exterior to the chamber and the temperature controlled to within a couple of degrees with the aid of a temperature controller. The reaction was cooled rapidly at the end of the experiment with the help of a cooling system fitted inside the high pressure reactors. The mode of operation was as follows: 120 gms (dry basis) of Illinois #6 coal was slurried in ammoniacal solutions to give a solids pulp density of 20 w/o. The autoclaves were sealed and the air purged with inert gas. This insured no reaction with the coal sulfur during the heatup period. The heater and stirrers were turned on and the temperature allowed to stabilize at 130°C. The system was then pressurized with oxygen to 300 psi, and the reaction permitted to proceed. The vapor space of the reactor was connected to a gas chromatograph for measurement of the gas phase for products of reaction.

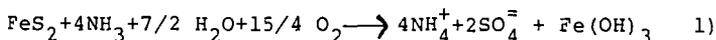
Minus 100 mesh coal was used, and the degree of agitation fixed to maintain the system in a kinetically controlled regime(2). Ammonia concentrations between 0.5 molar and 5 molar were studied. An analysis of the starting Illinois #6 coal is listed in Table I.

TABLE I -- Starting Coal Analysis

Total Sulfur 4.99%	Ash 19.27%
Pyritic Sulfur 2.06%	Vol. Matter 35.6%
Sulfate Sulfur 0.65%	Fixed Carbon 45.13%
Organic Sulfur 2.28%	BTU(maf) 13477

EXPERIMENTAL RESULTS

The chemical reaction for the oxidation of pyrite in an ammoniacal system is given by Equation 1).



where all of the sulfide sulfur is oxidized to soluble sulfates. Care was taken to insure that the NH_3/FeS_2 molar ratio for the experimental study was always in excess of the 4 required stoichiometrically: a range between 6.5 and 65 was considered.

The effect of retention time and ammonia concentration on sulfur removal from Illinois #6 coals is graphically displayed in Figure 1. Approximately 90% of the pyritic sulfur can be removed, and there appears to be no apparent effect of NH_3 concentration on pyrite removal. There appears to be a definite trend, however, in the organic sulfur removal as a function of NH_3 concentration. Measurements of total change in sulfur content of the coal, expressed as $\text{lbs. SO}_2/\text{MMBTU}$, shows a 50% change between the starting coal and the desulfurized coal. This compares against a 25% change after desulfurization of Illinois #6 coals when using the $\text{O}_2/\text{H}_2\text{O}$ system(2) where only pyritic sulfur is removed. The desulfurized coals, after an NH_3/O_2 treatment, also show no residual sulfate sulfur.

An important consideration in any chemical desulfurization process, in which the coal sulfur is oxidized, is the oxidant consumption. For this process the oxygen consumption to oxidize the coal sulfur species, and the coal itself, may be listed as follows:

- a) reaction with pyrite
- b) oxidation of organic sulfur
- c) oxygen uptake by the coal
- d) oxidation of coal to form CO and CO₂ in the gaseous phase
- e) formation of carbonates in solution.

The stoichiometric oxygen consumption for the pyrite reaction, given by Equation 1), calculates to be 1.0 lb.O₂/lb.FeS₂.

In the oxidation of pyrite with oxygen it is inescapable that oxygen will also react with the coal carbon. This oxidation of the coal usually results in the formation of CO and CO₂, together with soluble coal acids. There is a greater propensity for the formation of coal acids in basic systems than in acid systems. Furthermore, there is some pickup of oxygen by the coal to form an intermediate oxygen-coal complex.

The gases, as analyzed in the vapor space of the autoclaves, using a gas chromatograph, show that CO formation is negligible and that CO₂ is the major product of reaction. Some of the CO₂ formed due to carbon oxidation tends to dissolve in the ammoniacal liquor and report as carbonates in solution. To accurately determine the exact oxygen consumption for coal oxidation, solution analyses were conducted to measure this amount of carbonate formed. These analyses showed that the amount of carbonate measured in solution increased with increasing ammonia concentration. The total oxygen consumption for coal oxidation, both as CO₂ in the vapor space and carbonate in solution, as a function of retention time and ammonia concentration is shown in Figure 2. These results show that the coal oxidation is fairly insensitive to the ammonia concentration.

Due to the formation of an oxygen-coal complex, there is some oxygen tied up with the coal. This consumption is graphically displayed in Figure 3, which again shows no dependence on ammonia concentration. A minimum oxygen consumption for this process is tabulated in Table II.

TABLE II -- Minimum Oxygen Consumption

	<u>lbs.O₂/lb.coal</u>
O ₂ for pyrite reaction	0.0375*
O ₂ uptake by coal	0.034**
O ₂ for CO ₂ + CO	0.035**
	<u>0.1065</u>

* Based on 2% pyritic sulfur coal

** After 2 hours of sulfur removal

This table does not take into account any oxygen consumption for organic sulfur oxidation, which is difficult to measure. For a plant processing 8000 TPD of 2% pyritic sulfur coal (with a pyritic sulfur/organic sulfur ratio of 1), the oxygen demand, based on Table II, calculates to by 850 TPD. With a 25% contingency factor

to allow for organic sulfur oxidation, a 1000 TPD oxygen plant would be needed. This total oxygen duty is the same as that required for coal desulfurization using the O_2/H_2O system(2).

An important consideration for the viability of any desulfurization process is the overall thermal efficiency of the system. The BTU loss, on a moisture-ash-free basis, as a function of reaction time and ammonia concentration is presented in Figure 4. This graph shows that between 8% and 13% loss may be expected after two hours of sulfur removal. The pairing of the BTU loss as a function of ammonia concentration shown in Figure 4 is not immediately obvious. The loss of carbon during the desulfurization process is graphically displayed in Figure 5. In all cases the carbon loss is much greater than can be accounted for by CO_2 and carbonate formation.

This suggests that the difference reports in solution as coal acids. The formation of these acids is not surprising since the reaction of alkalis with coal to form humic acids is well known.

SUMMARY AND CONCLUSIONS

1. Increasing reaction time and ammonia concentration improved the extent of organic sulfur removal. For example, after 2 hours when using a 5 M NH_3 solution, 25% of the organic sulfur can be removed.
2. Changing the NH_3 concentration had no apparent affect on pyritic sulfur removal.
3. The oxygen consumption to oxidize the coal carbon (reporting as CO_2 in the gas phase and carbonae in solution) is fairly insensitive of the NH_3 concentration.
4. Ammonia concentration has no apparent affect on oxygen uptake by the coal.
5. Both the ammonia concentration and reaction time have an affect on the BTU and carbon values of coal. Increasing either one decreases the BTU and carbon value. As much as a 13% BTU and 10% carbon loss may be realized with using a 3 M NH_3 solution and reacting the coal for 2 hours. The large carbon losses are due to the formation of coal acids.

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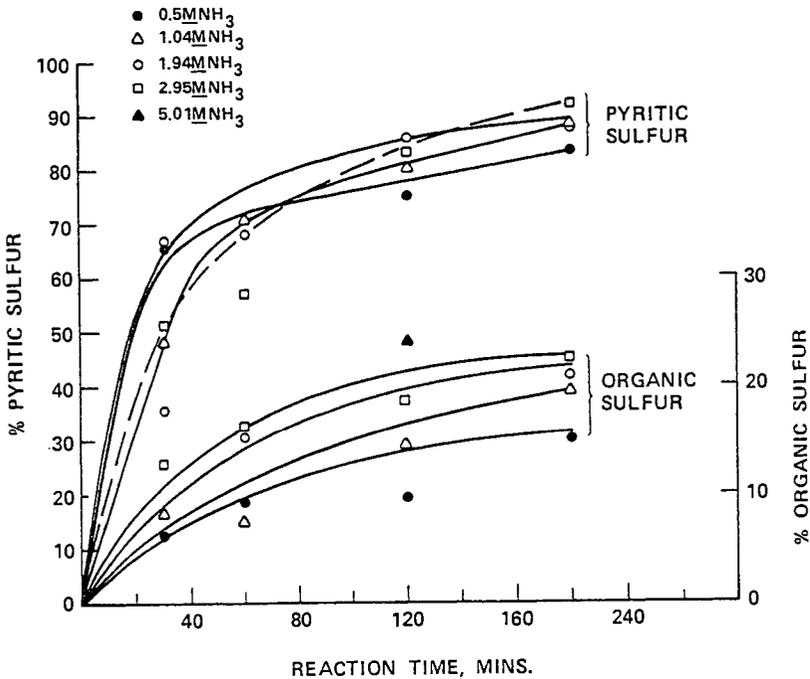


Figure 1. Sulfur Removal as a Function of Ammonia Concentration and Time.

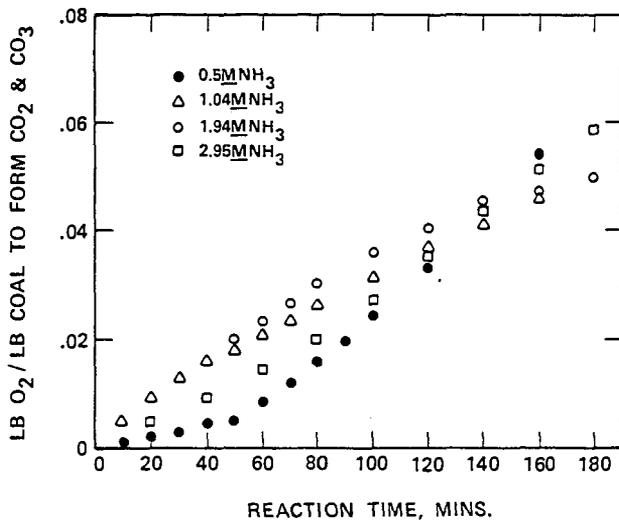


Figure 2. Oxygen Consumption for Coal Oxidation

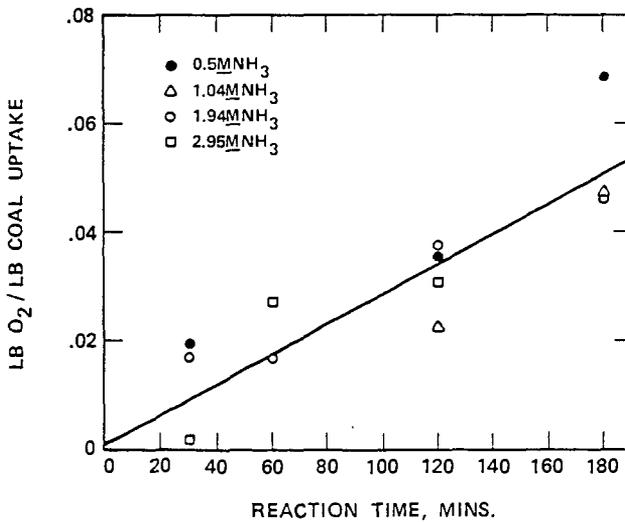


Figure 3. Oxygen Uptake by Coal

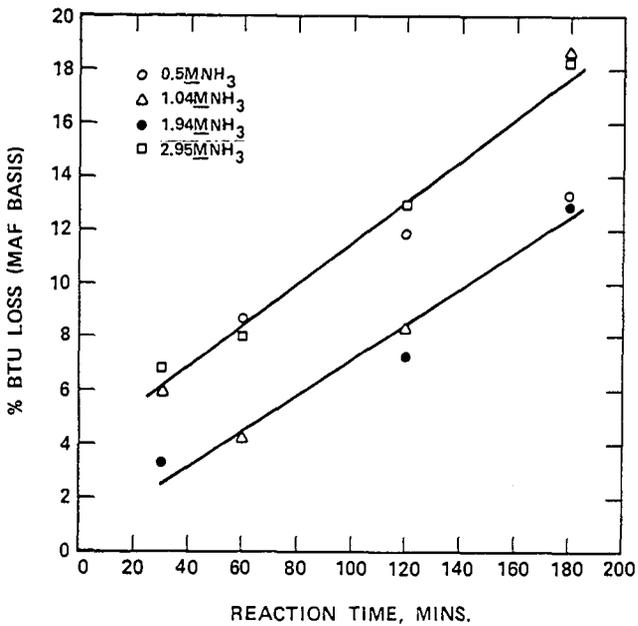


Figure 4. BTU Loss from Coals

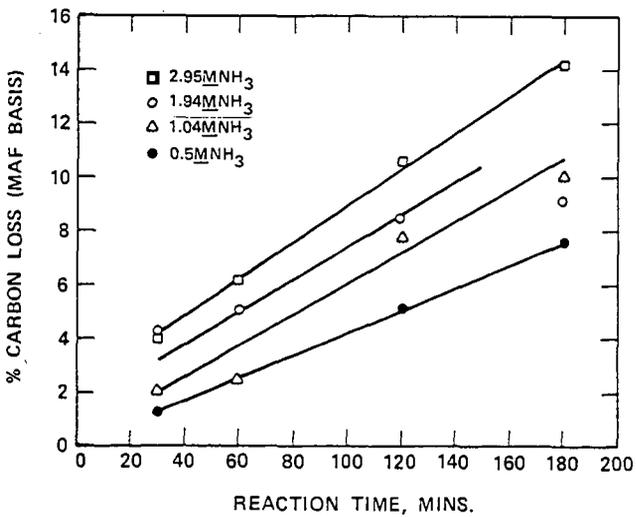


Figure 5. Carbon Loss from Coals