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The Controlled Oxidation of Lignite in a Fixed Bed

Leroy Dockter

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THE CONTROLLED OXIDATION
OF LIGNITE
IN A FIXED BED

by

Leroy Dockter

B. S. in Chemical Engineering
University of North Dakota, 1959

A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

June
1969

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This thesis submitted by Leroy Dockter in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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Title The Controlled Oxidation of Lignite in a Fixed Bed

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Date June 29, 1969

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ABSTRACT

The use of cooling coils or pipes to control the reaction zone temperatures when oxidizing lignite in a fixed bed was studied. The experimental procedures involved passing heated air through a bed of lignite to initiate spontaneous heating and then removing the heat generated using a water cooled coil. Variables investigated included the lignite moisture content, prior oxidation history, and lignite source.

Spontaneous heating was initiated in lignite from three different mines, and at initial moisture contents from bed moisture down to 10 percent by heating the lignite to 250-260 °F while passing air slowly through the bed. At moisture contents below 10 percent or after severe oxidation the temperature necessary to initiate spontaneous heating rose to over 300 °F.

The low thermal conductivity of the lignite bed was found to prevent adequate heat removal from the bed to permit satisfactory control of the oxidation of lignite. An equation describing the temperature distribution in the lignite between cooling pipes embedded in the oxidizing lignite was developed.

INTRODUCTION

The main objective of this thesis was to study the use of cooling coils or pipes to control the reaction zone temperature when oxidizing lignite in a fixed bed. The study was divided into two phases. The first phase included the development of a procedure by which rapid oxidation of lignite could be initiated in a fixed bed, and investigation of the factors which affect this rapid oxidation. The second phase of this study was the investigation of the heat transfer from oxidizing lignite via cooling coils or pipes as a method of keeping the bed temperature low enough to prevent combustion.

Interest in this project was prompted by the tantalizing possibility of uniting the North Dakota lignite mining industry with the state's farming industry. In the past, contact between the lignite industry and agriculture was limited to taking land out of agricultural production to facilitate the mining of lignite. The lignite mined has been used almost entirely as a fuel for electrical power generation. Recently however, evidence has been mounting that lignite might be put into a non-fuel use as a soil conditioner-fertilizer component.

To be useful as a soil additive the lignite must be partially oxidized to increase its humic acid content.

A literature survey indicated that very little information about the controlled oxidation of lignite was available. This thesis work is therefore a study of one method by which lignite can be oxidized.

CHAPTER I

BACKGROUND INFORMATION

Considerable work has been done in an effort to develop a good fertilizer from lignite coal in the past. Generally efforts were directed toward producing an ammoniated fertilizer which could compete with other mineral fertilizers. Young presents a bibliography of 13 papers and patents concerning the use of coals and coal derivatives as fertilizers.¹

A form of naturally occurring oxidized lignite called Leonardite has proved beneficial as a soil additive when ammoniated or acid washed.^{2,3} Since deposits of Leonardite are usually found in conjunction with lignite seams, it would be desirable if the lignite itself could be utilized as a raw material for a soil additive. One of the most recent investigations into the use of lignite as a soil additive was by Freeman, who studied the effects of coal-derived humates on plant growth.⁴ He reported that lignite, and in particular oxidized lignite, had potential as an agricultural soil additive and suggested that to take advantage of this capability one would probably have to accelerate the rather slow natural oxidation of lignite by oxidizing it rapidly under controlled conditions.

The rapid oxidation of lignite which was found desirable if lignite is to be used for agricultural purposes is the same reaction which has been plaguing the lignite industry since the first mine was opened. When lignite is exposed to the atmosphere, it reacts with oxygen liberating heat. If the proper conditions exist, this heat is not dissipated and as a result the local temperature rises. As the temperature rises the oxidation rate increases, resulting in an ever increasing spiral known as spontaneous heating. The temperature caused by this spontaneous heating may vary from a few hundred degrees to over 2000°F in glowing embers. The temperatures in these "hot spots", and the rate at which these "hot spots" grow are in part a function of the ease with which air can get into the hot region and the rate at which heat is transferred from it.

As can readily be understood, this form of uncontrolled rapid oxidation is very undesirable from the lignite industry's view point. Not only does this oxidation decrease the heating value of the lignite, but if left unattended a "hot spot" can grow until all the lignite stored in the pile is consumed. Once one of these "hot spots" has formed in a lignite pile, it is not an easy task to eliminate it. Experience has shown that the most expedient way to get rid of a "hot spot" is to literally dig out and spread the hot lignite into thin layers to cool off, and then return the cooled lignite to the pile. Consumers who stockpile lignite go to great extremes to prevent these "hot spots" from forming.

The Bureau of Mines has done considerable work on the procedures for preventing spontaneous combustion of lignite in storage piles.^{5,6}

A survey of the literature concerning the initiation and control of the oxidation of lignite indicated that some work had been done in this field. Unfortunately most of the work was oriented toward determining the spontaneous heating tendencies of lignite and the procedures necessary to prevent this. Elder, et al., studied the oxidation of various coals ranking from low-volatile bituminous to lignite.⁷ Their investigation was carried out in an externally heated rotating drum in which the effects of temperature, oxygen concentration, particle size, and moisture on the oxidation rate of coals were studied.

Sondreal presents a fairly comprehensive study of lignite oxidation at temperature levels of 25, 65, and 95 °C.⁸ Among the variables investigated were oxygen concentration, moisture content, particle size, and the effects of prior oxidation. Although the temperature ranges covered by Sondreal are considerably below those investigated in this thesis work, it might be interesting to note some of his conclusions. At lower temperatures oxidation of the lignite caused a progressive decrease in the oxidation rate; however, when the lignite was heated above 70 °C this deactivation was reversed. Large quantities of absorbed carbon dioxide were released and the lignite was as reactive, or more reactive, than it was prior to the initial oxidizing period.

Moisture removal increased the rate of oxidation until the moisture content was down to about 25 percent. Below 25 percent moisture the oxidation rate decreased, but never below that of the raw lignite. The oxidation rate was found to be directly proportional to the oxygen concentration, all other variables being constant. Over the temperature range investigated, the oxidation rate doubled for every 11 °C rise in temperature.

Sanderson studied the oxidation rate and the heat of oxidation for lignite in oxygen at temperatures of 20, 60, and 90 °C.⁹ He concluded, as did Sondreal, that temperature, size consist, and the extent of prior oxidation affected the rate of oxidation. The oxygen consumption rates obtained varied from 0.01 to 0.07 gram-moles oxygen per hour per kilogram of moisture and ash free (maf) lignite for the least reactive lignite at 20 °C and the most reactive lignite at 90 °C respectively. The heat of oxidation was not affected by moisture content or prior oxidation; however, his data indicated a small increase with temperature. He reported heat of oxidation values of 85 and 89 Kcal per gram-mole oxygen for temperatures of 60 and 90 °C respectively.

A literature search for information on the thermal conductivity of lignite yielded two sources which may give an order of magnitude estimate for the thermal conductivity of lignite. Lange's Handbook gives a value of 0.098 BTU/hr ft °F at temperatures below 32 °F for "coal".¹⁰ D. J. Millard using coking coals of minus one-half inch size gives

a range of 0.097 to 0.145 BTU/hr ft °F.¹¹ Although the information was not given, it may be assumed that the value from Lange's handbook is for monolithic coal while the values given by Millard are for a porous bed and would therefore more closely approximate the conditions presented in a bed of lignite. From these values we can see that lignite will probably have the thermal conductivity characteristics of a fairly good insulator. For the benefit of those who may be interested in this topic in the future, Sondreal is investigating the thermal conductivity of lignite at the Bureau of Mines Coal Research Laboratory in Grand Forks, North Dakota, concurrently with this project.

In summary, there is a large potential market for oxidized lignite as a soil conditioner-fertilizer for the agricultural industry; to take advantage of this use the natural oxidation of lignite must be accelerated; and this rapid oxidation can take place in lignite stockpiles under proper conditions, but if the air flow into the pile and the heat build-up due to oxidation are not controlled spontaneous combustion can occur.

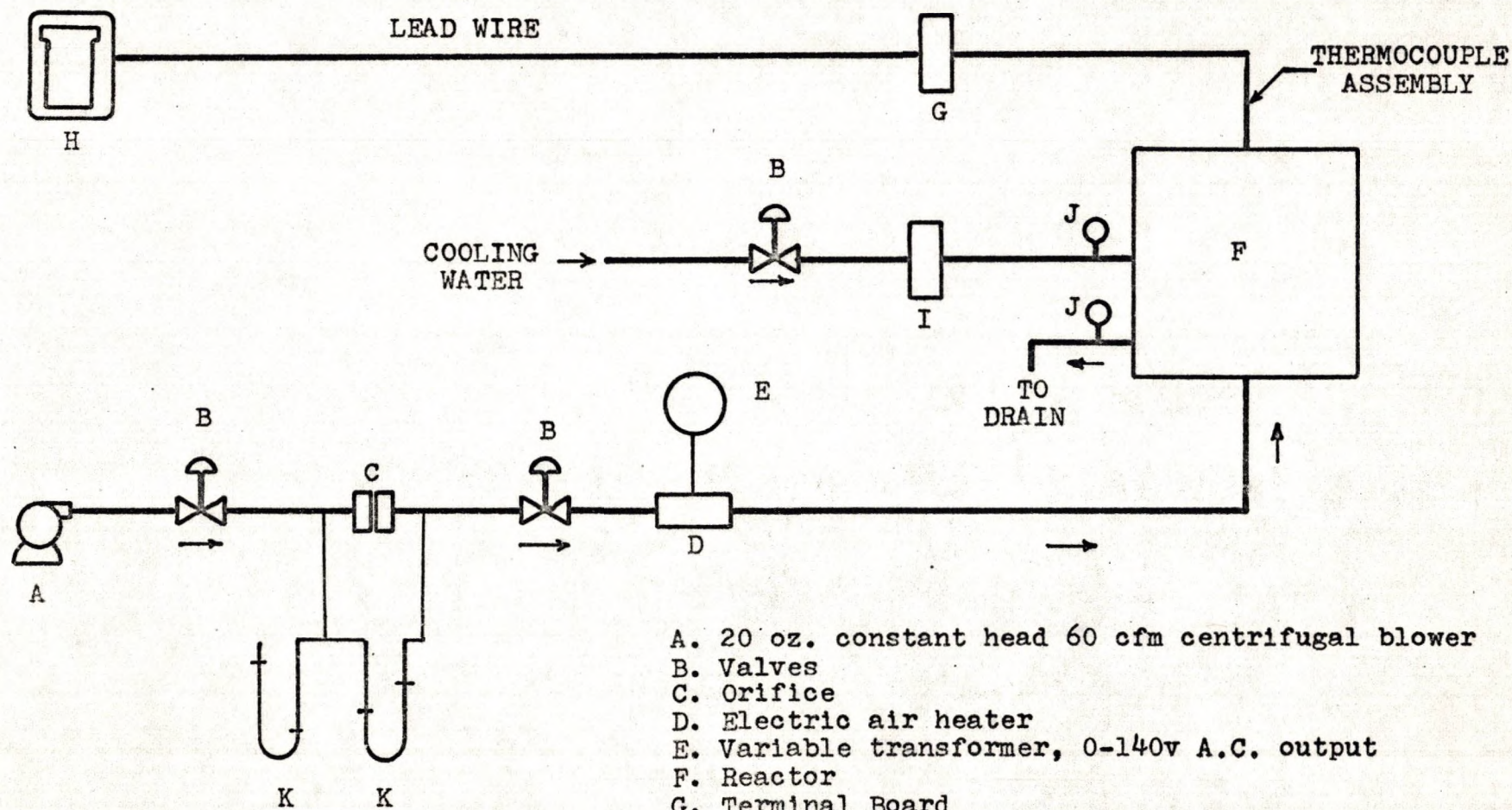
CHAPTER II

TEST EQUIPMENT

A schematic diagram of the test apparatus used for this research work is presented in Figure 1. The major components of the test set-up were a constant head centrifugal blower, an orifice for measuring air flow, a variable transformer, an electric resistance heater, a test reactor, two thermocouple assemblies, a 16 point temperature indicator-recorder, a rotameter to measure water flow, and a cooling coil. The test reactor will be described in detail later in this chapter.

The air flow rates were measured ahead of the air heater using an orifice plate and manometer system. The values presented in this thesis are at standard gas conditions of 60 °F and 30 inches mercury pressure. The orifice was calibrated in place using an American Meter Company low pressure orifice flow prover.

After passing through the orifice, the air was brought up to the desired temperature using a 600 watt electrical resistance air heater. The heating element was installed in a section of insulated pipe which was then filled with short ceramic tubes to create turbulence and furnish heat transfer area. The voltage to the heating element could be varied from 0 to 140 volts A.C. using a variable transformer.



- A. 20 oz. constant head 60 cfm centrifugal blower
 B. Valves
 C. Orifice
 D. Electric air heater
 E. Variable transformer, 0-140v A.C. output
 F. Reactor
 G. Terminal Board
 H. 16 point indicating recorder, 32-475 °F range
 I. Rotameter, 0-8 gph
 J. Bimetallic thermometers, 0-220 °F
 K. Manometers

Fig. 1.--Schematic diagram of test apparatus

The temperatures in the test reactor were recorded on a 16 point potentiometric indicating recorder which had a range of 32 to 475 °F. To compensate for differences in cold junction temperature, the instrument was equipped with a manual cold junction bias. The instrument was calibrated and cross-checked at intervals during the course of this investigation using a portable laboratory potentiometer.

A cross-sectional view of the test reactor with the cooling coil installed is presented in Figure 2. The reactor was essentially two nested cylindrical metal containers 10.5 inches and 15.5 inches in diameter. The annular space between the two containers was filled with light-weight vermiculite insulation. The bottom 5 inches of the inner container was used as a plenum and contained an air baffle plate directly over the air inlet pipe to prevent the air from channeling up the center of the lignite bed. To support the lignite bed, an expanded metal grid covered with two layers of ordinary window screen laid at 45° angles to each other was used. Prior to charging for a test, a layer of particles which had been screened from the lignite to be tested was placed on this base to reduce the loss of fines. This simple base was found to be a very satisfactory means of supporting the bed, as very little fines sifted through into the plenum during the course of a test. A conical metal hood placed on top of the reactor helped funnel the gases from the reactor toward an exhauster hose to keep the area clear of gases.

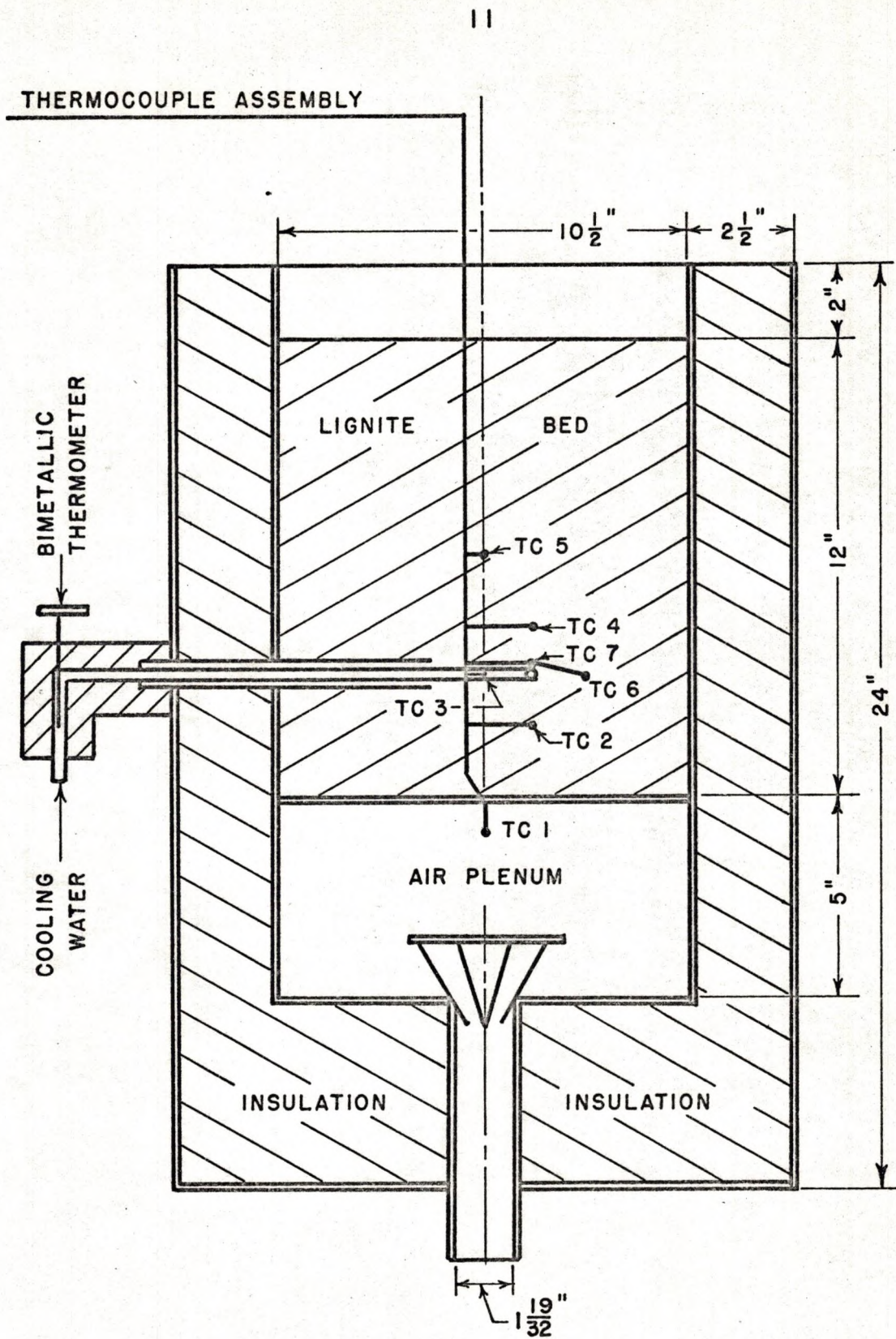


Fig. 2.--Cross-section of reactor with cooling coil installed.

All thermocouples used were fabricated from 24 B. & S. gage Type K Chromel-Alumel thermocouple wire with an asbestos and glass sheath. The thermocouples were made by fusing the fluxed ends of the two wires into a ball and were then checked for accuracy in boiling water using a portable laboratory potentiometer.

Different thermocouple assemblies were made for tests under Phase One and Phase Two. In place, the Phase One thermocouple assembly allowed temperature measurement of the air in the plenum below the lignite bed, at two inch intervals up the center of the bed, the gas above the bed, and a horizontal profile on two inch intervals at any level in the bed, for a total of 13 points. All thermocouple points were one half inch away from the assembly to prevent false readings due to air channeling or heat conductivity through the assembly.

The Phase Two thermocouple assembly which is shown in Figure 2 and shown partially in Figure 3 allowed measurement of the air temperature in the plenum, bed temperatures around a point midway along the length of the cooling coil, the surface temperature of the coil at the midway point, and the temperature at the center of the bed. Thermocouples TC1, TC2, and TC3 were each hooked up to three different recorder points, and TC4, TC5, and TC6 were each hooked up to two different recorder points. Using this method readings for most thermocouples were obtained about every seven minutes.

The cooling coil used to remove heat from the oxidizing lignite bed was fabricated from a 9 inch piece of 1/4 inch O.D. copper tubing as shown in Figure 3. To prevent heat transfer in the lines going to and from the coil, the lead-in lines were made from 3/16 inch O.D. stainless steel tubing which has about one-twentieth the thermal conductivity of copper. Each of these stainless lines was covered with ceramic insulators to further prevent heat transfer. Once outside the reactor, these lines were insulated with a light-weight castable insulation. Bimetallic thermometers were placed in the ingoing and outgoing cooling water lines as close to the reactor as possible. Also shown in Figure 3 is a cross-section of the cooling tube through the TC7 contact point and indicating the four surrounding thermocouple locations.

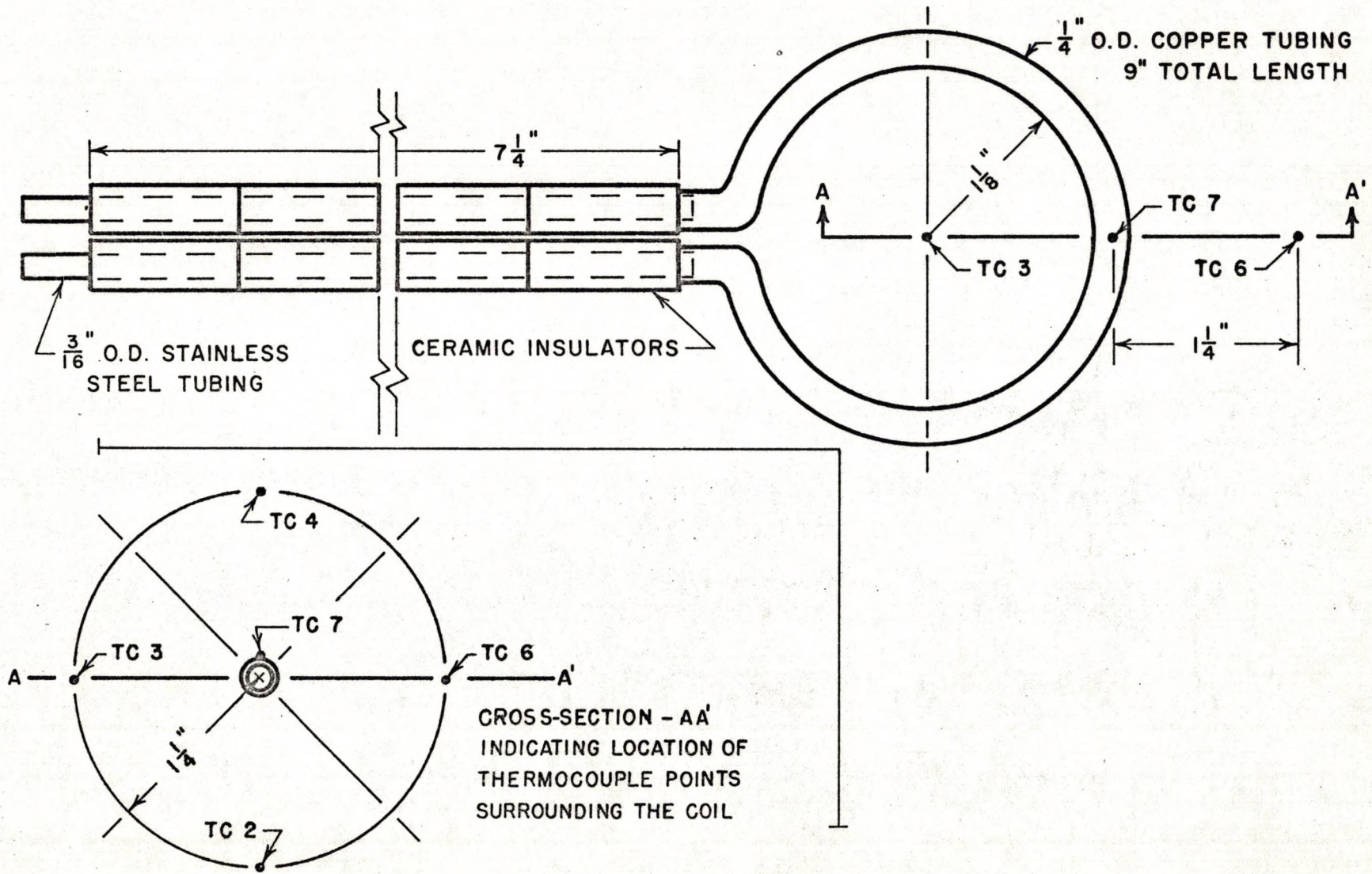


Fig. 3.--Cooling coil

CHAPTER III
EXPERIMENTAL PROCEDURES
Sample Preparation

All of the lignite used in this project was supplied by the Bureau of Mines Coal Research Laboratory where this research was performed. The mines from which the lignite originated and the analyses of these lignites are given in Appendix A.

Lignite as mined has a moisture content of about 30 to 40 percent. Upon exposure to air, it will lose a considerable portion of this moisture and as it dries the lignite chunks break into smaller pieces in a degrading process known as slacking. Because of this characteristic, it is almost impossible to dry lignite or expose it to air, and still retain the original size distribution. This means that in a commercial oxidizing venture even if the lignite mines were to produce a particular size fraction, such as 1/2 by 1/4 inch, by the time it arrived on site and had been charged to the oxidizing unit considerable size degradation would have occurred. Therefore, most of the tests in this work were performed on lignite which had been crushed to a certain top size fraction rather than using lignite screened to a certain size fraction.

The lignite as received had been crushed to a top size of 2 inches at the individual mines. It was then crushed again to a 3/4 inch top size. Unless otherwise stated, all tests performed were on lignite of this size consist. A screen analysis for the three different lignites used is given in Appendix A.

Reactor Charging

Prior to charging the reactor, a portion of the lignite to be used was screened to obtain sufficient plus 1/8 inch lignite to cover the reactor bottom with a layer of particles. The undersize generated during this screening was discarded. After assuring that the thermocouple assembly and cooling coil, if used, were in their proper location, the lignite which had previously been prepared and mixed was charged to the reactor. To prevent size segregation as the reactor was charged, small quantities of lignite were spread into the reactor in layers. As these layers were built up, grab samples were taken at intervals. These cumulative grab samples were used to obtain an analysis of the lignite charged.

Test Procedure

One of the major problems encountered in this research work was that of determining the temperature at which spontaneous heating was initiated, and how to measure the effect of different variables on this temperature. To measure this

temperature, it was necessary to raise the temperature of the lignite bed, while passing air through it, until the spontaneous combustion cycle was started.

Initial efforts to heat the lignite to various temperatures prior to charging to the reactor were unsuccessful due to cooling and other difficulties encountered in the charging procedure. External heating of the lignite bed was eliminated as a possibility because the low conductivity of the lignite would have produced a sharp temperature gradient across the diameter of the bed.

It was decided that the best method for heating the lignite was to heat the air before it was passed through the bed. Of course, this method had drawbacks, such as the drying effect of the hot air being used to heat the bed and a limit on the rate at which the bed temperature could be raised, but the heating rate was controllable and resulted in a fairly flat temperature profile across the lignite bed under "steady state" conditions. If the temperature of the incoming air was slowly raised as the bed warmed up, eventually the bed temperature passed the temperature of the incoming air. This "cross-over temperature" was used as an indication that spontaneous heating had been initiated. If the air flow was continued after cross-over, the bed temperature would rise until the lignite was burning.

For a perfectly insulated reactor and a low air flow rate, the heat built up from long term oxidation would probably raise the bed temperature enough to initiate spontaneous

heating even if the air temperature was fairly low. Since both air flow rate and the length of the oxidizing period effect the cross-over temperature, a constant air flow rate was used to determine the effects of the other variables tested.

To reduce the time necessary to initiate spontaneous heating higher air flow rates were used. An upper limit on the air flow, and consequently the heat input rate, was the flow velocity which caused entrainment of the smaller particles in the lignite bed. This flow rate was found to be about 14 to 15 cfm per square foot of reactor cross-section. Above this flow rate, considerable migration of the smaller sizes into the upper part of the bed was observed.

Although it was not measured, a lower limit on the air flow rate necessary to initiate spontaneous heating also made its presence known during the initial testing period. When the natural convection chimney effect was allowed to control the air flow rate after an initial warm-up period, all the oxygen was seemingly consumed by the first few layers of particles. During several of these low air flow tests, ash was found in the bottom one-half inch layer of the bed indicating combustion on the surface of the particles. The lignite two inches higher in the bed was, for all practical purposes, unaffected.

During the initial testing period, it was established that for the air flow rate range of 5 to 10 cfm/sq ft bed a temperature cross-over would not occur until after the

highest bed temperature was around 250 °F. Once this was established, the air temperature for further tests was rapidly brought up to about 230 °F and kept there until the 2 inch level bed temperature had risen to equilibrium. The air temperature was then raised slowly until the temperature at the 2 inch level in the bed passed the temperature of air coming in. This temperature was recorded as the cross-over temperature. Cross-over usually occurred about 5 to 7 hours after the start of a test.

During the experimentation under Phase one of this investigation, the air heater was shut off and the air flow was stopped after cross-over had been achieved. The reactor was allowed to cool down and then emptied using a vacuum cleaner to remove the charge layer by layer, thereby allowing sampling and observation of the effects of the test run.

The experimental procedure for tests under Phase Two was identical to that under Phase One until the cross-over point had been passed. For these tests the air flow was continued after cross-over, although the air heater was switched off. The vertical temperature profile in the bed was leveled out using a method developed by trial and error. In this method, the air flow was turned on and off at intervals which were determined by the changes necessary in the temperature profile. For instance, if the lower level bed temperatures were too high, short blasts of air at a high flow rate were used at intervals. If the reverse situation developed and the lower bed level temperatures dropped too

intervals of air flow at lower rates were used to raise the temperature in the lower portion of the bed. Once the desired temperature conditions were reached, the cooling water flow was started. After the desired data had been recorded, the cooling water flow was stopped and the reactor was allowed to cool. A vacuum cleaner was again used to remove the lignite from the reactor.

CHAPTER IV

DISCUSSION OF RESULTS

Perhaps it would be wise at this point to clarify the manner in which the problem studied in this thesis work was attacked. In the Introduction and in Chapter I, it was indicated that little literature was available in which the controlled oxidation of lignite at intermediate temperatures of 200 to 600 °F had been studied. There also was little information available on the thermal conductivity of a bed of lignite. It was therefore decided that rather than studying one small phase of the problem of controlling the oxidation of lignite in a fixed bed, such as extending to higher temperatures the previous data on the rates of oxidation, it would be more useful to obtain as much general information about the problem as possible. Once a background of experience and information becomes available the details of the trouble spots which may arise could be investigated later.

With this approach in mind the investigation was divided into two phases. Essentially, the purpose of the first phase was to determine whether a "hot spot" could be initiated and maintained under laboratory conditions and what variables affected it. The purpose of the second phase was to determine whether cooling pipes could be used to remove sufficient

heat from this heating zone once initiated to allow continued oxidation at a reasonable rate.

Phase One Results

The previously mentioned investigations by Sanderson and Sondreal indicated that in an atmosphere of oxygen the rate of oxidation for lignite rises sharply as the lignite temperature is raised beyond 200 °F. First efforts were therefore directed toward determining at what temperature a bed of lignite in an atmosphere of air will oxidize rapidly enough to initiate spontaneous heating. As was mentioned in the preceding chapter, the temperature at which the temperature of oxidizing lignite went above the temperature of the air being introduced into the bed was defined as an indication that spontaneous heating had been initiated.

To give the reader a better idea of the mode by which the temperatures at the various bed levels rose during a test Figure 4 is presented. This figure is a condensation of the recorder strip chart data obtained during a test and indicates the temperatures of the incoming air and the first four thermocouple levels (at the 2, 4, 6, and 8 inch bed depths) as the test progressed. This figure is representative of all tests in this phase with variations due to moisture causing a change in the time scale only. This particular test was on 3/4 inch top size Beulah lignite with an initial moisture content of 10.6 percent and an air flow rate of 5.2 cfm/sq ft bed. As can be seen, cross-over

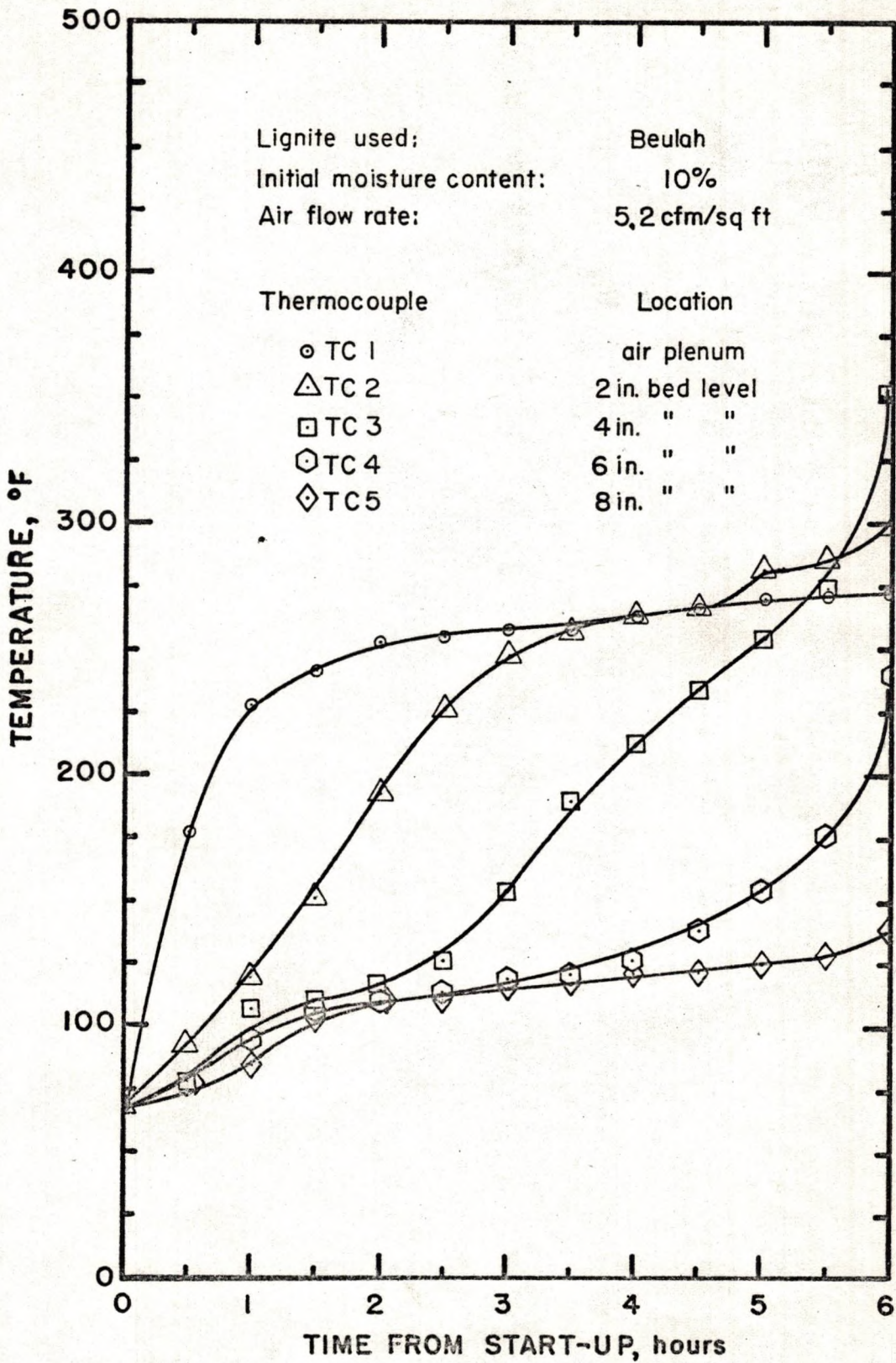


Fig. 4.--Temperature profiles during a test

occurred at 265 °F about 4 hours after startup. At cross-over the temperatures at points 4, 6, and 8 inches above the bottom of the bed were 210, 125, and 120 °F respectively. After cross-over the bed temperatures rose rather rapidly until about 6 hours after the start of the test when smoke poured from the top of the bed indicating combustion, at which time the test was stopped. In earlier tests it was demonstrated that when using an air flow rate of 5.2 cfm/sq ft the entire bed could be brought up to temperatures of about 230 °F without having a cross-over until a temperature of at least 250 °F was reached. Therefore the rapid increase in temperature of the incoming air was a time saving expedient which did not have a great effect on the desired results.

TABLE 1
EFFECTS OF MOISTURE ON THE CROSS-OVER TEMPERATURE^a

Moisture Content, percent	Cross-over Temperature, °F	Air Flow Rate, cfm/sq ft Bed
1.7	285	9.2
10.6	265	5.2
19.2	255	9.2
33.4	255	9.2

^aLignite used for these tests came from the Beulah Mine, Knife River Coal Mining Co., Mercer County, North Dakota.

From the data presented in Table 1, it can be seen that the moisture content of the lignite as charged to the

reactor seemed to have little effect on the cross-over temperature at the higher moisture levels. The increase in cross-over temperature at the lower moisture levels could be caused by a decrease in surface activity due to surface oxidation during the drying process.

The manner in which the lignite for this series of tests warmed up to, and entered the spontaneous heating cycle was quite similar at all moisture levels. In all cases a vertical moisture gradient was established as the warm-up took place. As the lignite in the lower level of the bed dried its temperature rose. One might interpret this phenomenon as a "dry front" moving up the bed. Temperatures were fairly low - below 100 °F - until this "dry front" had passed. As this front passed a point in the bed, the temperature at this point rose fairly rapidly until either a steady state or ignition was reached. The temperature at which this break from slowly rising temperatures to rapidly rising temperatures occurred was not at the boiling point of water as might have been expected, but at temperatures ranging between 100 to 120 °F.

The moisture content of the lignite bed was found to range from essentially zero percent moisture in the zone at the bottom of the bed, which had reached temperatures at or over the cross-over temperature, to just below the moisture content of the lignite as charged in the very top layers of the bed. The height to which the very low moisture zone reached depended on how long air flow was permitted after cross-over had been reached.

In Table 1, the test at the 10.6 percent moisture level was conducted using about one-half the air flow of the other tests in this series to determine what effects, if any, a reduction in air flow would have on the cross-over temperature. As can be seen, there was essentially no effect at this flow rate range.

Having established a temperature range to which lignite must be heated to initiate spontaneous heating, the next area of interest was whether the "deactivation" and resultant reduction in oxidation rate due to prior oxidation, which Sondreal and Sanderson both found to occur at low temperatures, extended into the temperature range needed for spontaneous heating. In Table 1, it can be seen that there was a 30 °F increase in cross-over temperature for the very low moisture lignite over the same lignite in the high moisture range. To determine whether this increase was caused by oxidation during the drying process or a change of reactivity due to reduced moisture content, a new series of tests was planned.

In this test series, the lignite from the cross-over determination at the 1.7 percent moisture level presented in Table 1 was subjected to repeated standard crossing point determinations without being removed from the reactor. After each determination, the reactor was allowed to cool until all temperatures measured reached room temperature. The cross-over temperature for this oven-dried lignite for four successive determinations were 285, 285, 285, and 320 °F

respectively. As can be seen there was no change in cross-over temperature due to cumulative oxidation before the fourth determination. This would indicate that deactivation caused by surface oxidation has reached a plateau level in the drying process and only very severe further oxidation causes greater deactivation.

A moisture analysis of the lignite after these tests indicated that the lignite had been completely dried over almost the entire depth of the bed. The moisture contents of the lignite at 4, 8, and 10 inches from the bottom of the bed were 0.1, 0.2, and 1.4 percent respectively.

Several interesting observations were made during this series that are worth noting. Although these tests had almost identical air flow and heating rates and cross-over occurred between the third and fourth hour of operation for all tests, the vertical temperature gradient decreased for each test. The temperatures at 2 and 10 inches from the bottom of the bed at cross-over for the four consecutive tests were 220 and 285, 230 and 285, 265 and 285, and 320 and 320 °F respectively. During the last test the temperature gradient actually reversed itself after cross-over, indicating that the less oxidized lignite in the upper portion of the bed was actually the more reactive.

The change in reactivity between raw lignite and well oxidized, dried lignite was vividly demonstrated during the third test. When it was noted that the temperature two inches below the top of the bed was above the temperature which

initiates spontaneous heating in raw lignite, a half inch layer of raw lignite was spread out on top of the reactor bed. Air flow was continued after cross-over had occurred to permit further oxidation. When the maximum bed temperature reached 340 °F (at the 10 inch level) the lignite which had been placed on top of the bed started smoking and glowing embers were observed. When the reactor was cleaned out after the fourth test, no ash or other evidence of combustion could be found in the bed proper, but considerable ash was found throughout the added layer.

To determine whether there was any major difference in cross-over temperature for different lignites a series of tests was conducted on three different lignites. The results for these tests are presented in Table 2. All of the lignites were air dried to the reported moisture contents prior to charging to the reactor. As can be seen, there is very little difference in cross-over temperatures for these three lignites.

TABLE 2

EFFECT OF LIGNITE SOURCE ON CROSS-OVER TEMPERATURE

Lignite Source	Moisture Content, percent	Cross-over Temperature, °F	Air Flow, cfm/sq ft bed
A	19.2	255	9.2
B	24.9	260	5.2
C	20.4	250	5.2

In an effort to use the analysis of the gas flowing from the top of the reactor bed as a measure of the amount of oxidation going on in the bed, the gas was analyzed for oxygen, carbon dioxide, and carbon monoxide content. The analyses and the maximum recorded bed temperature at the time of analysis for one of these tests is presented in Table 3. The temperatures above 315 °F are only approximate as the temperatures were rising very rapidly and the minimum time required to obtain a gas sample for later analysis was about two minutes. The maximum bed temperatures for the last two analyses presented were beyond the 475 °F maximum of the recorder used and are therefore unknown.

TABLE 3
ANALYSES OF GASES FLOWING FROM AN
OXIDIZING LIGNITE BED^a

Maximum Bed Temperature, °F	Oxygen Content, percent	Carbon Dioxide Content, percent	Carbon Monoxide Content, percent
255	21.0	0.0	0.0
270	20.9	0.0	0.0
275	20.9	0.0	0.0
280	20.8	0.0	0.0
285	20.9	0.0	0.0
300	20.6	0.0	0.0
315	20.0	1.0	0.0
340	18.5	2.0	1.0
350	18.0	3.5	0.5
?	16.5	5.5	0.5
?	11.6	7.4	2.0

^aLignite used for this test came from the Beulah Mine, Knife River Coal Mining Co., Mercer County, North Dakota.

At first glance, these gas analyses seem to present some rather startling conditions. First lignite was oxidized at temperatures of up to 300 °F without using any oxygen or producing any carbon dioxide; and second, at temperatures of over 340 °F carbon monoxide was produced in the presence of considerable quantities of oxygen.

In an effort to explain these events, Sanderson's data was extrapolated to 250 °F obtaining a value of 1×10^{-6} lb-moles oxygen consumed per minute per pound maf lignite in an atmosphere of oxygen.¹² Using Sondreal's conclusion that the oxidation rate is approximately proportional to the oxygen concentration, this value was reduced to 0.21×10^{-6} lb-moles oxygen/min lb maf lignite.¹³ The reactor charge averaged about 26 lb of lignite containing 20 percent moisture and 10 percent ash, or about 18.7 lb maf lignite, giving a value of 3.9×10^{-6} lb-moles oxygen consumed per minute assuming the entire lignite bed was at 250 °F. Immediately prior to cross-over most of the lignite was still below this temperature, but this does give an order of magnitude estimate of the maximum oxygen consumption rate. Air was passed through the bed at a rate of 6.3 cfm which is equivalent to $3,500 \times 10^{-6}$ lb-moles of oxygen per minute. Thus, the total reduction in oxygen content of the air passing through the bed was on the order of 0.1 percent. This concentration was at the lowest detectable limit for the instrument used, which was accurate to ± 0.1 percent.

As a cross-check for the oxygen consumption rate obtained above, the approximate temperature rise due to the heat generated by this oxidation rate was calculated. Using Sanderson's value of 162,000 BTU generated per lb-mole oxygen consumed, an approximate specific heat of 0.3 BTU/lb °F for lignite, and the oxidation rate of 0.21×10^{-6} lb-moles oxygen consumed/min lb maf lignite as calculated above, a temperature rise of 0.1 °F per minute was obtained. This value is quite reasonable as spontaneous heating has not been initiated at a temperature of 250 °F.

Phase Two Results

Having demonstrated that a spontaneous heating zone of oxidizing lignite can be generated and having investigated some of the major factors affecting the initiation of this spontaneous heating, the next step necessary was to investigate the possibility of removing sufficient heat from the reacting zone to prevent combustion while still supplying enough oxygen to allow rapid oxidation. For this phase of this thesis work the laboratory reactor was equipped with a copper cooling coil as described in Chapter II.

The location of this cooling coil was determined by the results obtained during tests conducted under Phase One. From a data analysis standpoint it would have been ideal to be able to place the cooling coil in a zone so that the temperature gradients in all directions from the coil were equal. Analysis of the data obtained in Phase One indicated

that the zone which had the least temperature variation was one extending vertically from the 2 inch level to the 4 inch level of the bed and horizontally from the center of the bed to about two inches from the reactor wall. The cooling coil was therefore designed so that it could be located within this zone.

The procedure used to bring the lignite bed up to the desired temperature for this series of tests was described in Chapter III. In preliminary testing, it was discovered the insulating qualities of lignite were even better than anticipated. The amount of heat which could be removed was so low that under low air flow conditions combustion temperatures existed only one or two inches away from the cooling coil which had a surface temperature of about 70 °F. Under higher air flow conditions, the areas further removed from the cooled zone heated to combustion temperatures when air flow was continued for any period of time after cross-over. To obtain heat transfer data, it was therefore necessary to bring the zone up to temperature, turn on the cooling water, and then stop the air flow. The data obtained from a series of tests using this procedure are presented in Table 4. The temperature values given are the averages of the temperature at the start and end of each test run for each point reported. The heat transferred was then a combination of the heat generated by the consumption of the oxygen in the air spaces between particles, plus some of the sensible heat content of the lignite as it cooled. It might be added that

the maximum temperature drop during the data collecting portion of a test run was 35 °F at TC3 during the 30 minute run of test 2.

In Table 4, the quantity of heat removed per square foot of tube outer surface area was calculated in the usual manner using the water flow quantities and the temperature increase of the water while passing through the coil.

If the lignite bed surrounding the cooling coil is divided into four quadrants as is indicated in Figure 3, and it is assumed the temperature measured in each quadrant is the average temperature at a 1-1/4 inch radius for that quadrant, an effective bed "background temperature" can be obtained by averaging the temperatures in the four quadrants. This average background temperature is given in Table 4 for the four test runs conducted and was used to calculate a modified over-all heat transfer coefficient, U^* , to get a more useful measure of the heat removal ability of the cooling coil. This hybrid number is the heat removed per hour per square foot of coil surface area per degree temperature difference between the water and the lignite bed 1-1/4 inches away from the coil. It represents a combination of the water-side film coefficient, the conductivity of the metal coil, the conductivity of the lignite bed, and the convective heat transfer coefficient for the air in the bed around the coil. The U^* calculated indicated that there was little difference in heat transfer capability between the 1/4 by 1/8 inch and the 1/8 by 0 inch size fractions.

TABLE 4
DATA AND RESULTS FROM PHASE TWO TESTS

Initial Moisture Content, percent	12.7		16.0	
Size Consist	1/8 by 0 inch		1/4 by 1/8 inch	
Test Number	1	2	3	4
Time of Test, minutes	15	30	10	10
Average Temperatures, °F				
TC1	202	170	198	125
TC2	317	435	405	444
TC3	318	376	399	388
TC4	385	388	377	321
TC5	525	425	309	298
TC6	306	353	355	285
TC7	92	106	112	100
Average Background Temperatures, °F	330	390	385	360
Water In, °F	69	70	72	69
Water Out, °F	86	99	105	97
Average Water Temperature, °F	78	84	88	83
Water Flow Rate, gph	0.22	0.22	0.22	0.22

TABLE 4--Continued

Test Number	1	2	3	4
Heat Removed, BTU/hr sq ft ^b	660	1,120	1,280	1,090
U*, BTU/hr sq ft °F ^b	2.6	3.7	4.3	3.9

^aLignite used for these tests came from the Baukol-Noonan Mine, Baukol-Noonan, Inc., Burke County, North Dakota.

^bBoth the Heat Removed and U* were calculated using the outside tube area. For U* the temperature difference used was between the cooling water and the average back-round temperature of the bed 1-1/4 inches from the tube.

SUMMARY AND CONCLUSIONS

In the course of this investigation considerable experience and information was accumulated on a subject which a literature survey indicated had been severely neglected. It was demonstrated that the inherently unstable condition present in the spontaneous heating of lignite can be overcome, allowing this phenomenon to be studied in the laboratory. It was demonstrated that spontaneous heating could be initiated by heating the lignite to temperatures of 250 to 260 °F while a moderate flow of air was maintained through the bed. When the lignite was dried to moisture contents below 10 percent, the temperature necessary to initiate spontaneous heating rose and severe oxidation at these low moisture levels raised this temperature to over 300 °F. The temperatures necessary to initiate spontaneous heating in lignite from three different mines were almost identical.

During tests designed to evaluate the possibility of maintaining a high rate of oxidation in a fixed bed of lignite by removing the heat generated by this oxidation with a cooling coil, it was demonstrated that lignite was a remarkably good insulator. Temperature gradients of over 300 °F per inch were easily maintained in the bed with only minor quantities of heat transferred through this distance.

A modified over-all heat transfer coefficient was determined for the test apparatus using two different lignite size fractions. The values obtained for this coefficient ranged from 2.6 to 4.3 BTU per hour per square foot of outside coil surface area per degree temperature difference between the cooling water and the lignite bed 1-1/4 inches away from the coil. There was little difference in heat transfer capability between the two consists tested.

The results of this investigation indicate that using cooling pipes to remove the heat generated by the oxidation of lignite in a fixed bed would, at best, be a poor method for controlling the oxidation rate.

RECOMMENDATIONS

Although the results of this investigation indicate that it would be difficult and probably impractical to use cooling pipes as a means of controlling the oxidation of lignite in a fixed bed, a situation might arise in which this method is the only alternative. Therefore, to help analyze the heat transfer from a fixed bed of oxidizing lignite a mathematical model of an ideal situation was derived. The derivation of, and the limits bounding this model are presented in Appendix B. The net result is an equation which gives the temperature at any point, R , between cooling pipes in the lignite bed:

$$T = (q/4k) \left[2R_m^2 \ln(R/R_p) - R^2 R_p^2 \right] + T_{\min}$$

where q is the heat generated by the oxidizing lignite, K is the thermal conductivity of the lignite bed, R_m is one-half of the center-to-center distance between cooling pipes, R_p is the pipe radius, and T_{\min} is the temperature at the surface of the cooling pipe. Using this equation, the maximum distance between cooling pipes can be determined for any given temperature limit desired between pipes if the heat generated by the oxidation and the bed thermal conductivity are known.

Since the information available concerning the oxidation rate of lignite is limited to temperatures under 200 °F, it is recommended that the temperature range from 200 to 600 °F be investigated. An investigation of the thermal conductivity of a bed of lignite in this temperature range is also needed. This information, when used with the equation presented above, would allow a mathematical analysis of the physical conditions present in an oxidizing bed of lignite containing cooling pipes.

APPENDIX A
ANALYSES OF LIGNITES USED^a

Lignite source: ^b	A	B	C
Proximate analysis, percent:			
Moisture content	30.17	28.17	28.15
Volatile matter	28.46	32.92	28.49
Fixed carbon	33.57	33.39	36.01
Ash	7.79	5.52	7.35
Ultimate analysis, percent:			
Hydrogen	6.24	6.61	6.17
Carbon	44.66	46.52	47.62
Nitrogen	0.75	0.71	0.88
Oxygen	39.83	40.03	37.65
Sulphur	0.73	0.61	0.33
Ash	7.79	5.52	7.35
Heating value, BTU/lb	7,350	7.860	7.880
Size consist:			
percent retained on 0.263 in. screen	10.4	12.2	29.0
percent retained on 0.0937 in. screen	41.0	59.7	40.1
percent retained on 0.0469 in. screen	22.3	11.8	12.9
percent passing a 0.0469 in. screen	26.3	16.3	17.9

^aProximate and ultimate analysis and heating value determinations were obtained from the Bureau of Mines Coal Research Laboratory, United States Department of Interior, Grand Forks, North Dakota.

^bLignite Source:

A. Beulah Mine, Knife River Coal Mining Co., Mercer County, North Dakota.

B. Center Mine, Baukol-Noonan, Inc., Oliver County, North Dakota.

C. Baukol-Noonan, Mine, Baukol-Noonan, Inc., Burke County, North Dakota.

APPENDIX B

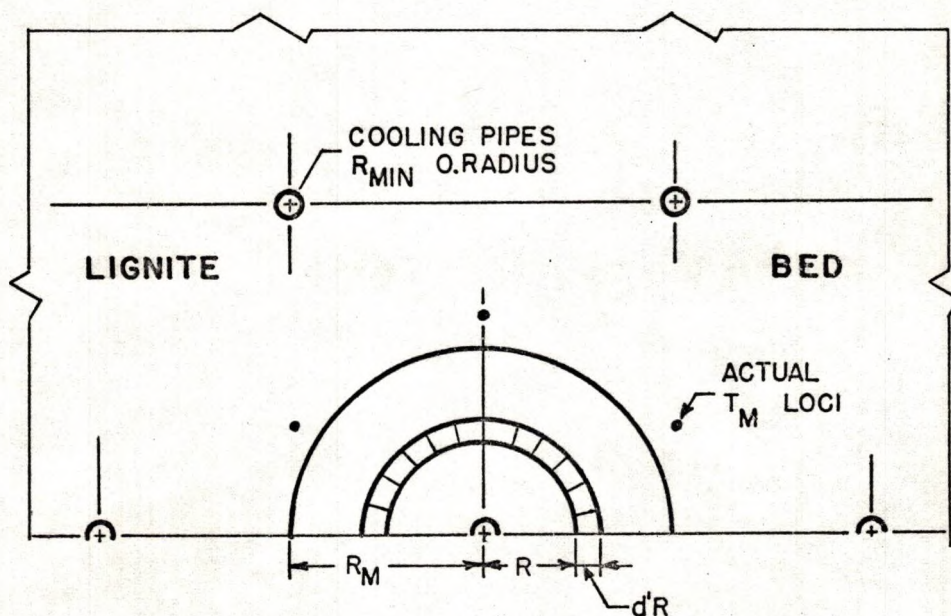
Derivation of Temperature Distribution Equation

The following simplifying assumptions were made to facilitate the derivation of the temperature distribution equation:

1. Infinitely long cooling pipes are placed into a fixed bed of lignite in an equilateral triangular pattern (see figure below).
2. The maximum temperature in the lignite surrounding a cooling pipe can be approximated by a temperature, T_m , at all points on a circle of radius R_m .
3. Heat is generated uniformly throughout the bed by the oxidizing lignite.
4. Steady state conditions can be achieved.
5. The amount of heat transferred due to air flow is negligible.

The assumed boundary conditions were:

1. $dT/dR = 0$ at $R = R_m$
2. $T = T_{min}$ at $R = R_p$



For mathematical convenience, it was assumed that heat flow was outward from the pipe. A heat balance over a concentric shell at radius, R , with thickness, $d'R$, is given by:¹

heat in through the left face + heat generated in the shell = heat out through the right face

or stated mathematically this heat balance is:

$$(1) -kA_R(dT/dR)\Big|_R dH + qVdH = -kA_{(R+d'R)}(dT/dR)\Big|_{(R+d'R)} dH$$

where:

k	= the effective thermal conductivity of the lignite bed, BTU/hr ft °F
dH	= time interval, hr
A_R	= area at radius, R
L	= unit length of cooling pipe, ft
$A_{(R+d'R)}$	= area at radius $(R+d'R)$, which is equal to $6.28(R+d'R)L$, sq ft
V	= volume of shell, which is equal to $6.28RLd'R$, cu ft
q	= uniform heat generation rate, BTU/cu ft hr
T	= temperature, °F
T_{min}	= temperature at the surface of the cooling pipe, °F

Using the mean value theorem to equate dT/dR at radius, R , to dT/dR at radius, $R+d'R$:

$$(2) \frac{dT}{dR}\Big|_{(R+d'R)} = \frac{dT}{dR}\Big|_R + \left[\frac{d}{dR}\left(\frac{dT}{dR}\right)\right]\Big|_M d'R \quad \text{where } M \text{ is between } R \text{ and } (R+d'R)$$

After substituting the proper values for the areas in Eq. (1), dividing through by $6.28LdH$, and making use of Eq. (2), the heat transfer equation simplifies down to:

$$(3) qR = -k \left[R \frac{d^2T}{dR^2}\Big|_M + \frac{dT}{dR}\Big|_R + \frac{d^2T}{dR^2}\Big|_M d'R \right]$$

As $d'R \rightarrow 0$, $M \rightarrow R$, Eq. (3) reduces to:

$$(4) qR = -k \left[R \frac{d^2T}{dR^2}\Big|_R + \frac{dT}{dR}\Big|_R \right]$$

Since:

$$\frac{d}{dR} \left[R \frac{dT}{dR} \right] = \frac{dT}{dR} + R \frac{d^2T}{dR^2}$$

¹Adapted from Principles of Heat Transfer, by Frank Kreith, International Textbook Co., 1964, pp. 39-44

Eq. (4) reduces to:

$$(5) \quad qR = -k \frac{d}{dR} \left[R \frac{dT}{dR} \right]$$

After integrating twice and evaluating the constants of integration at the assumed boundary conditions, Eq. (5) reduces to the desired equation for the temperature distribution in the lignite surrounding a cooling pipe:

$$T = (q/4k) \left[2R_m^2 \ln(R/R_p) - R^2 + R_p^2 \right] + T_{min}$$

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