CONF-7809119--1



ENERGY
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# COAL DESULFURIZATION
# BY LEACHING WITH ALKALINE SOLUTIONS
# CONTAINING OXYGEN

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September 11-15, 1978

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For presentation at EPA Symposium on Coal
Cleaning to Achieve Energy and Environmental Goals
Hollywood, Florida
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## INTRODUCTION

Chemical methods for the removal of sulfur from coal have received wide attention (Friedman and Warzinski, 1977; Meyers, 1977; Wheelock, 1977; Wheelock, 1978). Among the more promising are processes based on extraction of sulfur by leaching with aqueous solutions containing dissolved oxygen ( Agarwal et al., 1975; Friedman et al., 1977; Tai et al., 1977). The rate of extraction can be increased by operating at elevated temperature and pressure. Although generally the leaching solutions are acidic, either initially or as a result of the generation of sulfuric acid during the oxidation of pyritic sulfur, basic solutions containing ammonia have also been proposed (Agarwal et al., 1976; Sareen, 1977). Apparently, the use of basic solutions allows a significant extraction of the organic sulfur as well as the pyritic sulfur from coal under milder conditions. The leaching temperatures for basic solutions are relatively low, generally less than 150°C. The advantages of using alkaline conditions for leaching high-sulfur coals were also demonstrated by Tai et al.(1977).

A unique chemical desulfurization (oxydesulfurization) process is being developed at the Ames Laboratory, Iowa State

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University, which is based on leaching fine-size coal with a hot, dilute sodium carbonate solution containing dissolved oxygen under pressure (Wheelock et al., 1978). In this process, sulfur is extracted from coal by conversion into soluble sulfates. For pyrite the overall conversion reaction appears to be:

$$2 \, FeS_2 + 7.5 \, O_2 + 4 \, H_2O = Fe_2O_3 + 4 \, H_2SO_4.$$
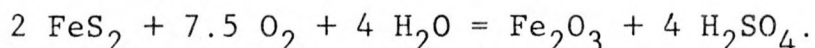
The pyritic iron remains as an insoluble iron oxide or hematite (Chen, 1978). The sulfuric acid generated in the process is immediately neutralized by the alkali as follows:

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O.$$
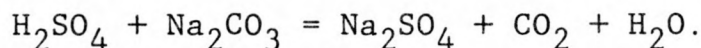
The mechanism for the extraction of a portion of the organic sulfur has not been established.

In this work, several high-sulfur bituminous coals were leached under various conditions. The effects of important parameters such as agitation, leaching time, temperature, oxygen partial pressure, and alkalinity on the process were studied. The results will be used to optimize the oxydesulfurization process.

## EXPERIMENTAL

### Apparatus

The leaching experiments were conducted in a 1-liter stirred autoclave reactor (Autoclave Engineers, Inc., Model AFP 1005) made of Type 316 stainless steel. The reactor was furnished with a removable, protective liner made of stainless steel, an electric heating jacket, a proportional temperature controller, an internal cooling coil, and a pressure gauge.

The contents of the autoclave was stirred by a gas-dispersing turbine agitator operated by a magnetic drive.

## Procedure

For each experiment, the autoclave reactor was charged with 40 g. of coal plus 400 ml. of the leach solution and sealed. The desired agitator speed was established, and the autoclave was purged with nitrogen gas while being heated up to temperature. When the desired temperature was reached, the flow of nitrogen was stopped, the autoclave was vented, and oxygen was introduced into the autoclave. The oxygen partial pressure (psia), the total pressure within the autoclave (psig), the temperature, and the stirrring rate were kept constant for the duration of the experiment. Some gas was bled continuously from the reactor to prevent any build-up of gaseous reaction products, while the system pressure was kept constant by supplying oxygen on demand. At the end of a run, the flow of oxygen was stopped, the system purged with nitrogen, and the reactor cooled. The leached coal was then recovered by filtration, dried at 90°C for 1 day, weighed, and analyzed for the various forms of sulfur, ash content, and heating value by standard ASTM procedures.

## Materials

Three of the coals used for leaching came from mines located in southeastern Iowa (Lovilia mine, Big Ben mine, and Scott coal from the Iowa State University demonstration mine). Another was a Western Kentucky coal (No.9 seam) from the Fies Mine in Hopkins Co., KY. The Iowa coals were high-volatile bituminous coals, high in sulfur content, and very heterogeneous

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in composition. The coals were dried at 90°C for 1 day, ground and sieved to the desired mesh size, and analyzed prior to leaching.

## Calculations

The heating value recovery, in percent, was calculated by the following equation:

$$\text{Recovery (\%)} = \frac{(\text{wt. coal recovered}) \times \text{heating value} \times 100}{(\text{wt. coal started}) \times \text{heating value}}$$

The specific sulfur content ($lb.S/10^6$ Btu), used in the tabular data, was calculated as follows:

$$\text{Specific sulfur content} = \frac{\text{percent sulfur} \times 10^6}{100 \times \text{heating value (in Btu/lb.)}}$$

There is a slight difference in the two forms in which the data are presented. In the tables, the percent of sulfur reduction is based on changes in the specific sulfur content ($lb.S/10^6$ Btu); in the graphs, it is based on the change in the weight percent of sulfur.

### RESULTS AND DISCUSSION

## Effect of stirring rate

In order to establish the effect of the stirring rate of the turbine agitator on the amount of sulfur removed from coal by leaching, Scott coal was leached for 1 hr. by 0.2$\underline{M}$ sodium carbonate at 150°C and 50 psia oxygen partial pressure. The results are presented graphically in Figure 1. The amount of

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pyritic and total sulfur extracted from coal increased steadily as the rotation speed was increased from 200 to 1200 r.p.m. Between 1200 and 1400 r.p.m., the amount of sulfur extracted (both pyritic and total sulfur) increased sharply. For agitator speeds above 1400 r.p.m., the amount of pyritic and total sulfur removed began to level off and approached a constant value between 1800 and 2100 r.p.m., being about 90 and 63% for pyritic and total sulfur, respectively. Within this range, the amount of extracted sulfur was independent of the agitator speed, indicating that the rate of extraction was no longer limited by the mass transfer of oxygen through the solution surrounding the individual particles.

A similar dependency on stirring rate was observed by Kosikov et al.(1973) during their study of the oxidation of pyrite by air in an autoclave. In their explanation, the effect of stirring is due to the amount of oxygen dissolved in the solution. With increased agitation, the amount of dissolved oxygen increases until it reaches a limiting value determined by Henry's law.

The study of the effect of agitator speed on the amount of sulfur extracted was repeated at a higher oxygen partial pressure, i.e. 200 psia. The data shown in Figure 2 indicate that above 800 r.p.m. the reduction in total sulfur content increased more steeply and then leveled off sooner, at about 1200 r.p.m., and at a higher sulfur reduction value, approximately 67%, than at the lower oxygen partial pressure of 50 psia. The reason for the steeper rise in sulfur removal may be higher solubility of oxygen in the alkaline leach solution at
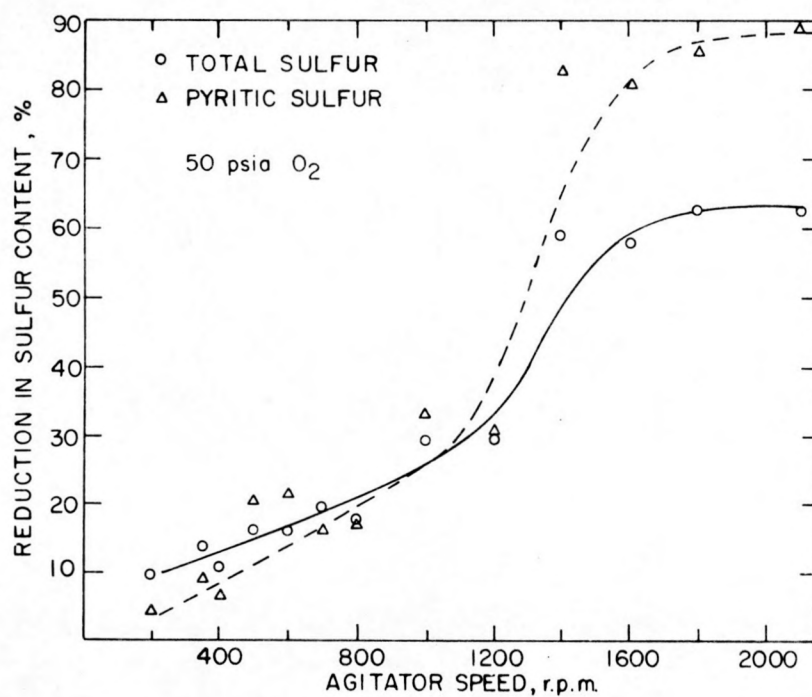
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Figure 1. Effect of agitator speed on the removal of sulfur from coal for 50 psia oxygen partial pressure.
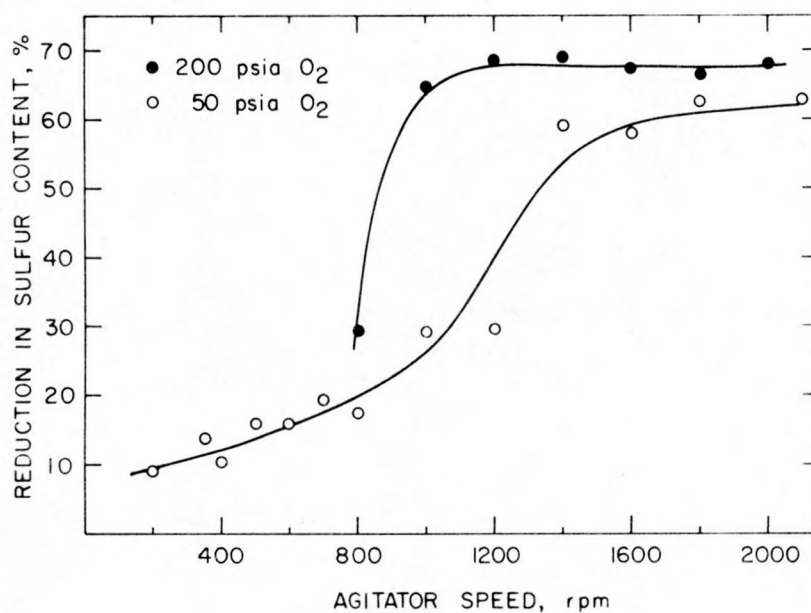


Figure 2. The interaction of agitator speed and oxygen partial pressure on total sulfur removal.

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higher pressure. Thus, with increased stirring rate the
mass transport is higher for the solution with the greater
oxygen concentration; as more oxygen is transported to the
particle surface, the reaction can proceed progressively faster.
At the plateau, some mechanism other than mass transport
through the external solution is rate-limiting, and further
increases in rotation speed do not increase the reaction rate.
To keep the leaching independent of the stirring rate, all
further experiments were conducted at 2000 r.p.m.

Effect of leach solution and oxidant

In the next set of experiments, the relative effective-
ness of alkaline versus acidic leaching conditions and of
pure oxygen versus air as the oxidant were compared. The four
run-of-mine coals, -200 mesh, were leached for 1 hr. at 150°C
and 50 psia oxygen partial pressure. Under alkaline conditions,
0.2$\underline{M}$ sodium carbonate was the leaching solution. For acidic
conditions, pure water was used; the sulfuric acid produced
during the oxidation of pyritic sulfur provided the acidity.
The oxygen partial pressure was the same (50 psia), regardless
of whether oxygen or air was supplied to the autoclave.

The results presented in Table 1 are averages for dupli-
cate runs. Although in each case the recovery in heating
value was high, it was slightly greater under acidic than under
alkaline conditions. However, it is apparent that the percent-
age sulfur reduction was higher for alkaline than for acidic
conditions. Since the relative merits of air versus oxygen
are more difficult to discern, the data were subjected to sta-
tistical analysis.

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Table 1. Leaching of coals (-200 mesh) with water and with alkali using air or pure oxygen.[a]

| Gas Type | H.V. Btu/lb. | Ash wt.% | lb.S/10⁶ Btu | | | | Tot. S Redn. % | H.V. Recov. % |
|---|---|---|---|---|---|---|---|---|
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| | 10,050[b] | 20.7 | 3.08 | 1.07 | 0.97 | 5.12 | (Lovilia Coal) | |
| O$_2$ | 10,320 | 17.1 | 0.92 | 0.51 | 1.15 | 2.58 | 49.6 | 95.3 |
| Air | 10,260 | 17.7 | 1.66 | 0.64 | 0.91 | 3.21 | 37.3 | 94.7 |
| O$_2$[c] | 9,520 | 23.5 | 0.56 | 0.22 | 0.71 | 1.49 | 70.9 | 86.9 |
| Air[c] | 9,420 | 23.6 | 1.11 | 0.22 | 0.85 | 2.18 | 57.4 | 88.3 |
| | 10,530[b] | 15.0 | 3.50 | 1.52 | 1.67 | 6.69 | (Big Ben Coal) | |
| O$_2$ | 11,003 | 11.3 | 1.18 | 0.38 | 1.66 | 3.22 | 51.9 | 97.1 |
| Air | 10,860 | 12.5 | 2.58 | 0.34 | 1.41 | 4.33 | 35.3 | 92.8 |
| O$_2$[c] | 10,260 | 17.3 | 0.72 | 0.34 | 0.97 | 2.03 | 69.7 | 88.2 |
| Air[c] | 10,140 | 18.3 | 0.81 | 0.32 | 1.02 | 2.15 | 67.9 | 86.3 |
| | 10,270[b] | 16.9 | 6.24 | 1.86 | 2.53 | 10.63 | (Scott Coal) | |
| O$_2$ | 11,260 | 12.4 | 1.42 | 0.34 | 3.21 | 4.97 | 53.2 | 93.9 |
| Air | 11,050 | 14.1 | 4.15 | 0.20 | 2.72 | 7.07 | 33.5 | 95.6 |
| O$_2$[c] | 10,520 | 18.2 | 1.93 | 0.22 | 1.94 | 4.09 | 61.5 | 93.2 |
| Air[c] | 10,340 | 19.6 | 2.78 | 0.30 | 1.85 | 4.93 | 53.6 | 91.7 |
| | 10,890[b] | 18.3 | 0.89 | 0.86 | 1.43 | 3.18 | (West. Ky. Coal) | |
| O$_2$ | 10,930 | 16.6 | 0.10 | 0.37 | 1.53 | 2.00 | 37.1 | 95.7 |
| Air | 11,180 | 16.3 | 0.13 | 0.33 | 1.63 | 2.09 | 34.3 | 95.7 |
| O$_2$[c] | 10,240 | 21.8 | 0.08 | 0.09 | 1.31 | 1.48 | 53.5 | 89.2 |
| Air[c] | 10,730 | 20.6 | 0.09 | 0.10 | 1.37 | 1.56 | 50.9 | 92.9 |

[a]Leached 1 hr. at 150°C and 50 psia O$_2$ partial pressure.

[b]Heating value, ash content, and sulfur distribution of unleached coal.

[c]Leach solution was 0.2M sodium carbonate.

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The general conclusion drawn from the statistical analysis is that the nature of the leaching solution (alkaline or acidic) has a greater effect on desulfurization than the nature of the oxidant (air or oxygen). Specifically, desulfurization is more effective, at the 99.5% confidence level, under alkaline than under acidic conditions. Also, at a slightly lower confidence level, namely 95%, oxygen can be said to be a better oxidant than air.

Closer scrutiny of the data in Table 1 reveals also that in almost every case both the pyritic and the organic sulfur contents were significantly lower for alkaline than for acidic leaching conditions. Use of air versus oxygen, however, produced no discernible difference in the organic sulfur content. For the pyritic sulfur content, use of oxygen tended to result in lower values than use of air.

The relative effectiveness of alkaline, neutral, and acidic conditions under various oxygen partial pressures will also be discussed further below.

Effect of leaching time

The effect of leaching time on the desulfurization of Lo-vilia coal is presented in Table 2 and in Figure 3. At 150 °C and 50 psia oxygen partial pressure, prolonged leaching with 0.2$\underline{M}$ sodium carbonate improved the extraction of sulfur at first. But after about 1.5 hr., the reduction in total sulfur leveled off at about 76-79%. The initial increase in extraction seemed due to the removal of additional pyritic sulfur, since the amount of organic sulfur removed appeared fairly constant

Table 2.  Oxydesulfurization of coal as a function of
leaching time.[a]

| Time hr. | H.V. Btu/lb. | Ash % | lb.S/$10^6$ Btu | | | | Tot. S Redn. % | H.V. Recov. % |
|---|---|---|---|---|---|---|---|---|
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| 0 | 10,175[b] | 18.6 | 3.84 | 0.92 | 1.02 | 5.78 | - | - |
| 0.5 | 9,686 | 22.5 | 0.92 | 0.24 | 0.67 | 1.83 | 68.3 | 86.9 |
| 1.0 | 9,601 | 23.2 | 0.76 | 0.15 | 0.87 | 1.78 | 69.2 | 86.1 |
| 1.5 | 9,674 | 22.6 | 0.56 | 0.25 | 0.55 | 1.36 | 76.5 | 81.3 |
| 2.0 | 9,706 | 22.4 | 0.39 | 0.22 | 0.74 | 1.35 | 76.6 | 81.6 |
| 2.5 | 9,414 | 24.7 | 1.03 | 0.34 | 0.70 | 2.07 | 64.2 | 76.6 |
| 3.0 | 9,651 | 22.8 | 0.53 | 0.22 | 0.48 | 1.23 | 78.7 | 80.9 |

[a]Lovilia coal (-200/+250 mesh), leached with 0.2$\underline{M}$ Na$_2$CO$_3$ at 150°C
and 50 psia O$_2$.
[b]Heating value, ash content, and sulfur distribution of unleached
coal.

(from an initial 1.02 lb.S/$10^6$ Btu down to an average of 0.67
lb. S/$10^6$ Btu).  At the same time, the heating value recovery
decreased with increasing leaching time.  Thus, the small
advantage in removal of some additional pyritic sulfur was offset
by a higher loss in heating value.

Effect of oxygen partial pressure

The beneficial effect of increased oxygen partial pressure
on the desulfurization of coal has already been observed in Fig-
ure 2.  A set of experiments was then designed to study this ef-
fect over the range of 25-200 psia oxygen partial pressure by
leaching Lovilia and Western Kentucky coals with 0.2$\underline{M}$ sodium
carbonate at 150°C.  From the results shown in Table 3 and in

Table 3. Effect of oxygen partial pressure on alkaline leaching of Lovilia coal (-200/+250 mesh).[a]

| $O_2$ Press. psia | H.V. Btu/lb. | Ash % | lb.S/$10^6$ Btu | | | | Tot. S Redn. % | H.V. Recov. % |
|---|---|---|---|---|---|---|---|---|
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| - | 10,175[b] | 18.6 | 3.84 | 0.92 | 1.02 | 5.78 | - | - |
| 25 | 9,522 | 23.9 | 0.78 | 0.22 | 0.91 | 1.91 | 67.0 | 86.6 |
| 50 | 9,600 | 23.2 | 0.76 | 0.15 | 0.87 | 1.78 | 69.2 | 86.1 |
| 75 | 9,588 | 23.3 | 0.57 | 0.23 | 0.78 | 1.58 | 72.7 | 86.2 |
| 100 | 9,619 | 23.1 | 0.57 | 0.25 | 0.83 | 1.65 | 71.5 | 86.3 |
| 125 | 9,449 | 24.4 | 0.93 | 0.22 | 0.93 | 2.08 | 64.0 | 86.2 |
| 150 | 9,716 | 22.3 | 0.34 | 0.22 | 0.76 | 1.32 | 77.2 | 86.9 |
| 175 | 9,676 | 22.6 | 0.40 | 0.26 | 0.69 | 1.35 | 76.6 | 87.0 |
| 200 | 9,618 | 23.1 | 0.36 | 0.23 | 0.78 | 1.37 | 76.3 | 84.1 |

[a]Leached 1 hr. with 0.2$\underline{M}$ $Na_2CO_3$ at 150°C.
[b]Heating value, ash content, and sulfur distribution of unleached coal.

Figure 4, it is evident that the reduction in the total sulfur of Lovilia coal increased from 67% up to 76-77% by increasing the oxygen partial pressure. The slight improvement can be attributed to additional removal of both pyritic and organic sulfur. By contrast, the improved desulfurization of Western Kentucky coal with increasing oxygen partial pressure was due to the increased removal of organic sulfur and not pyritic sulfur (data shown in Table 4 and Figure 5). There is no ready explanation for this difference in the behavior of the pyritic sulfur of the two coals. Lovilia coal seems also unique in that
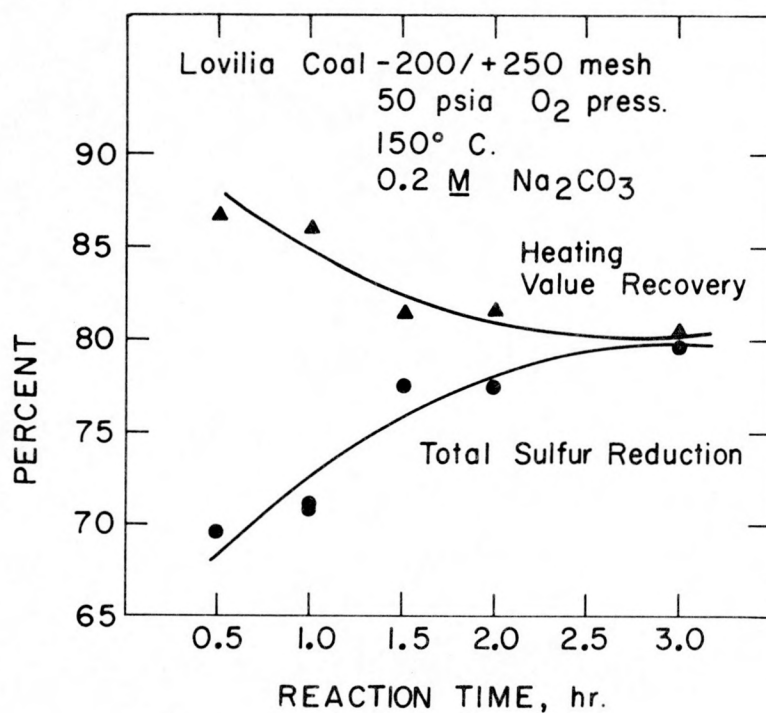
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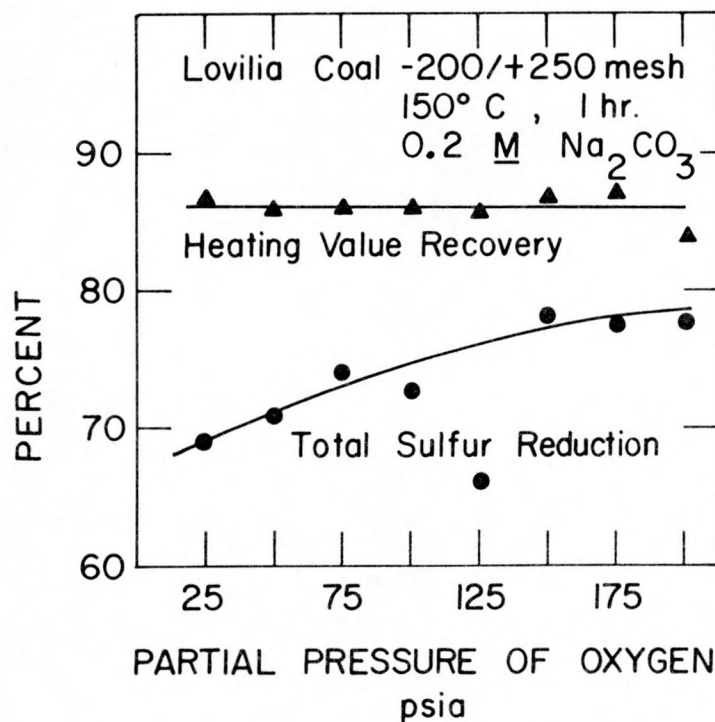Figure 3. Effect of leaching time on oxydesulfurization of coal.



Figure 4. Effect of oxygen partial pressure on oxydesulfurization of coal.

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Table 4. Leaching Western Kentucky Coal (-200 mesh) at different oxygen pressures.[a]

| $O_2$ Press psia | H.V. Btu/lb. | Ash wt.% | lb.S/10⁶ Btu | | | | Tot. S Redn. % | H.V. Recov. % |
|---|---|---|---|---|---|---|---|---|
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| | 10,890[b] | 18.3 | 0.89 | 0.86 | 1.43 | 3.18 | -- | -- |
| 50 | 10,237 | 21.8 | 0.08 | 0.09 | 1.32 | 1.49 | 53.3 | 89.2 |
| 100 | 10,370 | 21.9 | 0.16 | 0.08 | 1.22 | 1.45 | 54.6 | 89.4 |
| 150 | 10,375 | 21.9 | 0.17 | 0.09 | 1.15 | 1.41 | 55.9 | 89.5 |
| 200 | 10,383 | 21.8 | 0.13 | 0.14 | 1.12 | 1.38 | 56.5 | 90.2 |

[a]Leached 1 hr. by 0.2$\underline{M}$ $Na_2CO_3$ at 150°C. Data are averages of duplicate runs.

[b]Heating value, ash content, and sulfur distribution of unleached coal.

the pyritic sulfur content was almost never reduced to a level below about 0.4%. In Western Kentucky coal, on the other hand, the pyritic sulfur was decreased to as low as 0.13%. For both coals, however, the heating value recovery was almost unaffected by the increased oxygen partial pressure, remaining at about 86 and 90% for Lovilia and Western Kentucky coal, respectively.

The effect of oxygen partial pressure on the desulfurization of coal was studied also under alkaline, neutral, and acidic leaching conditions. The data in Table 5 and Figure 6 are for Western Kentucky coal, leached for 1 hr. at 150°C by 0.2$\underline{M}$ sodium carbonate, 0.2$\underline{N}$ sulfuric acid, or water at pressures from 50 to 200 psia oxygen.

Table 5.  Effect of oxygen partial pressure on the leaching of
coal with alkaline,neutral or acidic solutions[a].

| $O_2$ Press psia | H.V. Btu/lb. | Ash % | lb.S/$10^6$ Btu | | | | Tot. S Redn. % | H.V. Recov. % |
|---|---|---|---|---|---|---|---|---|
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| | 10,890[b] | 18.3 | 0.89 | 0.36 | 1.43 | 3.18 | --- | --- |
| 0.2$\underline{M}$ Na$_2$CO$_3$ | | | | | | | | |
| 50 | 10,322 | 21.7 | 0.10 | 0.07 | 1.32 | 1.49 | 53.1 | 90.0 |
| 100 | 10,368 | 21.9 | 0.15 | 0.07 | 1.21 | 1.43 | 55.0 | 87.8 |
| 150 | 10,344 | 22.1 | 0.20 | 0.09 | 1.13 | 1.42 | 55.3 | 86.9 |
| 200 | 10,230 | 22.9 | 0.13 | 0.13 | 1.19 | 1.45 | 54.4 | 90.2 |
| water[c] | | | | | | | | |
| 50 | 10,885 | 16.8 | 0.12 | 0.28 | 1.49 | 1.89 | 40.6 | 97.2 |
| 100 | 10,090 | 16.4 | 0.13 | 0.27 | 1.41 | 1.81 | 43.1 | 95.0 |
| 150 | 11,138 | 16.1 | 0.16 | 0.22 | 1.29 | 1.67 | 47.5 | 96.7 |
| 200 | 11,148 | 16.0 | 0.14 | 0.20 | 1.27 | 1.61 | 49.4 | 96.2 |
| 0.2$\underline{N}$ H$_2$SO$_4$ | | | | | | | | |
| 100 | 11,212 | 15.5 | 0.10 | 0.44 | 1.41 | 1.95 | 36.7 | 98.5 |
| 150 | 11,204 | 15.6 | 0.11 | 0.38 | 1.34 | 1.83 | 42.4 | 95.9 |
| 200 | 11,185 | 15.7 | 0.11 | 0.43 | 1.31 | 1.85 | 41.8 | 96.8 |

[a]Western Kentucky coal (-200 mesh), leached 1 hr. at 150°C.

[b]Heating value, ash content, and sulfur distribution of uncleachd coal.

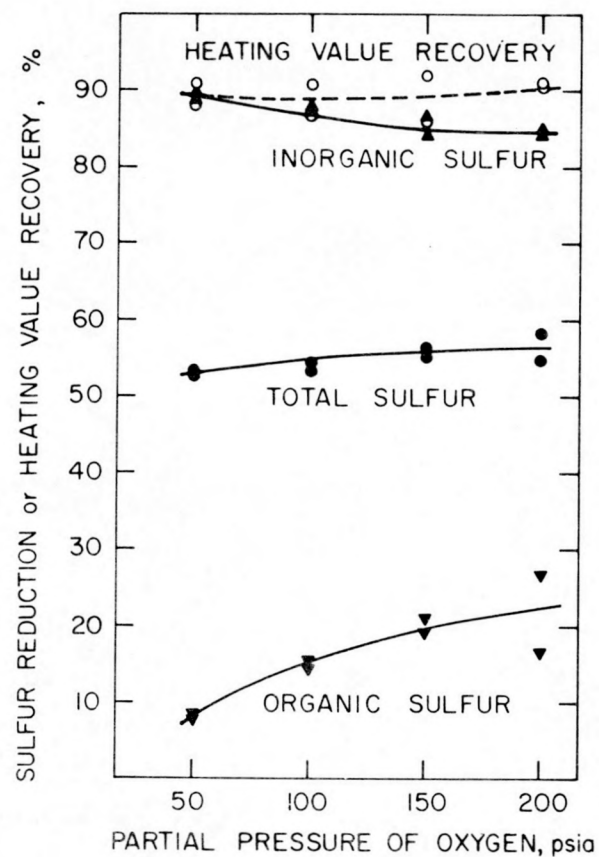[c]Initial solution, becomes acidic as leaching proceeds.

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Figure 5. Effect of oxygen partial pressure on leaching of Western Kentucky coal.
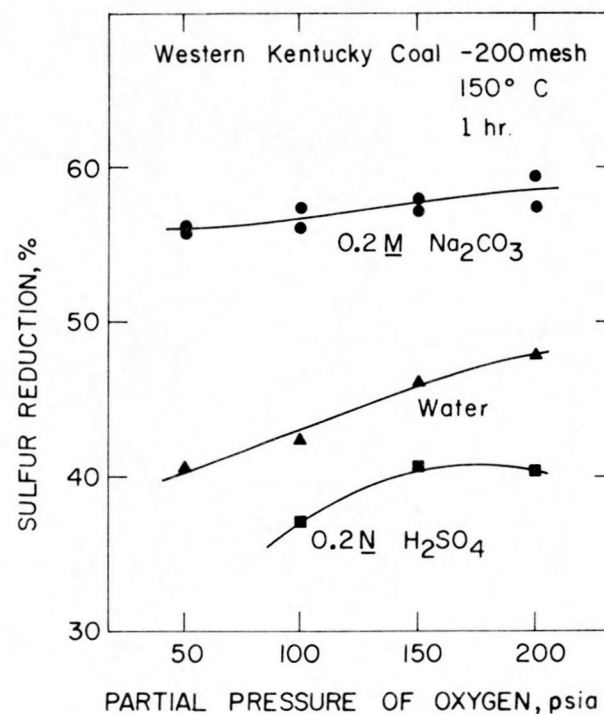


Figure 6. Effect of oxygen partial pressure on oxydesulfurization of coal by leaching with alkaline, neutral or acidic solutions.

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When water was used as the leachant, the initially neutral solution became acidic during the leaching process because of the production of sulfuric acid. Under these conditions, the reduction of total sulfur increased almost linearly with increasing oxygen pressure, from 40.6% at 50 psia to 49.4% at 200 psia oxygen partial pressure. When the leachant was initially acidic (0.2$\underline{N}$ sulfuric acid), the reduction of total sulfur was less favorable, ranging from 36.7% at 100 psia, through 42.4% at 150 psia, to 41.8% at 200 psia oxygen partial pressure.

When 0.2$\underline{M}$ sodium carbonate was the leachant, the total sulfur reduction was much higher; however, it seemed to increase only slightly with increasing oxygen partial pressure, from 53.1 to 55.3%. The amount of organic sulfur in the leached residue was less than that for the other leachants and appeared to decrease with increasing pressure. The heating value recovery, on the other hand, was lower under alkaline conditions (87-90%) than under acidic conditions (96-99%).

It should be noted that none of the coal samples removed from the autoclave were washed with water after the leaching treatment. This obviously had an effect on the residual levels of sulfate in the leached coal, amounting to about 0.2 lb.S/$10^6$ Btu. In the case of sulfuric acid as the leachant, this effect was even more noticeable with residual sulfate levels of about 0.4 lb. S/$10^6$ Btu. In addition to improving the total sulfur reduction, a washing step would also decrease the ash content of the leached coal. The benefits of washing leached coal by water or by dilute acid were recognized by Tai et al. (1977).

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## Effect of alkali concentration

The data in Table 6 and Figure 7 show the effect of the alkali concentration on the desulfurization of Lovilia coal at 150°C and 50 psia oxygen partial pressure for 1 hr. With no sodium carbonate present in the leach solution, the reduction of total sulfur was 58%. The presence of even a small amount of alkali, i.e. 0.05$\underline{M}$ sodium carbonate, improved the total sulfur reduction significantly, to 66%. Further increases in alkali concentration resulted in only slight improvement, while at higher concentrations the reduction of total sulfur even declined. The optimum concentration seemed to be 0.15-0.2$\underline{M}$ sodium carbonate, resulting in approximately 71% reduction of total sulfur. For this same concentration range, the residual amounts of pyritic, sulfate, and organic sulfur appeared to be minimum. Higher concentrations of alkali were also detrimental to the heating value recovery, causing a decline from 92.7 to 78.9% in the recovery by increasing the sodium carbonate concentration from 0.05 to 0.5$\underline{M}$. Even worse heating value recoveries were observed at higher alkali concentrations (Wheelock et al., 1978).

## Effect of temperature

The results of the effect of the leaching temperature on the desulfurization of Lovilia coal are presented in Table 7 and Figure 8. With increasing temperature, the total sulfur reduction increased at first, then passed through a broad maximum, after which it decreased at an accelerating rate. The optimum temperature range was approximately 120-150° C; up to 71.4%

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Table 6. Effect of sodium carbonate concentration on leaching of coal.[a]

| Conc. $Na_2CO_3$ M | H.V. Btu/lb. | Ash % | lb.S/$10^6$ Btu | | | | Tot.S Redn. % | H.V. Recov. % |
|---|---|---|---|---|---|---|---|---|
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| -- | 10,418[b] | 18.0 | 3.24 | 0.90 | 0.99 | 5.13 | -- | -- |
| 0[c] | 10,982 | 13.4 | 1.08 | 0.29 | 0.80 | 2.17 | 58.0 | 91.7 |
| 0.05 | 10,833 | 14.1 | 0.68 | 0.36 | 0.71 | 1.75 | 66.2 | 92.7 |
| 0.10[d] | 10,401 | 17.9 | 0.73 | 0.24 | 0.72 | 1.69 | 67.4 | 89.2 |
| 1.15[d] | 10,156 | 19.9 | 0.62 | 0.20 | 0.71 | 1.53 | 70.5 | 88.2 |
| 0.20[d] | 9,858 | 22.2 | 0.82 | 0.21 | 0.81 | 1.84 | 64.4 | 86.7 |
| 0.25 | 9,680 | 23.6 | 1.14 | 0.22 | 0.93 | 2.29 | 55.7 | 86.2 |
| 0.30[d] | 9,340 | 25.8 | 0.82 | 0.28 | 0.86 | 1.96 | 61.7 | 84.4 |
| 0.40[d] | 9,246 | 26.5 | 0.74 | 0.21 | 0.84 | 1.99 | 61.2 | 80.2 |
| 0.50[d] | 9,186 | 27.0 | 0.70 | 0.46 | 0.80 | 1.96 | 61.9 | 78.9 |

[a]Lovilia coal (-200/+250 mesh), leached 1 hr. at 150°C and 50 psia $O_2$.

[b]Heating value, ash content, and sulfur distribution of unleached coal.

[c]Leach solution was initially water; became acidic as leaching proceeded.

[d]Values are averages of duplicate runs.

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Table 7. Effect of temperature on the leaching of coal with alkali.[a]

| Temp. °C | H.V. Btu/lb. | Ash % | lb.S/$10^6$ Btu | | | | Tot.S Redn. % | H.V. Recov. % |
| | | | Pyr. | Sulf. | Org. | Tot. | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| -- | 10,047[b] | 19.6 | 3.90 | 0.94 | 0.93 | 5.77 | -- | -- |
| 100 | 9,666 | 22.6 | 1.25 | 0.28 | 0.69 | 2.22 | 61.5 | 89.7 |
| 120 | 9,634 | 22.9 | 0.80 | 0.29 | 0.56 | 1.65 | 71.4 | 88.2 |
| 130 | 9,662 | 22.7 | 0.88 | 0.23 | 0.64 | 1.75 | 69.7 | 89.2 |
| 150[c] | 9,268 | 25.9 | 1.42 | 0.20 | 0.70 | 2.32 | 59.9 | 83.6 |
| 170 | 9,205 | 26.3 | 1.51 | 0.27 | 0.59 | 2.37 | 58.9 | 80.2 |
| 180[c] | 9,016 | 27.8 | 1.71 | 0.22 | 0.98 | 2.91 | 49.7 | 75.9 |
| 200 | 8,950 | 28.4 | 2.69 | 0.23 | 0.98 | 3.90 | 32.4 | 78.2 |
| -- | 10,390[b] | 18.3 | 3.12 | 0.94 | 1.03 | 5.09 | -- | -- |
| 110[d] | 9,783 | 23.1 | 0.59 | 0.25 | 0.89 | 1.73 | 66.0 | 90.2 |

[a]Lovilia coal (-200/+250 mesh), leached 1 hr. with 0.2$\underline{M}$ $Na_2CO_3$ at 50 psia $O_2$.

[b]Heating value, ash content, and sulfur distribution of unleached coal.

[c]Average of duplicate runs.

[d]Control sample for this run was sample immediately above.
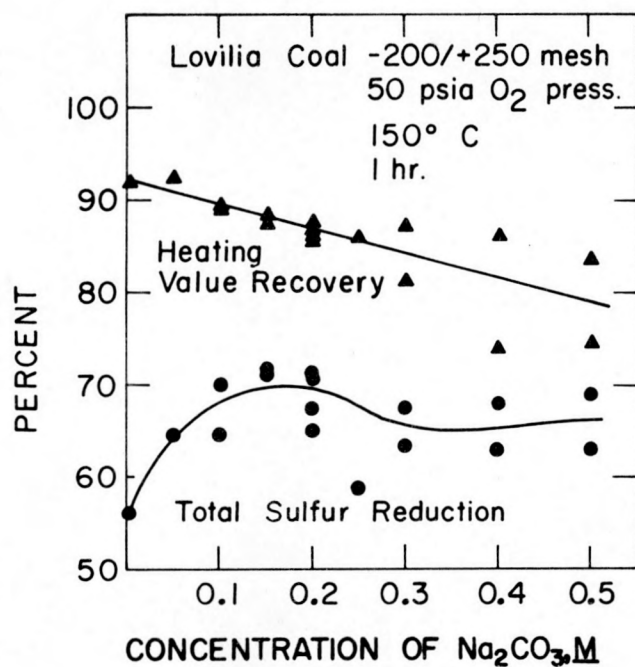
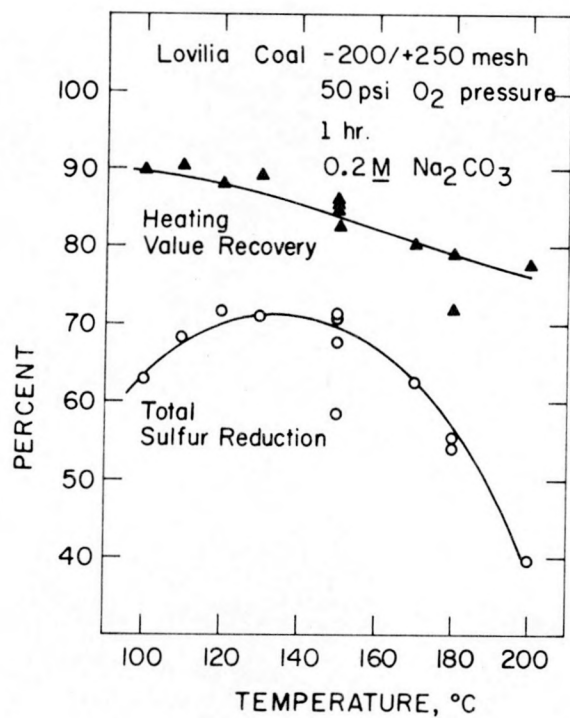Figure 7. Effect of sodium carbonate concentration on oxydesulfurization of coal.



Figure 8. Oxydesulfurization of coal as a function of temperature.

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of the total sulfur was extracted in this region. At 200 °C, the total sulfur reduction had decreased to 32.4%. The relative reductions in pyritic and organic sulfur seemed to parallel the reduction curve for total sulfur. Only sulfate sulfur appeared to have a constant residual value of about 0.2 lb. S/10$^6$ Btu. The heating value recovery declined steadily with increasing temperature, from 90% down to 78%, probably because of partial oxidation of coal.

At the present time, it is not certain what causes this unusual temperature effect. It may be due to a decrease in the solubility of oxygen in the sodium carbonate solution at higher temperatures. Or perhaps it may be caused by a thermally induced change in the structure of coal itself. Alternatively, there may be a change in the reaction mechanism or kinetics, possibly caused by the thermal decomposition of a reactive intermediate.

## CONCLUSIONS

It has been demonstrated with a small autoclave reactor that leaching of high-sulfur bituminous coals with hot, dilute solutions of sodium carbonate containing dissolved oxygen under pressure can remove most of the inorganic sulfur and a portion of the organic sulfur. Dilute alkaline leach solutions have been shown to be more effective than neutral or acidic solutions. More concentrated alkaline solutions are less beneficial and even detrimental, causing lower reduction in sulfur and decreasing the heating value recovery. The desulfurization reaction becomes independent of the stirring rate at high stirring speeds.

Leaching longer than 1-1.5 hr. results only in a modest increase in sulfur removal, but the advantage is offset by a decrease in heating value recovery. Increasing the oxygen partial pressure improves the extraction of sulfur without a noticeable decrease in the heating value recovery. The improvement is due mainly to an increase in the removal of organic sulfur, amounting to 30% in some cases. An optimum temperature range has been observed at about 120-150°C for which the reduction of sulfur is maximum. At higher temperatures, both the extraction of sulfur and the heating value recovery decline significantly.

The overall Ames oxydesulfurization process has been shown to be effective in removing almost all of the inorganic sulfur and a significant portion of the organic sulfur under relatively mild conditions. The moderate temperatures and pressures do not require extraordinary equipment, and the alkaline conditions provide a non-corrosive environment. With proper regeneration of the leaching solution, the process should prove an economical method for the chemical cleaning of high-sulfur coal.

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# CONVERSION TABLE TO INTERNATIONAL (SI) SYSTEM UNITS

1 Btu    =  1,055 joules

1 lb.    =  453.6 g

1 Btu/lb. = 2.324 joules/g

1 psi    =  6.89 kPa

1 r.p.m. = 0.105 rad/sec