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DIFFERENTIAL THERMAL ANALYSIS
OF LIGNITE ASH

BY

Robert G. Bredahl

B.S. in Chemical Engineering, University of North Dakota, 1963

A Thesis
Submitted to the Faculty
of the
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in partial fulfillment of the requirements
for the Degree of
Master of Science

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August
1965

This thesis submitted by Robert G. Bredahl in partial fulfillment of the requirements for the Degree of Master of Science in the University of North Dakota, is hereby approved by the Committee under whom the work has been done.

(signed) Wayne R. Kube
Chairman

(signed) Robert C. Ellman

(signed) James L. Elder

(signed) Woodrow H. McBride

(signed) A. M. Cooley

Dean of the Graduate School

ABSTRACT
DIFFERENTIAL THERMAL ANALYSIS OF LIGNITE ASH

by

Robert G. Bredahl, Master of Science

The feasibility of applying differential thermal analysis techniques to relate variance in the chemical analysis of fouling and non-fouling lignite ashes to specific differential temperature peaks was investigated.

Analysis was accomplished by heating powdered samples (minus 200 Tyler mesh) at an average heating rate of 13° F per minute from ambient conditions to 1,850° F in an oxidizing atmosphere. The samples were contained in a cylindrical nickel sample cell and temperature was monitored with chromel-alumel thermocouples.

Boiler flyash samples, laboratory ashed samples of natural lignite and synthetic ash mixtures based on the chemical analysis of the natural lignites were prepared and subjected to DTA analysis.

Reactions, transitions and melting points were characterized using cumulative synthetic mixtures. Peaks were obtained for silica, magnesium oxide, calcium oxide, potassium sulfate and sodium sulfate.

The fouling properties of the original lignites could not be detected by DTA analysis of boiler flyash samples. The natural fouling and non-fouling ash samples exhibited dissimilar DTA curves during initial heatings which could be used to differentiate fouling lignite from non-fouling lignite. It was found, however, that the differences observed in the DTA curves were eliminated after repeated high temperature exposure.

Before definite conclusions concerning the acceptance or rejection of a lignite based on the differences in DTA curves, the effect of prior temperature exposure must be thoroughly examined and additional natural lignite ash samples must be analyzed.

DTA techniques show considerable promise as a means of determining fouling properties of lignite and the technique should be used at higher temperatures to enable DTA analysis during the fusion of the lignite ash.

ACKNOWLEDGMENTS

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The author also wishes to thank Professor Wayne R. Kube and Mr. Robert C. Ellman, of the Bureau of Mines staff, for their counsel and guidance throughout the investigation.

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Introduction

The primary objective of this investigation was to determine the feasibility of applying differential thermal analysis (DTA) techniques in an ash study program being conducted at the Bureau of Mines Lignite Research Laboratory. Specifically, the study was to determine if DTA methods could relate variance in the chemical analysis of lignite ash to differential temperature peaks obtained with the DTA technique and to determine if these peaks could be identified with a specific mineral or combination of minerals present in the ash.

The vast lignite deposits in North Dakota comprise 18 percent of the worlds solid fuel reserves (1)[1]. This resource is not being utilized to any extent except in North Dakota and northwestern Minnesota. Within this area lignite is used primarily as fuel in electric power generating facilities. These facilities have occasionally experienced severe fireside fouling in the boilers which result in loss of efficiency and require frequent periods of down-time to clean boilers. Lignites from certain mines may cause trouble, yet no problems have been observed using lignite from other mines. However, in some instances, lignite from different areas of the same mine may be troublesome. An ash study program is in progress to determine the characteristics of lignite ash, and to relate these characteristics to fouling or non-fouling properties which can serve as a basis for determining the acceptability of a lignite for use in powerplants. The characterization of these properties is a subject of mutual interest to the Lignite Research Laboratory and the Chemical Engineering Department, University of North Dakota. This mutual interest prompted the investigation of DTA as the subject of a jointly sponsored research fellowship in Chemical Engineering at the University of North Dakota.

The scope of the project was to design, construct or procure necessary equipment to investigate DTA as an analytical tool to temperatures of 1,700° C; but, due to problems and expenses anticipated, the temperature limit was reduced to 1,000° C. Samples of mineral constituents in lignite ash were to be analyzed both before and after oxidation to establish characteristic peaks. Lignite and flyash samples corresponding to fouling and non-fouling conditions were to be prepared and subjected to DTA analysis. The data obtained were to be correlated, based on composition and fusability characteristics, in terms of fouling or non-fouling properties.

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[1] Numbers in parenthesis refer to items in List of References.

CHAPTER 1
THE DIFFERENTIAL THERMAL ANALYSIS METHOD

Origins

Analysis of temperature induced reactions in solids and liquids began in the last half of the nineteenth century. In early phases, transformations and reactions were observed by measuring the time rate of change in temperature of a sample being heated at a constant rate. Le Chatelier (1887) was a principal contributor to this new analytical tool with his work on devising a method for classifying clays (2). The differential temperature measurement concept was first developed by Roberts-Austen in 1889 for use in metallurgical studies (3). Application of DTA techniques was limited and was focused primarily on classification of clay and clay minerals until the early 1930's. During this period techniques and equipment were developed and refined. Beginning in 1934, yearly DTA publications, which indicate activity in the field, began increasing and rose to 170 by 1952, compared with 5 in 1934 (4).

The early equipment, designed and developed by the individual experimenters, lacked any standards or specifications for uniformity and was usually designed with one particular application in mind. This lack of uniformity resulted in data obtained and interpreted using one unit, which could not be obtained or reproduced with a different unit. Difficulties arose when comparison of the early data was attempted from the published results. Several commercial DTA units are currently manufactured, but the large capital expenditure necessary to purchase a unit results in many researchers designing and constructing their own equipment. The problem of obtaining accurate and reproducible data for comparison therefore is still present, but the availability of comprehensive literature surveys and bibliographies such as those of Murphy (5,6), Smothers and Chiang (4), and Mackenzie (7) result in a more thorough knowledge of problem areas before the equipment is constructed. These surveys serve to form a loose standard or specification for the construction of individual DTA units and as a natural result, data comparison can be accomplished easier and with far more accuracy.

DTA now provides useful data in many areas of research (soils, metallurgy, ceramics, solid fuels and propellants, pharmaceuticals, and polymers), and its usefulness as an analytical tool is being established very firmly.

Theory of Operation

General principle

In differential thermal analysis a sample to be analyzed and an inert reference material are contained in symmetrical partitions

Whether metal or ceramic materials are used, no reactions should occur between the cell and the sample.

Thermocouples. - The temperature measuring thermocouples should utilize materials which will be unreactive with the samples, have an easily measured emf and provide a long operational life at the temperatures used. Chromel-alumel couples find the widest application for temperatures up to 1,000° C. At higher temperatures platinum, platinum-rhodium couples are required. Care must be used while assembling and installing the differential couple to assure that bead sizes are identical and that the location of the couple is symmetric to the furnace heating coil and to itself. The differential couple is assembled to measure the temperature difference between the sample leg and the reference leg. Since the system is complete by itself, a cold junction is not required.

Furnace. - Any controllable heat source may be used in designing the furnace, but electrically heated furnaces are used almost without exception. A properly designed unit should provide a zone of uniform heat so that no large temperature gradients exist. The unit must also be able to establish a temperature driving force large enough to provide the heating rate desired. Furnaces are either internally or externally wound on a ceramic core and then insulation, as required, is packed around the core. Some devices have utilized radiation shielding in place of standard insulation.

Resistance wire used in the construction falls into three categories: (a) up to 1,000° C, (b) 1,000° C to 1,750° C, and (c) 1,750° C to 2,000° C. In category (a), Nichrome and Kanthal wires or strips are used extensively. Category (b) required platinum wire exclusively until recently when Kanthal began producing wire capable of operation to 1,300° C. Category (c) requires molybdenum wire surrounded by a hydrogen atmosphere. Two high temperature ceramic-metal heating elements, Globars and Kanthal Super, can be used as high as 1,700° C. Whatever the choice for the heating element, the furnace will have a much longer life if the element is not underrated.

Heating rate control. - This control must be selected to provide a reproducible heating rate. A transformer driven by a variable speed motor is the most common control. Manual control is used where cost or availability prohibit an automatic control, but results are not always satisfactory.

Recording instrumentation. - Accuracy and rapid response are the primary requirements for selecting instrumentation. Galvonometers were used in early systems but required visual recording of deflections. The oscillograph system, which couples the galvonometers

Packing. - The variation in the density of the sample or reference inert around the thermocouple beads due to non-uniform packing techniques should be minimized. Tight packing is preferred to loose packing as the former produces a more pronounced peak (4). No procedures are mentioned concerning the packing of the sample and it is assumed that any method used which affords uniformity is acceptable.

Furnace atmosphere. - The atmosphere in which the sample is analyzed will have considerable effect on the reactions which occur (oxidation reactions will not occur in a reducing atmosphere, etc.) If reactions are to be examined, the equipment must have provisions for maintaining the actual environmental atmosphere which the sample is subjected to in use. Melting points and phase transitions are not affected to a great extent by the atmosphere. To use DTA quantitatively or qualitatively to determine the presence of compounds in an admixture, the melting or transition points of the compounds should be used if possible (4,7).

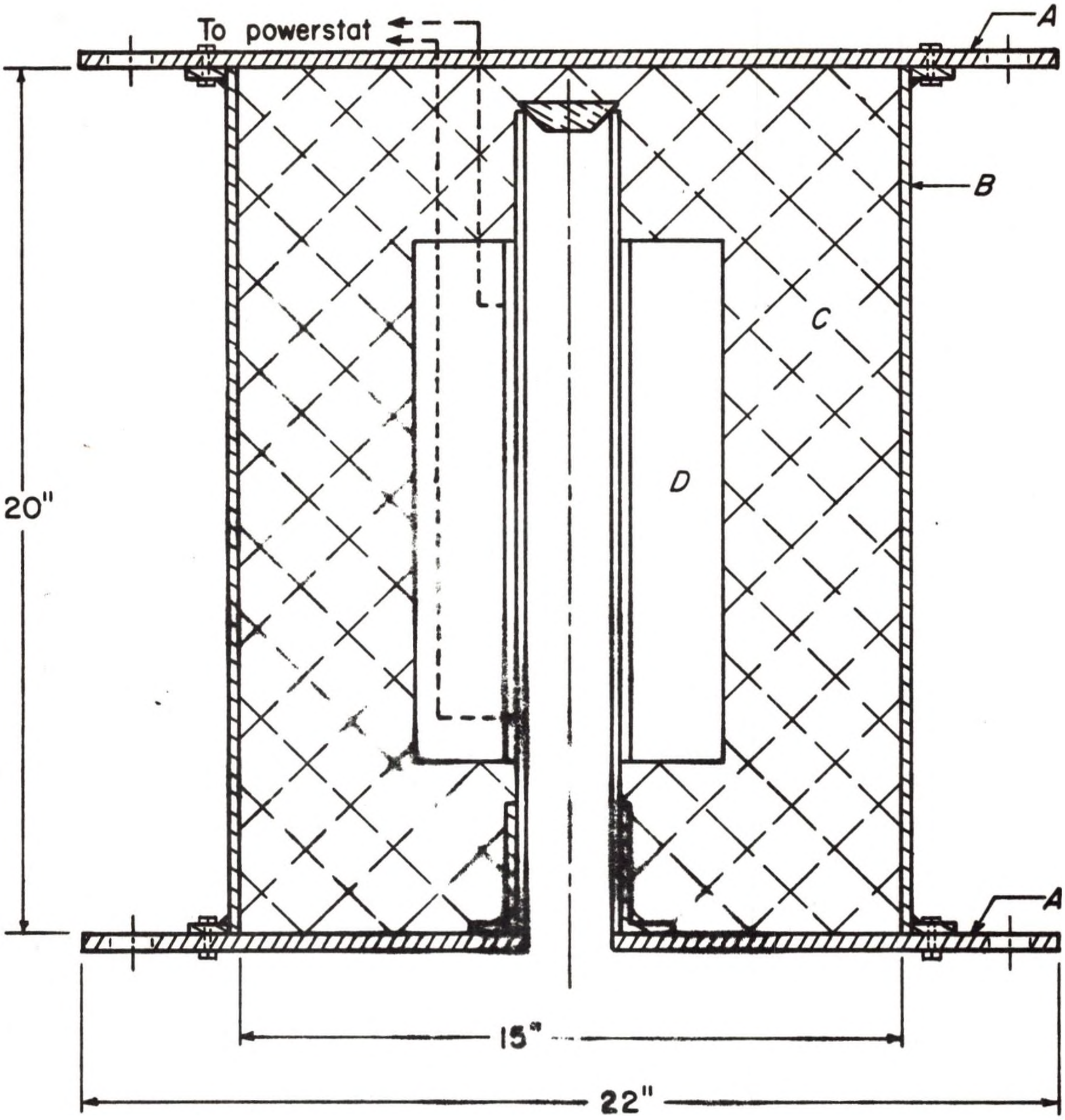
Prior Applications of DTA

Differential thermal analysis techniques have been employed in many areas of mineralogical research, with most applications in the field of clay and clay minerals. No articles dealing with DTA applications to coal ashes were found in the literature. Several articles which discussed application in analysis of coals were found (11-15). These articles described DTA as a tool to establish the rank or coking characteristics of coal and as such are concerned only with the temperature of occurrence of exothermic and endothermic peaks and not with the mineral(s) or organic reaction which cause the peaks (11,12,14). Gaines and Partington (13) investigated effects caused by addition of inorganic compounds used to inhibit swelling which briquets of low rank coals displayed upon carbonization. DTA techniques have been applied by Warne (15) to specifically identify effects of certain mineral constituents in coal. Analysis was accomplished in an atmosphere of nitrogen to eliminate oxidation reactions and the effect of the mineral(s) and minimum detectable concentrations were determined.

CHAPTER II

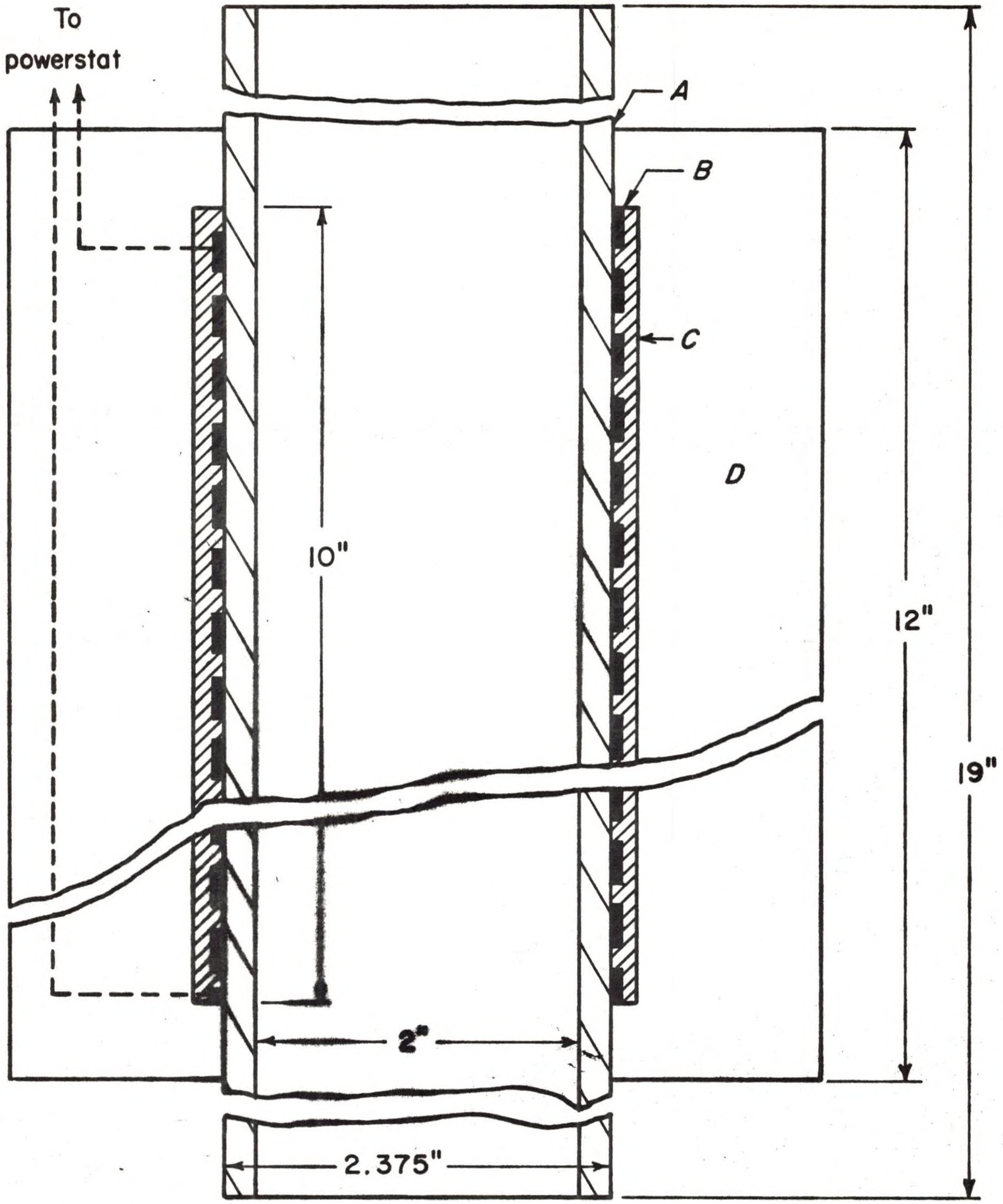
DESIGN OF APPARATUS

The apparatus was designed to provide reproducible operating characteristics to a maximum temperature of 1,000° C. The discussion presented herein is centered on the final design and covers basically the furnace, sample probe components and instrumentation. Certain problem areas which developed during the investigation will be discussed.



A Transite board
B Rolled sheet steel
C Fiberfrax insulating blanket
D Heating element : see details in Fig 2

Fig I Assembly drawing for DTA furnace.



A Ceramic core

B Heating element, Kanthal A-1 resistance strip, $\frac{1}{4}$" x .015" x 20' long.

C Norton 1162 high temperature refractory

D Silicon carbide refractory

Fig 2 Assembled heating element.

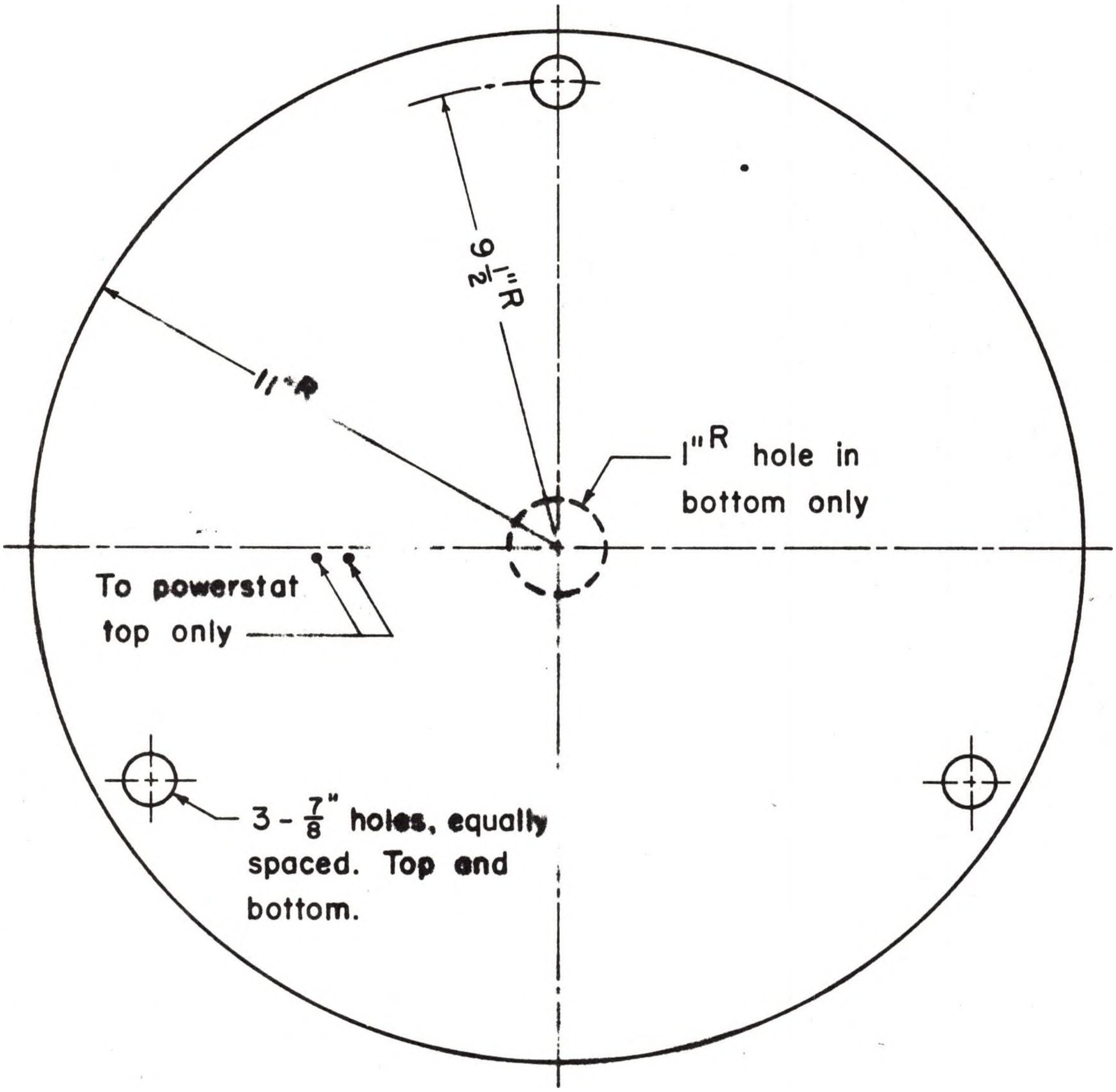


Fig. 3 Top and bottom covers for DTA furnace.

Sample Probe System

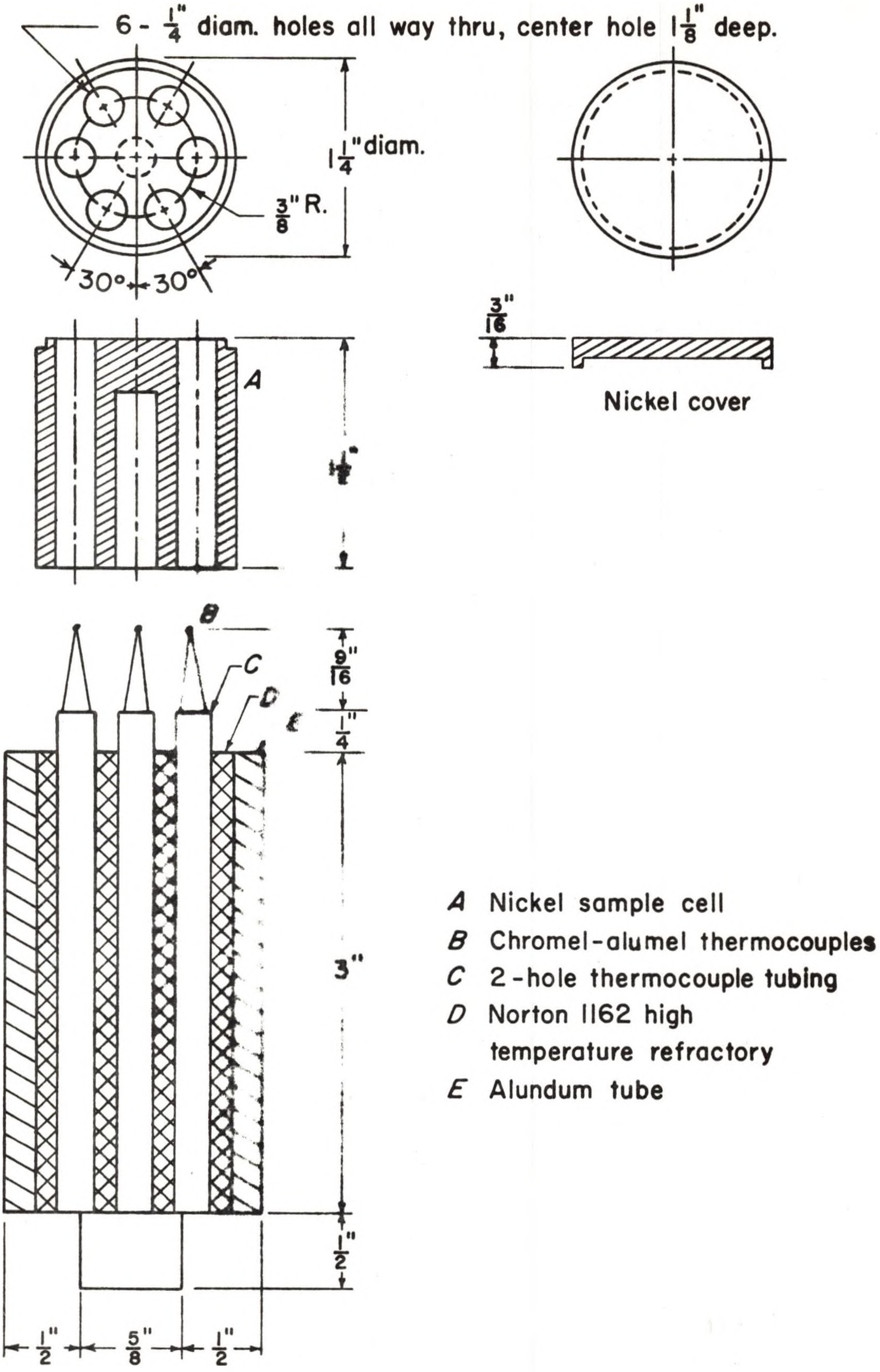
This system, consisting of a nickel sample cell, a ceramic support and thermocouples, is shown in Figure 4. Initial plans called for multiple sample testing and the cell was so constructed. Lack of proper instrumentation curtailed this idea and as a result single sample testing was required using the original multiple sample cell. The center hole in the cell contains the system thermocouple and any two symmetric holes in the six hole radial arrangement can be used to contain the sample and reference materials and thermocouples. The thermocouple tubing in the alundum tube is held in place by a high temperature refractory. The tube shown is the top portion of the complete probe, the bottom of which is used to support the components at the proper height in the furnace and to lead the thermocouple wire out of the furnace. The probe was designed in two portions to facilitate removal of the thermocouple system from the unit when replacement was necessary. The two 1/2-by 5/8-inch tips, in the figure, are used to correctly position these two portions of the probe.

The thermocouples were chromel-alumel with one differential set and a system temperature couple required. Initially, the couples were made using a twisted junction in which the bead is obtained by twisting the two wires together and welding in an oxy-acetylene flame with a borax flux. This type of junction is very strong and should have a long life. Difficulties in obtaining identical bead sizes and the high stresses developed in this type of junction were troublesome. A butt type junction was found to be superior for this service as this junction provides a small, easy to reproduce bead which does not have the high stress present in the twist junction.

The nickel sample cell was sized to hold approximately 0.8 to 1.4 grams of lignite ash, depending on the density of the ash, which has an observed range of 13 to 23 grams per cc.

Instrumentation

Figure 5 is a block diagram of the instrumentation system used. A list of the instruments is presented in Table 1.



A Nickel sample cell

B Chromel-alumel thermocouples

C 2-hole thermocouple tubing

D Norton 1162 high temperature refractory

E Alundum tube

Fig 4 Sample probe components.

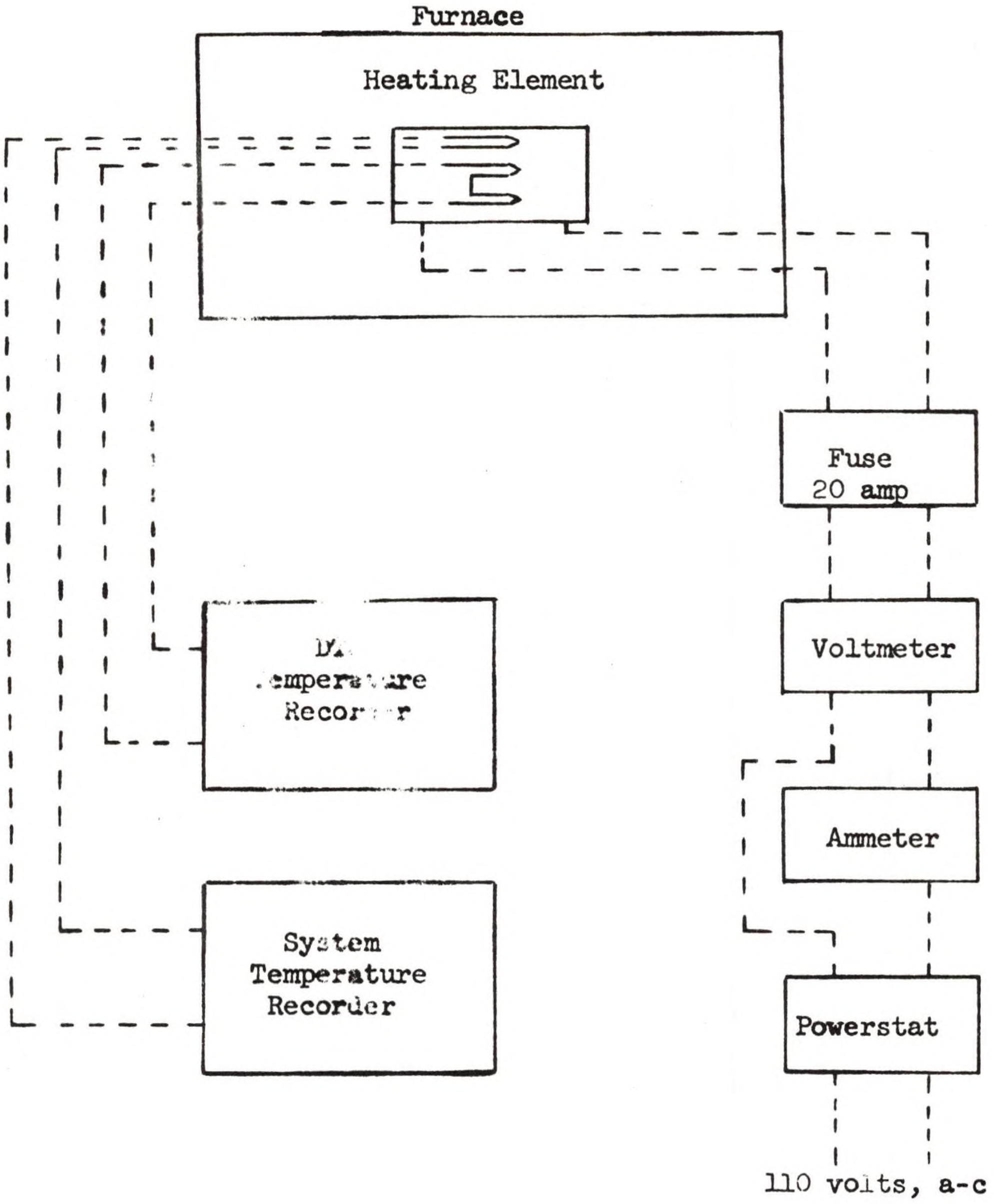


Fig. 5. - Block diagram of DTA instruments.

TABLE 1

DTA INSTRUMENTATION

Instrument	Manufacturer	Range
Voltmeter a-c	Weston	0 to 130 volts
Ammeter a-c	Weston	0 to 30 amps
Powerstat	Superior Electric Co.	0 to 120 volts 0 to 20 amps
Differential recorder	Minneapolis Honeywell	-0.1 to 1.0 mv
System recorder	Minneapolis Honeywell	0 to 2,500° F

Problem Areas

The furnace heating element and the differential thermocouples are the main areas where problems can be expected to develop. The difficulties which occurred and the corrective action(s) taken as well as alternate methods are in the following paragraphs.

Care must be observed during construction of the heating element to insure against reactive foreign material being in contact with the coil. Most high temperature resistance wire will react at high temperatures with most metals, and care must be exercised during the assembly of the element not to contaminate the wire. The first element assembled burned out after eight cycles of operation. Examination of the element after disassembly indicated that the cause of failure was twofold. One, the exit of the electrical leads from the element out of the furnace resulted in sharp bends in the strip causing points of high stress which were not properly protected with refractory. Secondly, the protective inert refractory had not covered the coil completely and silicon carbide refractory had contaminated the element. The second element was constructed with these problem areas corrected and has operated successfully for 53 complete cycles.

The differential thermocouple temperature measuring system was constructed so that the thermocouples would be immersed in the sample and reference materials. This type of design results in contamination of the thermocouple if a slagging sample is analyzed or in some instances minerals present in the sample will attack the thermocouple causing spurious data. After repeated cycling to temperature, all thermocouple metals become brittle to some extent and must eventually be replaced. In addition, the type of welded junction used has an effect on the useful life of the couple. The ashes analyzed during the course of the investigation were not heated to slagging temperatures so this particular problem was not experienced.

The furnace refractory was cured by slowly heating the assembled furnace. The heating rate and the maximum temperature limits of the system were investigated before actual testing of samples was begun.

The symmetry of the sample cell was established to the maximum operating temperature. This symmetry determination, which checks the drift of the differential thermocouple from the null position of zero mullivolts, was accomplished by placing inert alumina in both the reference and the sample cells. When the cells were filled with alumina a reproducible base line could be obtained. Consequently, the symmetry of the cell was determined with both cells empty except for the required thermocouples. The problem experienced with the packed alumina resulted in a solid ceramic inert being used as the reference material. Thus, any variance in data which might occur from using a powdered reference material which would have to be replaced and repacked following each run was eliminated.

At temperatures above 1,400° F, deviation from the base line occurred because of an induced electrical potential in the differential couple from the a-c current in the heating coil. This effect was partially eliminated by grounding the couple through a 0.1 mfd capacitor.

Base line drift was not completely eliminated because the inert and sample did not have identical thermal properties and the induced potential in the thermocouple could not be entirely suppressed.

An acceptable heating rate was established. By making incremental changes in the amperage applied to the heating element every 15 minutes, a satisfactory and reproducible heating rate could be maintained. Heating rates of about 13° F per minute when the furnace was heated from ambient conditions and of about 15° F per minute when consecutive runs were made on the same day, could be maintained. The heating curve was linear except at the initial and final stages of the run.

A gross, minus 200 mesh (Tyler series) sample for DTA analysis was randomly mixed and placed in the sample cell. The cell was filled in increments and each portion was packed with a ceramic probe. No specific weights were established because of the large variations in the density of the lignite ashes analyzed. Instead, the density of the sample surrounding the thermocouples was kept constant by uniform packing in the cell.

Smothers and Chiang (4) and Mackenzie (7) in their comprehensive bibliographies indicate that the effects of heating rate, particle size and packing density are secondary in establishing a workable procedure. The main requirement is that a procedure be developed samples was investigated. The basis of the work was simply that fouling flyash exhibited higher sinter strengths than did the non-fouling upon heating. It was found that the addition of calcium and sodium sulfates to the non-fouling flyash increased its sinter strength to the same level as observed for the fouling. This study therefore suggested that fouling properties observed may be the result of sodium or calcium sulfate concentrations in the original lignite. An acceptable synthetic ash was obtained by substituting calcium and sodium sulfates in stoichiometric proportions to the amount of sulfur reported in the oxide analysis of the natural ash. The synthetic was prepared by replacing all reported sodium oxide by sodium sulfate, including the balance of the sulfur as calcium sulfate and the balance of the calcium as calcium oxide. The remaining portion of the synthetic prepared consisted of the oxides of the minerals present in the chemical analysis of the natural ash. Trace elements reported were not included and all of the potassium was added in the sulfate form. The DTA curves for these synthetic ashes were found to exhibit satisfactory characteristics when compared to the natural ashes. (Discussion of the curves will be presented later.) Characterization of the peaks observed in the natural ashes was therefore possible using the derived synthetic mixtures. Table 2 compares the synthetic and natural ash compositions for fouling and non-fouling operation.

TABLE 2

COMPARISON OF SYNTHETIC AND NATURAL
ASH CHEMICAL COMPOSITIONS

	Natural ash		Synthetic ash	
Analysis, percent	fouling	non-fouling	fouling	non-fouling
Silica	20.4	27.2	20.4	27.2
Aluminum oxide	10.1	10.8	10.1	10.8
Ferric oxide	6.6	6.4	6.6	6.4
Titanium oxide	0.3	0.5	---	---
Phosphorous pentoxide	0.1	0.3	---	---
Calcium oxide	35.2	36.7	33.7	30.4
Calcium sulfate	---	---	3.5	15.2
Magnesium oxide	7.3	7.3	7.3	7.3
Sodium oxide	7.6	0.6	---	---
Sodium sulfate	---	---	17.4	1.4
Potassium oxide	0.5	0.6	---	---
Potassium sulfate	---	---	0.9	0.6
Sulfur trioxide	11.9	9.6	---	---

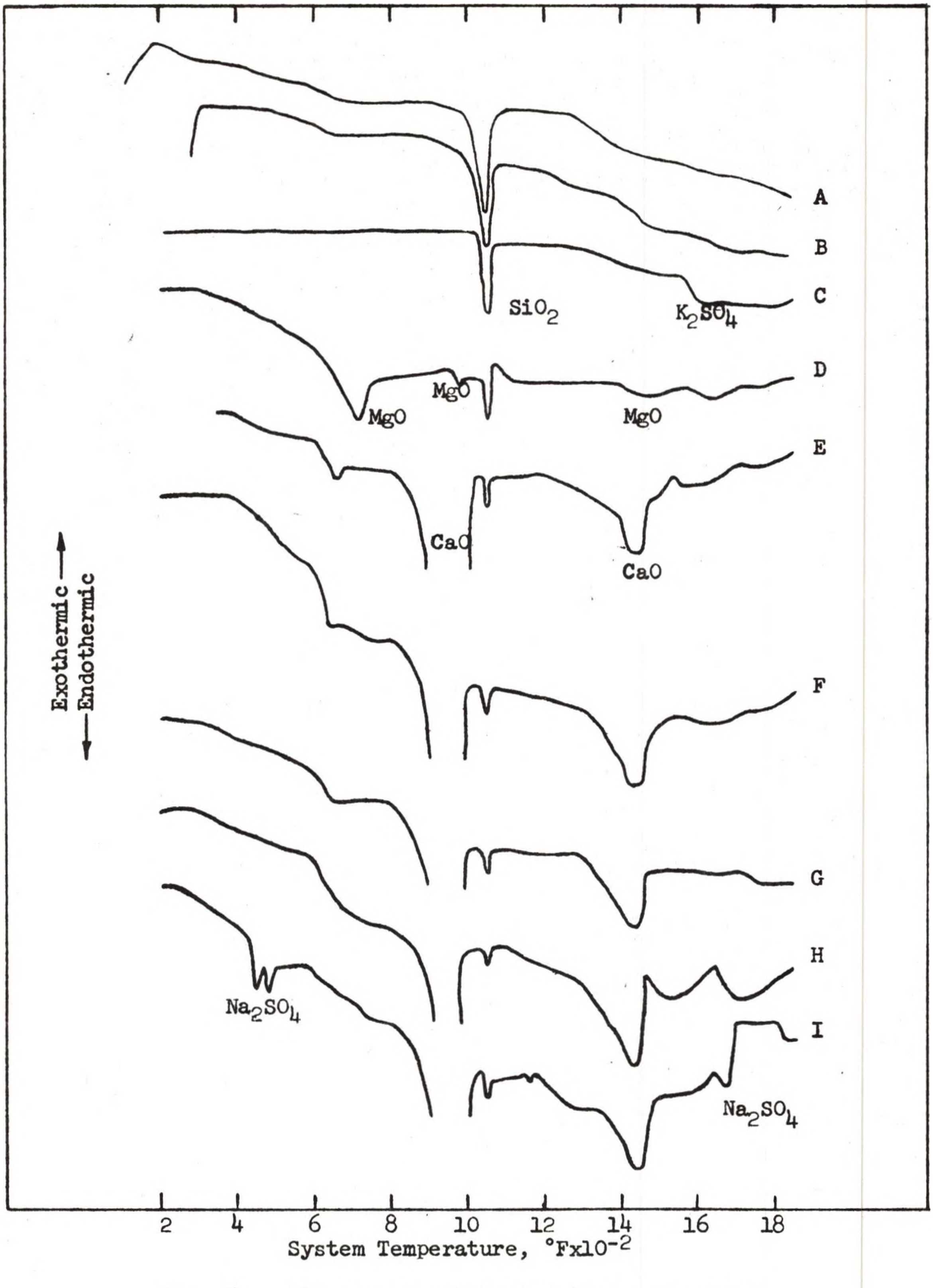


Fig. 6. - DTA curves obtained during cumulative characterization of synthetic fouling and non-fouling ash.

Aluminum oxide. - (Curve B) No reactions or phase transitions were observed in the temperature range investigated.

Potassium sulfate. - (Curve C) A very weak endotherm is observed at 1,600° F. The peak cannot be related to either a transition or melting point and is therefore assumed to be a reaction in which a complex silicate such as orthoclase ($KAlSi_3O_8$) has been formed. No definite substantiation of such a conclusion is possible, nevertheless, the peak was observed in following characterization curves thus ruling out the possibility of erroneous data.

Magnesium oxide. - (Curve D) Three distinct endotherms were obtained. The peaks, one at 720° F, one at 980° F, and one weak broad peak beginning at 1,420° F, were not identified with respect to any reactions or transitions.

Calcium oxide. - (Curve E) The addition of the large percentage of calcium oxide to the cumulative sample resulted in slight suppression of the 720° F magnesium oxide and the silica peaks. An extremely strong endothermic peak at 980° F and a weaker endotherm at 1,430° F completely mask previous effects noted for magnesium oxide. No identification as to specific transitions or melting points was possible and the peaks are assumed to be the result of reactions indicating the formation of complex calcium silicates.

Ferric oxide and calcium sulfate. - (Curves F and G) No additional reactions or transitions were observed.

Sodium sulfate. - (Curves H and I) The two curves presented are for the complete non-fouling and fouling synthetic ashes. The non-fouling synthetic has a low sodium sulfate concentration and the fouling has a high concentration.

The non-fouling synthetic sample, curve H, exhibits two weak endotherms in addition to previously discussed peaks. The first, beginning at 1,470° F, is the result of base line drift induced by the step power change supplied to the heating element every 15 minutes. The second, beginning at 1,640° F, is the melting of the sodium sulfate in the sample. This peak is in close agreement with the actual melting point of 1,622° F.

The fouling synthetic, curve I, exhibits a double endotherm beginning at 450° F due to phase transitions. The melting endotherm at 1,640° F is much sharper because of the high concentration in the sample.

A summary of the peaks attributed to each mineral used in the preparation of the synthetic ashes is presented in table 4.

Representative DTA curves shown in figure 7 indicate that the similarity observed in the composition also exists in the DTA curves. Essentially, five separate peaks are detected. The endothermic peak occurring from 200 to 600° F is due to moisture in the samples. The exothermic peaks occurring near 830° F in both samples, at 1,020° F in the fouling and at 1,240° F in the non-fouling samples were not identified. These peaks are believed to be caused by the same mineral(s) as evidenced by identical shapes. The difference in the temperature at which the peaks occur is apparently due to a greater concentration of the minerals causing the peaks in the non-fouling sample.

Lignite Ash

The chemical analysis of the ash samples investigated in this study was presented earlier in table 2. Comparison of this data indicates that the non-fouling ash has a low sodium content, 0.6 percent, compared with 7.6 percent for the fouling ash and that the sulfur content is slightly less, 9.6 versus 11.9 percent. All other minerals are present in equivalent percentages with the exception of silica, which comprises 27.2 percent of the non-fouling versus 20.4 percent in the fouling.

Representative DTA curves are shown in figure 8. Both curves exhibit the spurious thermocouple peaks discussed earlier. Apparent peaks, indicated by question marks on the curves, are assumed to be the result of either an uncharacterized mineral or an induced emf in the differential thermocouple.

The fouling DTA curve is relatively featureless with the exception of the weak calcium oxide-magnesium oxide endotherm at 1,420° F and the sodium sulfate endotherm beginning at 1,500° F.

The non-fouling DTA curve exhibits the same mineral peaks as present in the fouling with one exception. A strong endotherm at 940° F due to calcium oxide. Note that a weak inversion endotherm for silica was obtained.

A modification of the regular DTA was performed on the fouling and non-fouling ashes. In this approach the non-fouling ash was placed in the sample cell and the fouling ash was placed in the reference inert cell. This procedure results in the canceling of DTA peaks for common materials in both samples and as a result only the difference existing between the samples is evident. The resulting DTA curve is shown in figure 9 and reveals that calcium and/or magnesium oxide is present in the non-fouling ash to a much greater extent than it is present in the fouling ash. The apparent sodium sulfate endotherm beginning at 1,630° F is due to the previously mentioned step change in power supplied periodically to the heating element.

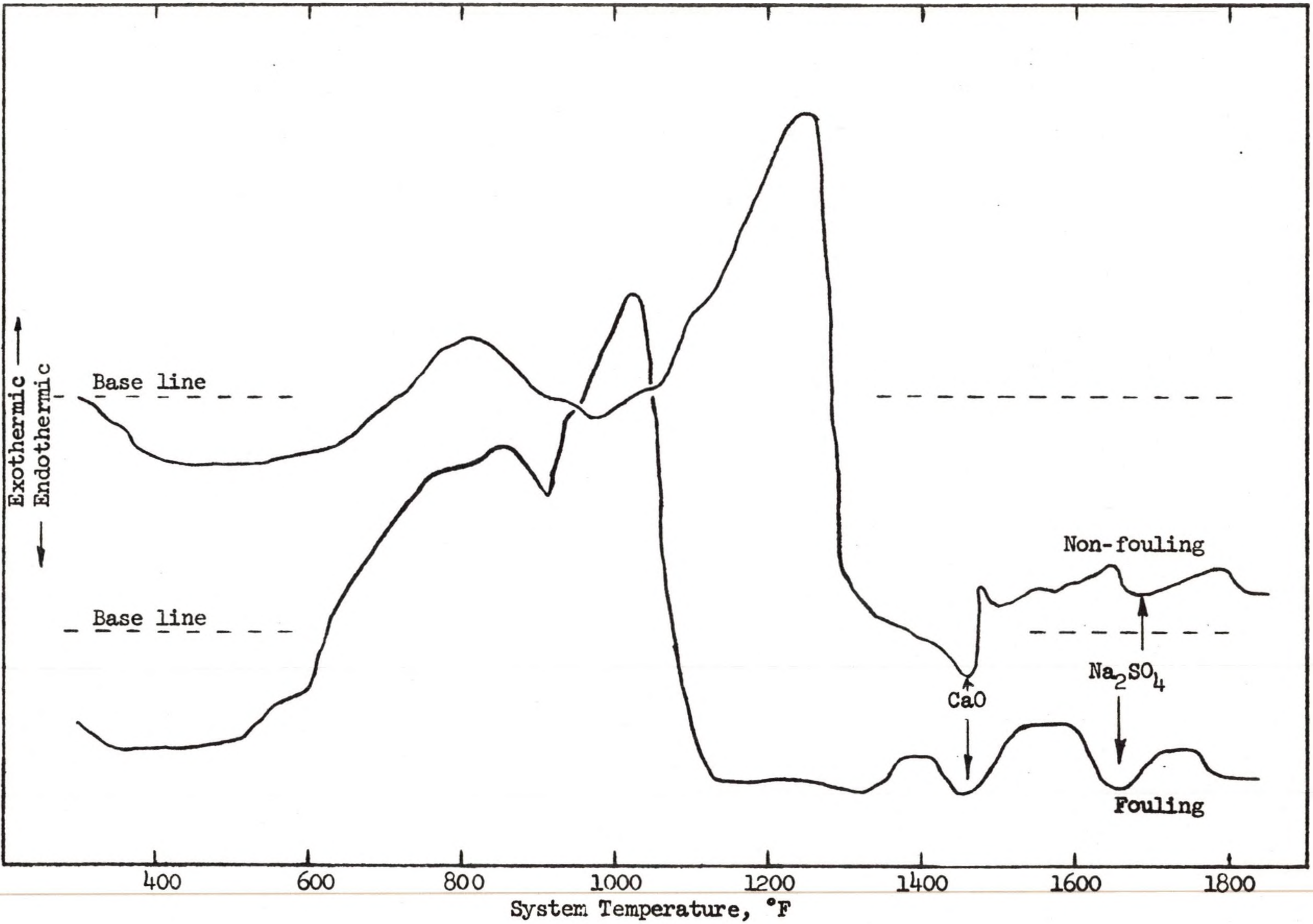


Fig. 7. - DTA curves obtained for fouling and non-fouling boiler flyash.

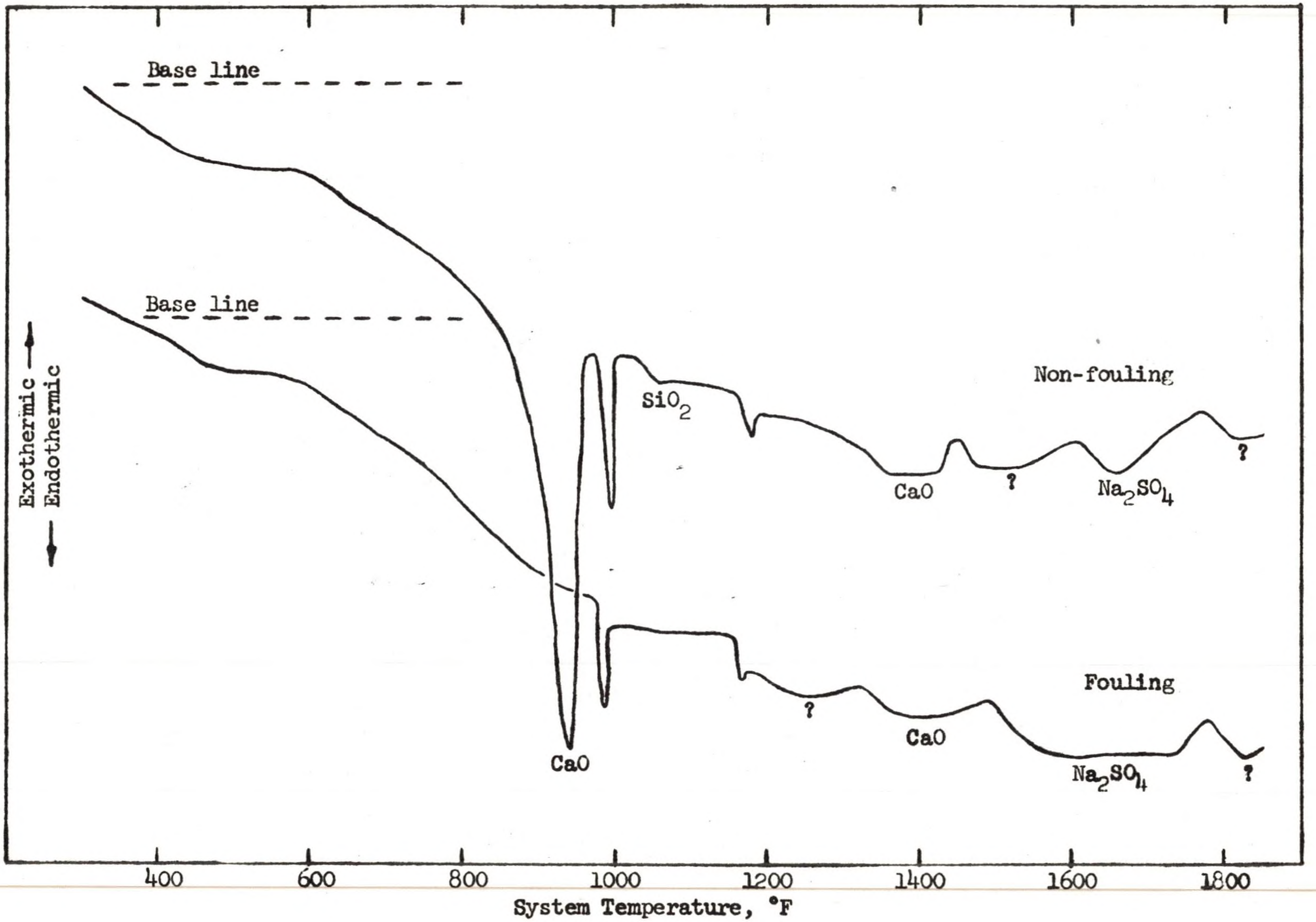


Fig. 8. - DTA curves obtained for fouling and non-fouling natural ash.

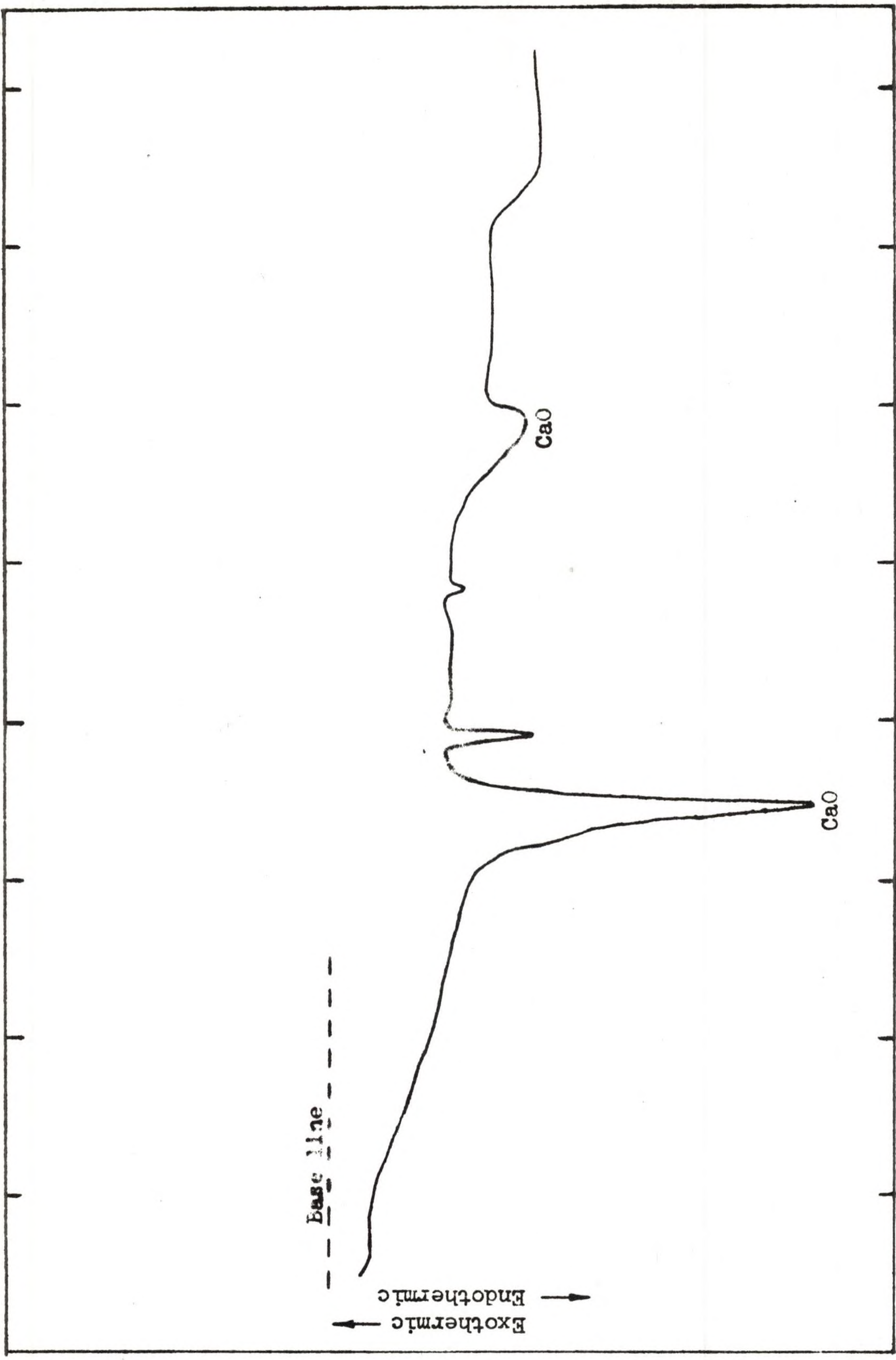


Fig. 9. - **DTA curve** obtained for differential analysis of fouling and non-fouling natural ash.

The differences observed in the DTA curves for the non-fouling and fouling natural ashes investigated are slight. The strong calcium oxide endotherm at 940° F which is observed for the non-fouling but not for the fouling appears to be the only major difference. The strength of the melting endotherm for sodium sulfate is more pronounced and broader for the fouling ash.

Synthetic ash

This section is concerned with discussing the DTA curves obtained during the analysis of the synthetic ashes. The curves shown in figure 10 present the data to be discussed.

The preparation of synthetic ashes corresponding to fouling and non-fouling natural ash was discussed in the characterization section and the chemical composition of these ashes is given in table 2. The two synthetics differ mainly in amounts of sodium sulfate, calcium sulfate and silica. The non-fouling synthetic has low sodium sulfate, 1.4 percent, and high calcium sulfate, 15.2 percent, compared to the fouling synthetic which has high sodium sulfate, 17.4 percent, and low calcium sulfate, 3.5 percent. The amount of silica in the non-fouling is 6.9 percent greater than in the fouling synthetic ash.

Curves A (fouling) and B (non-fouling) in figure 10 were obtained during the initial heating of the synthetic ash. The noticeable differences between the two curves are the double endotherm at 450° F and the melting endotherm at 1,640° F for sodium sulfate and a slightly more pronounced calcium oxide peak at 1,430° F in curve A. The transition peak due to silica and the large endotherm at 990° F which indicates the presence of calcium oxide were the same for both samples. Comparison of curves A and B for the synthetic and curves G and H for the natural ashes indicates that the synthetics are not satisfactory based on the data obtained during the initial heating. The fact that natural ash is heated to a high temperature, 800° F, during preparation suggested that the effect of temperature on the synthetic ash DTA curves should be examined before different compositions were prepared and analyzed.

Curves C (fouling) and D (non-fouling) were obtained during the second heating of the initial samples which had been used to obtain DTA curves A and B. The non-fouling synthetic still exhibits strong calcium oxide endotherms but these peaks are no longer observed for the fouling synthetic. Note also the disappearance of the double sodium sulfate endotherm at 450° F in the fouling sample and the reduction in the height of the silica peaks in both samples. Comparison of these curves to those for the natural ash indicates that the synthetic ashes provide DTA curves which are quite similar to the corresponding natural ash curves.

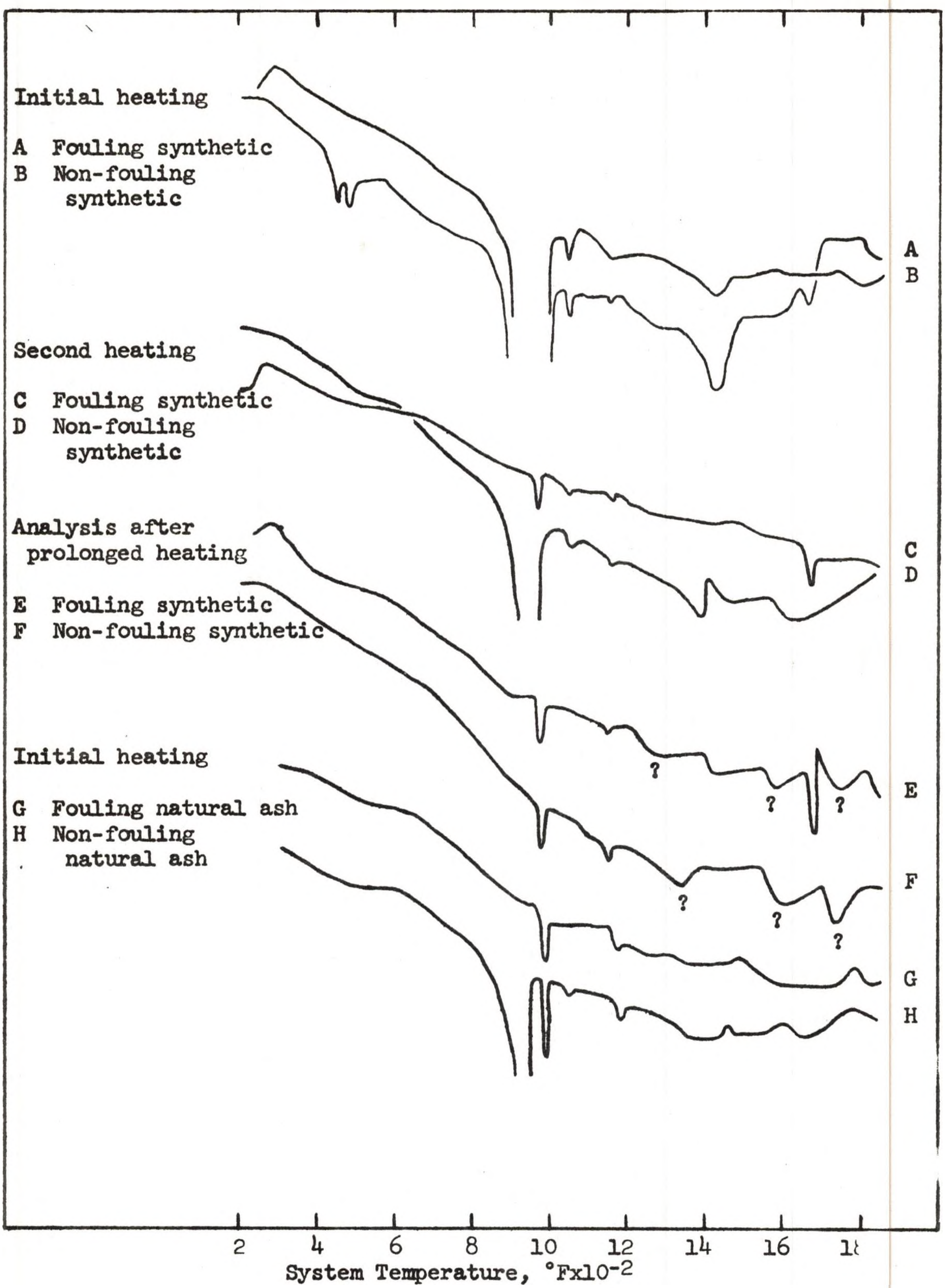


Fig. 10. - DTA curves showing the effect of prior heating on fouling and non-fouling synthetic ashes.

The effect of prior heating on the synthetic ash DTA curves was investigated further by testing synthetics which had been heated at 1,850° F for 14 hours. Curves E (fouling) and F (non-fouling) compare the DTA curves thus obtained. Note the similarity in the shape of the curves. The only characterizable peaks are two endotherms present in the fouling synthetic curve. One peak at 1,420° F corresponding to calcium oxide and another at 1,670° F is caused by the sodium sulfate melt. The three endotherms indicated by question marks in curves E and F occur at about the same temperature and are attributed to the formation of complex silicates during the prolonged heating at 1,850° F. These compounds apparently undergo reactions or transitions during DTA analysis. The assumption concerning the formation of the silicates is borne out by the fact that the transition peak for silica is missing from both curves, indicating that all of the silica originally present in the samples has been reacted. No characterization of these peaks was possible during the course of the present investigation. The major observation resulting from the DTA analysis of the synthetic ashes which had been subjected to prolonged heating is that both the fouling and non-fouling synthetic curves approximate the DTA curve obtained during the analysis of the fouling natural ash.

Alteration of non-fouling ash

A brief examination into the possible alteration of the non-fouling natural ash DTA curve was performed. The alteration was attempted by adding sodium sulfate to the non-fouling natural ash so that the sodium content of this ash would be equivalent to that of the fouling natural ash. The sample was prepared by mixing sodium sulfate with the non-fouling natural ash. The resulting mixture was then analyzed twice in the DTA apparatus. The first analysis was to observe if additional transitions or reactions might occur during the initial heating of the sample. The second analysis was to observe the effect that the addition had on the DTA curve after these possible reactions had occurred.

The DTA curves which resulted are shown in figure 11. The initial curve shows the peaks expected for the non-fouling natural ash plus additional sodium sulfate peaks. The second curve, obtained by reheating the first sample analyzed, appears to duplicate the fouling natural ash curve as indicated by the featureless curve obtained. A control DTA analysis was performed using unaltered, non-fouling natural ash. The purpose of the control was to assure that changes observed in the DTA curve of the altered ash were the result of the addition and not due to completion of reactions which could occur in the unaltered natural ash when the sample was heated to a high temperature. The data obtained from these two runs is presented in figure 12. Unfortunately, the second heating resulted in a DTA curve similar to the curves obtained for the fouling natural ash. This indicated that reactions possible in the non-fouling ash were completed by heating to 1,850° F and that no detectable

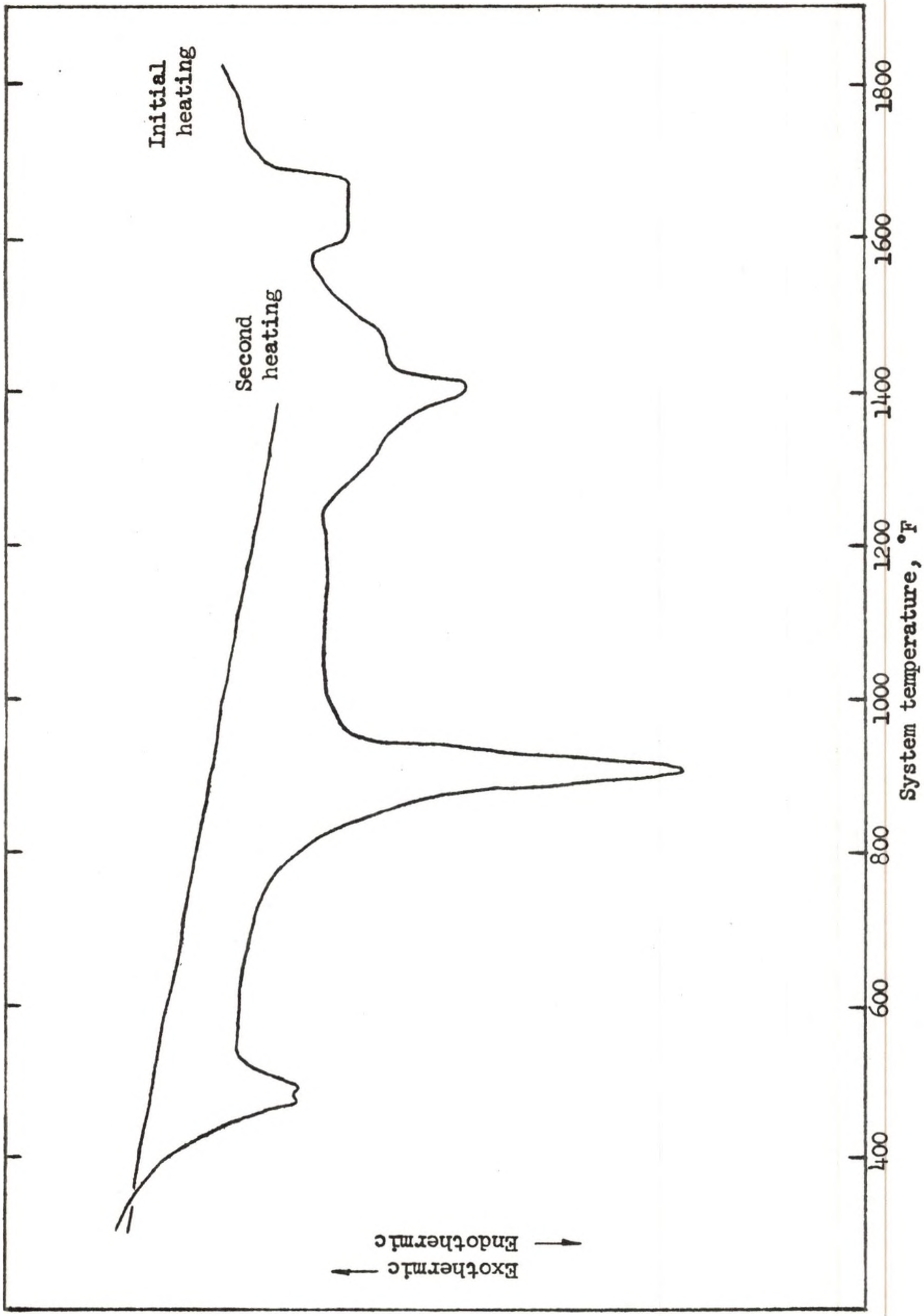


Fig. 11. - DTA curves obtained for initial and second heatings of natural non-fouling ash altered by addition of sodium sulfate.

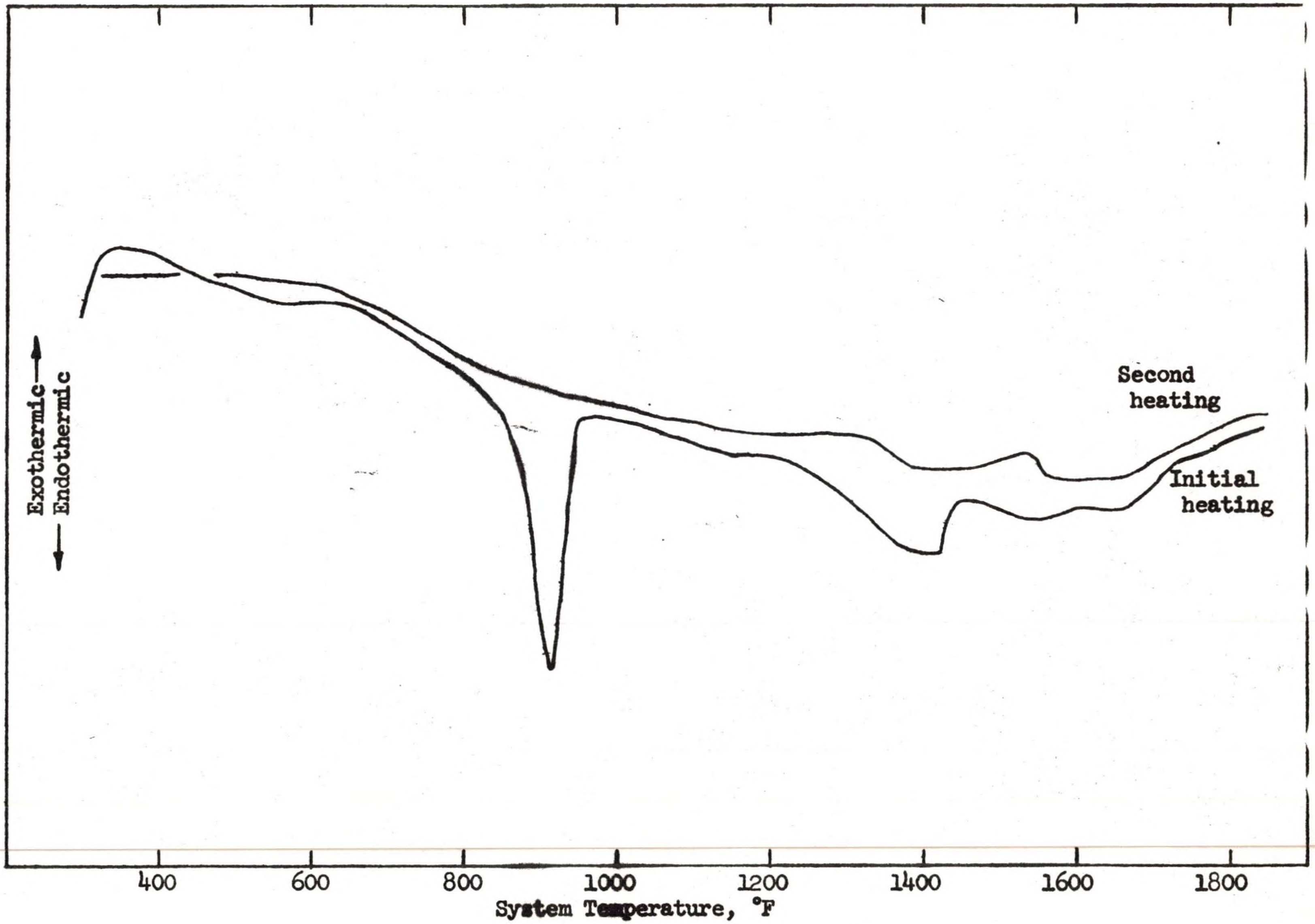


Fig. 12. - DTA curves obtained for initial and second heatings of natural non-fouling ash.

differences could be established between the fouling and the non-fouling natural ashes once they were heated to this high temperature. Because of this, it was impossible to ascertain the effects of the sodium sulfate addition on the non-fouling natural ash DTA curve and this type of study was left for future investigations.

SUMMARY AND CONCLUSIONS

Characterization

Endothermic reactions, transitions and melting points were observed for silica, magnesium oxide, calcium oxide, potassium sulfate and sodium sulfate. No effects were noted for aluminum oxide, ferric oxide, or calcium sulfate.

The peaks for silica and sodium sulfate were definitely related to known transition and melting points. The silica endotherm at 1,055° F is caused by the transition of silica from the α to the β form. The double endotherm beginning at 450° F is the result of phase transitions and the endotherm at 1,640° F is the melting point for sodium sulfate. The three endotherms for magnesium oxide at 720° F, 980° F and 1,420° F, the two endotherms for calcium oxide at 980° F and 1,430° F, and the single endotherm at about 1,600° F for potassium sulfate were not identified with respect to either transition or melting points and were assumed to be indicative of reactions in which complex silicates are formed.

The cumulative addition procedures developed, using synthetic ash mixtures, for characterizing natural ashes resulted in the successful identification of the major peaks observed on the DTA curves. Similar methods may be satisfactory when applied to more complex systems in which silicates believed to be present in natural ash are added.

Flyash

The flyash samples from fouling and non-fouling boiler operation exhibited DTA curves completely unrelated to those obtained for the corresponding natural ashes. The synthetic ashes developed were not useful in the characterization of flyash.

The DTA curves obtained were essentially exothermic with similar peaks near 830° F in both samples. The strong exotherms observed at 1,020° F in the fouling and at 1,240° F in the non-fouling samples have similar shapes suggesting that the peaks were caused by the presence of similar minerals. The difference in the temperature at which peaks occur is attributed to differing concentrations of these minerals. Endothermic peaks obtained in both samples indicated the presence of calcium oxide and sodium sulfate.

The second heating of the altered sample provided a DTA curve very similar to the curve for the fouling natural ash. A control DTA analysis in which an unaltered sample was heated and reheated by the same procedures provided a DTA curve during the second heating which was also similar to the fouling natural ash DTA curve. Therefore, no conclusion regarding the effect of the alteration could be made.

Prior exposure at high temperatures was concluded to have significant effects on the DTA curves obtained for fouling and non-fouling synthetic and natural ashes. The effect observed was that the DTA curves obtained for non-fouling samples after prolonged exposure to high temperatures were quite similar to fouling natural ash DTA curves.

The natural ash samples prepared in the laboratory appeared to exhibit dissimilar DTA curves during the initial analysis of the samples. These peaks could be used to differentiate fouling lignite from non-fouling lignite. The differences in the DTA curves for the two types of lignite ash appear to be affected considerably by prior temperature exposure and cannot be confidently used to establish correlations concerning fouling properties until this temperature effect on the DTA analysis can be completely established.

The primary conclusion of the investigation is related to the disappearance of peaks from the synthetic ash mixtures as they were analyzed after consecutive heatings. Certain peaks observed during the analysis of the samples were attributed to the formation of complex silicates or other compounds. Based on the data available, it appears that the fouling ash reacts to form these compounds at a much faster rate than the non-fouling ash. This rapid conversion could be a plausible explanation as to why fouling occurs. The temperature of combustion and the residence time at this temperature may allow the complete conversion of the fouling lignite ash content to silicates and other compounds which can melt and deposit on boiler surfaces. The non-fouling lignite does not react as rapidly and its ash cannot be converted completely. As a result, no severe fouling conditions occur.

RECOMMENDATIONS

The following recommendations are made.

(1) The manual heating rate control system used in the present investigation should be replaced by an automatic system. This change will eliminate large base line drift every time a step change is made in the power supplied to the heating element.

APPENDIX A

CALCULATIONS FOR INSULATION AND HEATING ELEMENT

Insulation

The insulation dimensions were determined for Fibrefrax insulating blanket having a thermal conductivity (k) of 0.188 Btu/hr ft ° F at 2,000° F and a density () of 6 lb/ft^3. The furnace was cylindrical with a height of 20 inches and diameter determined by the insulation thickness required. The insulation calculations assumed steady-state operation at a heating element temperature of 3,200° F and an outside wall temperature of 70° F.

Definitions

q_1 = longitudinal end losses, Btu/hr

q_2 = radial losses, Btu/hr

q_3 = heat capacity of insulation, Btu

r_i = radius of heating element, inches

r_o = radius of cylinder, inches

k = thermal conductivity, Btu/hr ft °F

l = height of cylinder, inches

L = longitudinal length, inches

T_i = heating element temperature, °F

T_o = outside wall temperature, °F

Calculations

The insulation was sized to allow 3,413 Btu/hr in radial losses from the furnace.

$$q_2 = \frac{2\pi kl\ (T_i - T_o)}{\ln(r_o/r_i)} = 3{,}413\ \text{Btu/hr}$$

Solving for ln (r_o/r_i)

$$\ln(r_o/r_i) = \frac{2\pi kl\ (T_i - T_o)}{q_2} = \frac{2\pi\ 0.188\ \frac{\text{Btu}}{\text{hr ft °F}}\ \frac{20}{12}\text{ft}\ \ (3{,}030°\ \text{F})}{3{,}413\ \frac{\text{Btu}}{\text{hr}}} = 1.751$$

APPENDIX B

TABULATED SUMMARY OF ALL DTA RUNS

Run	Date	Temp. °F	Ave. heating rate, °F/min.	Purpose
A	Feb. 16	1,080	2.73	Heat cure furnace refractory
B	18	1,640	3.07	Heat cure furnace refractory
C	23	1,730	6.07	Heat cure furnace refractory
D	25	1,735	9.38	Heat cure furnace refractory
E	Mar. 2	1,510	7.74	Determine heating rate
F	9	2,160	11.07	Determine heating rate
G	11	2,160	12.56	Determine heating rate
H	23	2,160	13.85	Determine heating rate
1	April 8	1,850	12.85	Check base line drift
2	9	1,850	13.21	Analyze non-fouling flyash
3	15	1,850	13.12	Base line drift
4	16	1,850	13.50	Base line drift
5	19	1,850	13.12	Base line drift
6	20	1,850	13.21	Base line drift
7	21	1,850	13.31	Analyze non-fouling flyash
8	22	1,850	13.12	Analyze fouling flyash
9	23	1,980	12.86	Analyze non-fouling flyash
10	27	1,850	13.03	Analyze fouling flyash
11	27	1,670	13.92	Analyze non-fouling flyash
12	29	1,850	13.21	Base line drift
13		1,850	13.41	Analyze fouling flyash
14	May 4	1,850	13.31	Analyze non-fouling flyash
15	4	1,850	13.91	Analyze low temperature lignite ash
16	11	1,850	14.01	Analyze non-fouling lignite ash
17	13	1,850	13.12	Analyze high temperature lignite ash
18	18	1,850	13.12	Analyze non-fouling synthetic
19	20	1,850	12.94	Analyze non-fouling lignite ash
20	20	1,850	13.50	Analyze fouling lignite ash
21	21	1,850	13.70	Analyze non-fouling synthetic
22	June 1	1,850	12.42	Analyze non-fouling lignite ash
23	1	1,850	13.12	Analyze fouling lignite ash
24	2	1,850	13.41	Analyze non-fouling synthetic
25	2	1,850	13.12	Differential DTA of lignite ashes
26	3	1,850	13.12	Analyze non-fouling synthetic
27	4	1,850	13.21	Analyze fouling synthetic
27a	4	1,850	13.31	Reheat run 27
28	7	1,850	12.50	Reheat run 26
29	8	1,850	12.25	Analyze non-fouling synthetic
30	8	1,850	13.41	Analyze fouling synthetic
31	9	1,850	13.12	Analyze non-fouling synthetic
32	10	1,850	---	Analyze fouling synthetic

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