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# Fusibility Characteristics of Synthetic and Natural Coal Ashes

James A. Medaris

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FUSIBILITY CHARACTERISTICS OF SYNTHETIC  
AND NATURAL COAL ASHES

by

James A. Medaris

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

A Thesis

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of the

Graduate School

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University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

June  
1960

This thesis submitted by James A. Medaris 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.

T1960  
M46  
Eng.

A. M. Cooley  
Chairman

D. E. Severson

Philip A. Rognlie

James L. Elder

Walter H. Oppelt

Christopher J. Hamre  
Dean of the Graduate School



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## INTRODUCTION

Coal ashes are composed of a variety of minerals, including clays, shales, complex carbonates and silicates, and pyrites (16). Upon heating the ash, individual minerals are at least partially decomposed to form minerals not originally present in the ash. The minerals in this complex mixture have melting points extending over a very wide temperature range. Hence, a further increase in temperature will cause a dissolution of molten and solid minerals which produces additional interaction of the minerals (17). Further heating will cause a continuation of this process until the ash has been entirely melted.

Not much is known of the complex process that takes place during melting and all correlations of physical properties have been made in terms of composition as pure oxides rather than the minerals actually present. This has been due to the method of analysis which reports the composition as pure oxides.

Correlation attempts have also been hindered by the fact that with natural ashes, it is not possible to vary one constituent independently of the others. This makes statistical studies of the effect of single constituents extremely difficult.

The primary purpose of this investigation was to devise a method for preparing a synthetic ash having the same fusion temperature and composition (as oxides) as a natural occurring ash. The synthetic ashes prepared were then used to substantiate previous work as well as provide a means by which later statistical studies of the effect of individual components could be made.

The present use of correlations of fusion temperatures and composition is very limited. In practice it is much more simple and accurate to determine the fusion temperature of the ash directly since chemical analysis of the ash is tedious. The primary interest, therefore, is the theoretical aspects of fusion and the possibility of future use of fusion characteristics and chemical composition in predicting viscosities of molten ash (1). The study of ash fusion temperatures is a prerequisite for this goal. When fusion characteristics have been satisfactorily explained work can commence on the more difficult aspect of correlation of viscosities with composition and fusion temperatures.



## CHAPTER I

### METHOD OF DETERMINING ASH FUSION TEMPERATURES

Natural ash preparations and fusion temperature determinations were made in accordance with U. S. Bureau of Mines Bulletin No. 492 (7) as outlined below. This method is in agreement with the ASTM method.

The coal was fired in an electric furnace at 800-900° C under an air flow until the ash maintained a constant weight. The completely oxidized ash was pulverized to minus 200 mesh (74 microns) in a ball mill using agate stones. The pulverized ash was formed into triangular pyramids 3/4 inch high and 1/4 inch on each side of the triangular base. A solution of 10% dextrin and 0.1% salicylic acid was used as a binder to form the pyramids. The pyramids were dried, heated to approximately 800° C for 30 minutes to drive off the dextrin, and then mounted in platinum bases.

The fusion temperatures were determined in a gas fired furnace using an optical pyrometer. The rate of temperature rise was maintained between 5 and 10° C per minute after 1800° F was attained. Three fusion temperatures were determined: (1) the initial deformation temperature at which the apex of the pyramid rounds or deforms as shown by pyramid 1 of Figure 1, (2) the softening temperature at which the pyramid has been reduced to a hemispherical lump as shown by pyramid 3 of Figure 1, and (3) the fluid temperature at which the pyramid has spread over the base in a flat layer as shown by pyramid 5 of Figure 1.

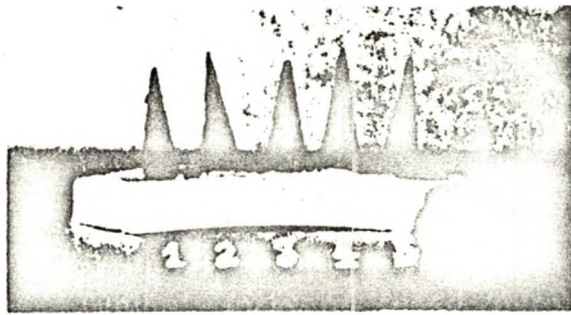
The use of platinum bases rather than the mixture of kaolin and alumina as specified by ASTM and Bureau of Mines Bulletin No. 492 was necessitated by the reaction of some of the samples with the refractory type base.

The Leitz Heating Microscope shown in Figure 2 was used with a few selected samples to give a pictorial record of the melting process as well as provide a limited comparison of the results obtained with the two types of equipment. The ash was prepared in the same manner as for the conventional furnace. It was then pressed into 3mm cube samples, without the binder, by means of a spring loaded hand press to a pressure of 300 psi.

## CHAPTER II

### BRIEF HISTORY OF CORRELATIONS

There have been many attempts to correlate ash fusion temperatures with composition since Le Chatelier and Chantetre (12) first investigated this relationship in 1902. None have been entirely successful although some of the reasoning does prove useful.



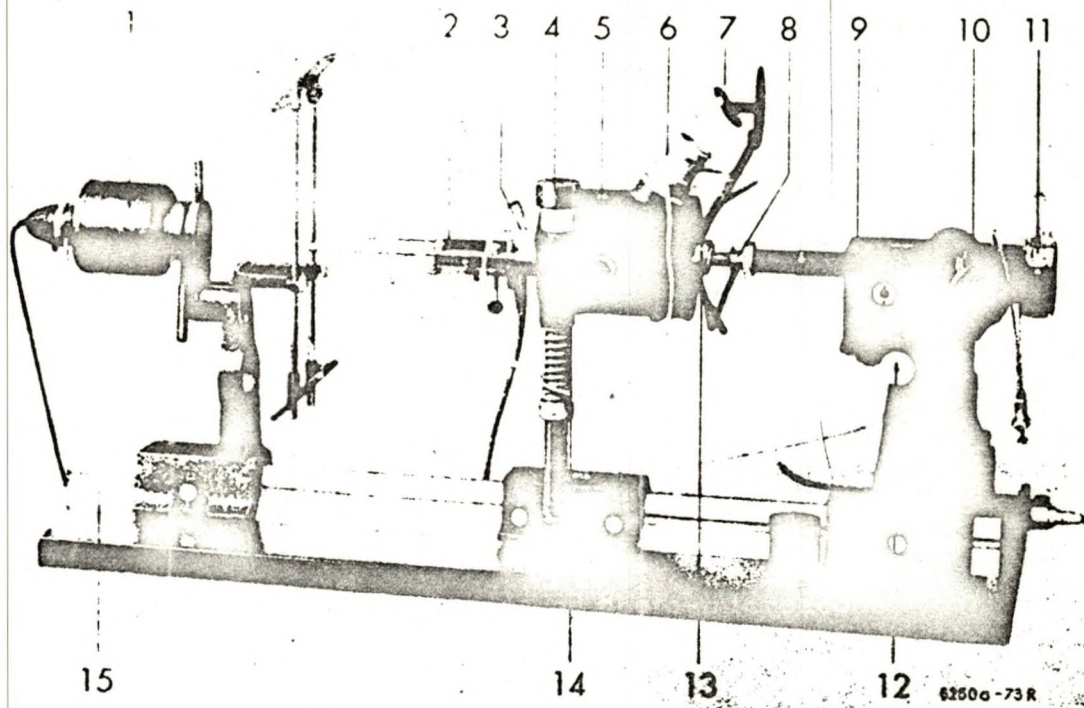
*A*



*B*

Fig. 1 A. Pyramids mounted on base.  
B. Typical form of fused pyramids.





Heating Microscope Outfit II A

- 1 Low voltage filament lamp
- 2 Specimen wagon
- 3 Rear cooling chamber
- 4 Screw for vertical adjustment
- 5 Furnace housing
- 6 Aperture for oblique illumination
- 7 Mirror for oblique illumination
- 8 Objective
- 9 Observation and photo-microscope
- 10 Mirror reflex system
- 11 LEICA housing
- 12 Rack and pinion drive for focusing
- 13 Forward cooling chamber
- 14 Screw for lateral adjustment
- 15 Prismatic rail

Fig. 2 Leitz heating microscope. (19)

The major problem in correlations is determination of the significance of each component reported in the analyses. Table I lists the components normally reported and the normal range of these components (15).

TABLE I  
TYPICAL LIMITS OF ASH ANALYSES OF U. S. COALS

Component	Range for Lignite - %	Range for Bituminous - %
SiO <sub>2</sub>	5 - 35	20 - 60
Al <sub>2</sub> O <sub>3</sub>	3 - 25	10 - 35
Fe <sub>2</sub> O <sub>3</sub>	3 - 25	5 - 35
CaO	15 - 35	1 - 20
MgO	2 - 15	0.3 - 4
Na <sub>2</sub> O plus K <sub>2</sub> O	1 - 6	1 - 4

The alkalis, Na<sub>2</sub>O and K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>, if reported, comprise only a small portion of the ash and have usually been disregarded for correlation purposes. The SO<sub>3</sub> is normally present in the form of sulfates so that all or nearly all of it is driven off before fusion takes place (4). The Al<sub>2</sub>O<sub>3</sub> is normally present in the form of clays which have a weight ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> of 1.18 (5). An examination of 290 available analyses revealed only ten cases where their ratio was less than 1.18 (5). It is assumed that any SiO<sub>2</sub> in excess of this ratio is in the form of very complex silicates (5), some of which have been identified (18) although no correlations have been attempted using this basis.

The iron may occur in any of its oxidized states depending upon the degree of oxidation during firing and the atmospheric conditions during the fusion temperature determinations. There is considerable doubt as to the actual state of the iron in any given case since it depends upon such factors as temperature, reducing conditions of the atmosphere, porosity of the sample, and history of the sample. Some workers have tried to determine a ratio of the various states for each sample (14), but in most correlations 100% Fe<sub>2</sub>O<sub>3</sub> is assumed (5).

All correlations use the softening temperature as the basis because it is the most significant variable in judging ash behavior (13). It is also the critical temperature used in predicting the flow properties of the slag formed from the fused ash (10).

Joseph Harrington (8) made a correlation using a basis of the ratio of the sum of SiO<sub>2</sub> plus Al<sub>2</sub>O<sub>3</sub> to the sum of the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO plotted against the softening temperatures for numerous ash analyses. This correlation predicted softening temperatures which varied as much as 300° F from the experimental values and so cannot be considered satisfactory. It does, however, show a definite trend and produces some



interesting results. The parabolic shape of the curve, with the minimum temperature where the basis ratio is approximately 1/2, shows that two ashes of entirely different analyses may have the same softening temperature. The portion of the curve for low ratios corresponds to lignites while the portion for high ratios was obtained from high-rank coal ashes. Thus, increasing the sum of the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> would decrease the softening temperature for lignite ashes but would increase it for bituminous coal ashes. This fact has been known for some time and has been utilized in the iron industry by adding fluxes to the blast furnace charge to produce a more fluid slag.

Nicholls and Selvig (8) proposed a general correlation using an index of:

$$R\% = \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}$$

This correlation gave results very similar to that of Harrington's, as might be expected from the similarity of the ratios used as an index.

Schaefer (2) proposed an index which supposedly represents the fluxing ability of the individual components. This index is the ratio:

$$R_s = \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} \left[ \frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{FeO} + 0.6(\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \right]$$

When R<sub>s</sub> was plotted against the softening temperature for 98 ashes from American coals an average deviation of 48° F from the curve of best fit was obtained. However, when Brown (3) used this index with Australian coal ashes an extremely poor correlation resulted.

Recently Mazumdar, Banerjee, and Lahiri (3) proposed an index based on molar percentages rather than weight percentages. This index was calculated to be the ratio:

$$R_m = \frac{3.33 \text{ SiO}_2 + 1.96 \text{ Al}_2\text{O}_3}{2.5 \text{ Fe}_2\text{O}_3 + 3.57 \text{ CaO} + 5.00 \text{ MgO} + 3.22(\text{K}_2\text{O} + \text{Na}_2\text{O})}$$

This ratio produced a better correlation than either the Schaefer (R<sub>s</sub>), or the Nicholls and Selvig (R%) index when used with Indian Coals.

The best correlation found in the literature was the prism plot developed by Estep and Seltz (4). This correlation was made by plotting the weight percentages of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> along the height and three sides of a triangular prism. The CaO content was computed on the basis of 100% for the four components mentioned and plotted along



the height of the prism. The percentages of the remaining three were recomputed disregarding all other components and plotted on the triangle formed by the base of the prism. The resulting solid figure contains isotherm planes which must be plotted in three dimensions. To simplify the correlation Estep and Seltz cut the prism into horizontal sections, each of which is a triangular plot of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ , with the  $\text{CaO}$  constant within one percent. In this way the isotherm planes can be represented as isotherm lines in each section. This correlation proved very good for bituminous ashes with which it was developed. However, it cannot be used for lignite ashes since the area of the ternary which was developed does not include the section corresponding to typical lignite ash compositions.

The author (9), in his Bachelor's thesis and subsequent work not included in the thesis, developed a correlation using only one ash and mixtures of this ash with  $\text{Al}_2\text{O}_3$  and/or  $\text{SiO}_2$ . The index for this correlation was the sum of the  $\text{SiO}_2$  and effective  $\text{Al}_2\text{O}_3$  equivalents. The effective  $\text{Al}_2\text{O}_3$  was defined as the portion of the  $\text{Al}_2\text{O}_3$  equivalents present which was required to neutralize the ash when the  $\text{SiO}_2$  is considered acidic, the  $\text{Fe}_2\text{O}_3$  and  $\text{CaO}$  are considered basic, and the  $\text{Al}_2\text{O}_3$  is considered amphoteric. This correlation is reproduced in Figure 3. It is very limited however, because the ratios between all components except  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were constant for all samples. Therefore, it can be expected that it would produce only a trend curve when applied to a selection of natural ashes.

### CHAPTER III

#### EXPERIMENTAL METHODS AND RESULTS

In preparing the synthetic ash from pure oxides it was necessary to use the carbonates of calcium and the alkalies since their oxides are very hygroscopic causing extreme difficulties in weighing the samples accurately. Great care had to be used even when using the carbonates to prevent water absorption by the remaining oxides before they were mixed. This was done by heating them at  $600\text{-}700^\circ\text{C}$  to constant weight and allowing them to cool in a sulfuric acid desiccator.

After the oxides were weighed in the right proportions and mixed they were heated at  $1000^\circ\text{C}$  to constant weight, taking two to four hours, to drive off the  $\text{CO}_2$  from the carbonates. This was done under a flow of air to purge the  $\text{CO}_2$  and to provide sufficient  $\text{O}_2$  to prevent reduction of the  $\text{Fe}_2\text{O}_3$ .

A synthetic ash was prepared in the above manner to conform to the reported analysis of Custer lignite ash. The analysis of this ash is given in Table II.

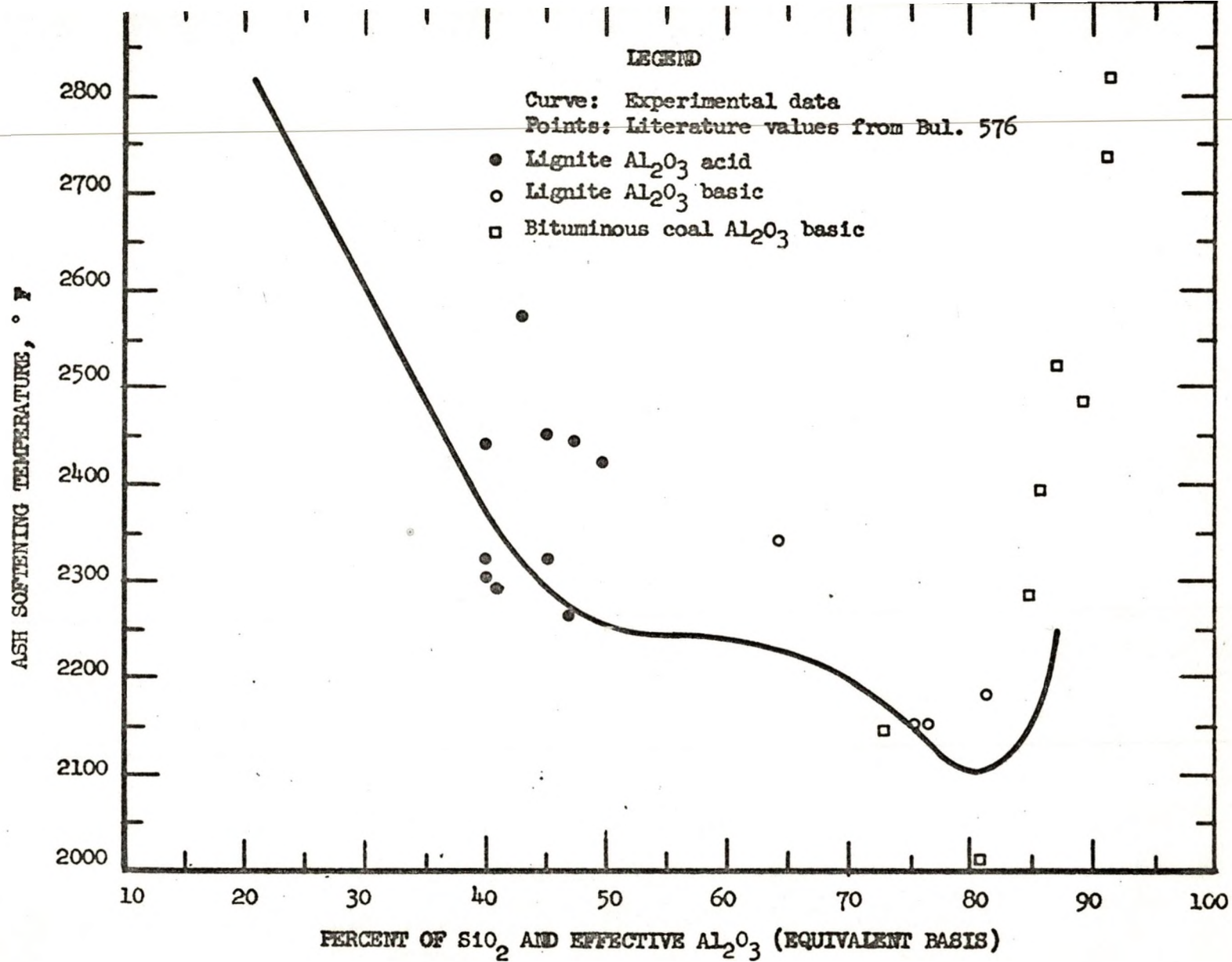


Figure 3: Effect of  $SiO_2$  plus  $Al_2O_3$  on ash softening temperature.



TABLE II

## CUSTER LIGNITE ASH ANALYSIS

Component	Weight Percent
SiO <sub>2</sub> .....	12.9
Al <sub>2</sub> O <sub>3</sub> .....	9.8
Fe <sub>2</sub> O <sub>3</sub> .....	9.4
CaO.....	31.7
MgO.....	7.3
BaO.....	0.8
Na <sub>2</sub> O.....	8.3
K <sub>2</sub> O.....	0.5
SO <sub>3</sub> .....	19.2

The SO<sub>3</sub> was not included in the synthetic ash because it is impossible to determine its form from the reported analysis and also because sulfates will decompose below fusion temperatures, as previously mentioned.

Fusion temperature determinations were made on this synthetic ash as well as mixtures containing additional SiO<sub>2</sub> and/or Al<sub>2</sub>O<sub>3</sub> identical to those used in the author's Bachelor's thesis. The fusion temperatures from these mixtures did not follow any apparent pattern. In fact the softening temperatures for all samples were between 2120° F and 2250° F except for those mixtures to which only Al<sub>2</sub>O<sub>3</sub> had been added. These showed an almost linear increase of softening temperature with increasing Al<sub>2</sub>O<sub>3</sub> concentration. Also, the softening temperature for the synthetic Custer ash was 360° F below that which was reported for the natural Custer ash. This is a good indication that they do not reflect the natural ash fusion characteristics.

From this result it was concluded that the synthetic ash required additional processing before it could be used in ash fusion studies. A heat treating process was selected because it was believed that high temperatures would allow the oxides to interact to form complex compounds closer related to those found in natural ash. To follow the progressing interaction, a test was devised based on the fact that HF will volatilize pure SiO<sub>2</sub> which can be driven off with heat application. HF was to be added to the heat treated ash and then the water, acid, and any portion of the ash volatilized by the acid driven off. It was hoped that any silicate SiO<sub>2</sub> would not be affected by the HF so that the weight loss due to the acid treatment could be used as an indication of the extent of the reaction of the SiO<sub>2</sub>. In this way it could be determined when a heat treated synthetic ash was equivalent to a natural ash. However, acid treatment of three selected natural ashes to be used as controls showed



that no relation existed between the SiO<sub>2</sub> content and the weight loss due to HF treatment. In fact no relation could be found between the weight loss and any component oxide. The weight loss in all three ashes was greater than expected and covered a much greater range than had been anticipated. The range of the weight losses was from six to thirty one percent.

A trial and error method was then used to obtain a heat treating process that would produce the desired results. After numerous trials it was found that heat treating the ash at 2100 - 50° F in the gas fired fusion furnace for 2.5 hours made the synthetic Custer ash exhibit the same fusion temperatures as the natural Custer ash. In order to determine the reproducibility of this method, nine additional synthetic ashes were prepared in the same manner using compositions given in U. S. Bureau of Mines Bulletin No. 567. The fusion temperatures obtained from these samples are compared with those listed in Bulletin No. 567 in Table III on page 16.

Gas samples were taken from the combustion chamber of the gas fired furnace, as close to the sample as possible during the heat treating to determine how well the atmosphere was controlled. Table IV on page 16 lists the amounts of CO<sub>2</sub>, CO, and H<sub>2</sub> obtained at various temperatures.

TABLE III  
COMPARISON OF FUSIBILITY CHARACTERISTICS  
OF NATURAL AND SYNTHETIC ASH

Mine <sup>1/</sup>	Initial Deformation, ° F		Softening Temperature, ° F		Fluid Temperature, ° F	
	<sup>2/</sup>	<sup>3/</sup>	1	2	1	2
	Beulah	2,080	2,100	2,340	2,350	2,370
Baukol-Noonan	2,080	2,130	2,150	2,200	2,180	2,220
Kincaid	2,080	2,080	2,150	2,190	2,210	2,400
Dakota Star	2,420	2,390	2,450	2,420	2,490	2,440
Dakota Star	2,260	2,300	2,310	2,350	2,420	2,400
Dakota Star	2,100	2,100	2,260	2,280	2,360	2,420
Zap	2,030	2,250	2,290	2,300	2,310	2,330
Lehigh	2,210	2,240	2,400	2,390	2,500	2,490
Custer	2,300	2,250	2,470	2,470	2,530	2,570
Dakota Star	2,380	2,410	2,440	2,460	2,470	2,490

<sup>1/</sup> Source for location, analyses, and fusibility of natural ash was Bureau of Mines Bulletin 567.

<sup>2/</sup> 1 - indicates natural ash.

<sup>3/</sup> 2 - indicates synthetic ash.



TABLE IV  
ANALYSES OF GAS SAMPLES FROM FUSION FURNACE

Temperature, ° F	CO <sub>2</sub> %	CO %	H <sub>2</sub> %
1500	5.8	6.7	10.9
2000	7.9	8.4	6.4
2000	5.3	6.0	10.9
2000	6.6	10.9	9.2
2000	7.7	9.4	7.6
2100	8.6	7.7	5.5
2100	6.5	10.9	10.3
2100	6.4	11.2	10.3
2100	6.3	11.8	10.7
2100	6.6	11.1	10.7
2100	6.3	11.7	11.2
Average	6.7	9.6	9.4

Some methane and ethane were present in concentrations always less than one percent. The remainder of the gas was nitrogen.

The table of gas analyses shows a considerable variation in gas composition. This undoubtedly is due to the fact that the atmosphere is controlled by the height and color of the flame emitted from the furnace as outlined by ASTM and Bureau of Mines Bulletin No. 492.

In an attempt to further substantiate the use of the heat treatment, infrared absorption spectra of the natural Custer ash and four synthetic Custer ashes which had been heat treated at various temperatures for varying lengths of time were made. These spectra are shown in Figure 4. Spectrum 1 is that of natural Custer ash. Spectrum 2 is that of synthetic Custer ash heated to 1500° F for one hour. Spectrum 3 is that of synthetic Custer ash heated to 2000° F for one hour. Spectrum 4 is that of synthetic Custer ash heated to 2000° F for two and one half hours. Spectrum 5 is that of synthetic Custer ash heated to 2100° F for two and one half hours.

The band at 2.9 microns on all the spectra is caused by water, apparently water of crystallization. As would be expected, the height of this band and hence the concentration of the water, decreases as temperature and curing time increase. The band at 6 - 7 microns in all spectra is due to the CO<sub>2</sub> radical. Again this decreases with temperature and time. The presence of the CO<sub>3</sub> radical is evidently caused by absorption of CO<sub>2</sub> from the air before heat treating or by reactions with the CO<sub>2</sub> of the gas in the fusion furnace. The band at 8 microns in the natural ash spectrum is due to the SO<sub>4</sub> radical and is absent in the synthetic

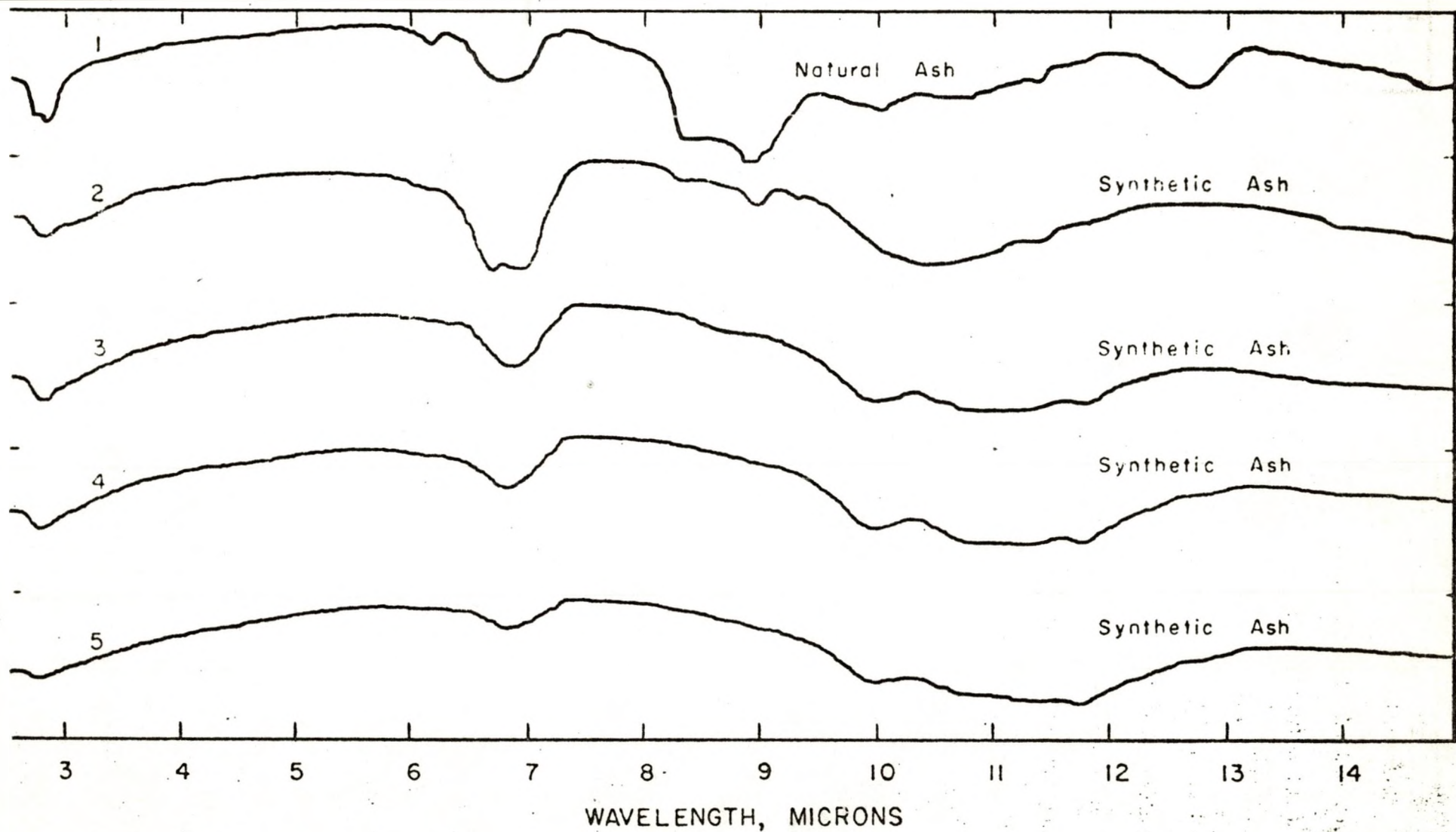


Figure 4: Spectrum of natural and synthetic Custer ashes.



ash spectrum since no sulfate  $\text{SO}_3$  was included in these mixtures. The band at 9 microns in spectrum 1 and 2 is due to the  $\text{SiO}_3$  radical. The band at 9.2 microns in spectrum 2 is due to  $\text{SiO}_2$ . This band has disappeared in spectrum 3, 4, and 5, indicating complete reaction of  $\text{SiO}_2$  to form silicates. The broad band from 10 - 12 microns is caused by the  $\text{SiO}_3$  radical. Thus, as temperature and time increase in the heat treatment the  $\text{CO}$  radical content decreases, the  $\text{SiO}_2$  disappears completely, and the  $\text{SiO}_3$  radical makes its appearance. Although the spectra of the natural ash and the synthetic ash which had been heat treated at  $2100 \pm 50^\circ \text{F}$  for two and one half hours do not coincide, it can be seen that all the  $\text{SiO}_2$  of the synthetic mixture has formed silicates producing compounds that are more likely to reflect natural ash behavior than the untreated mixture. The assumption that the natural ash and synthetic ash are equivalent after heat treatment is therefore based on complete reaction of the  $\text{SiO}_2$  as well as the exhibition of like fusion characteristics.

Three series of fusion temperature determinations were made using synthetic Custer ash with admixtures of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . The heat treatment was accomplished after the admixtures were made. Series I contained additions of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in the ratio in which they occurred in the original ash. Series II contained additions of  $\text{SiO}_2$  only. Series III contained additions of  $\text{Al}_2\text{O}_3$  only. All series were made so that the sum of the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  weight increased by 6 percent increments. Series I and II were continued until a rise in softening temperature was noticed between successive samples. Series III was continued until the softening temperature was above the range of the equipment. Table V lists the fusion temperatures obtained from these samples. The fluid temperatures are not listed for some of the samples because of the hindrance of the platinum base preventing precise observation of that point.

Attempts to correlate the softening temperatures with the compositions of these three series showed that no correlation existed using Harrington's factor, the  $R_f$  index, or the  $R_s$  index. When the  $R_m$  index was used it was found that Series I and II followed nearly identical curves but the curve for Series III was entirely different. This correlation is shown in Figure 5.

The ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  is rarely less than 1.18 in natural ashes, but was less than 1.18 for all the synthetic samples of Series III. It was therefore felt that there was justification for disregarding this series, or if possible, for providing a factor in the index to compensate for the excess  $\text{Al}_2\text{O}_3$ . If Series III were disregarded the correlation would be the curve for Series I and II in Figure 5. A factor which apparently compensates for the excess  $\text{Al}_2\text{O}_3$  is:

$$R_c = \frac{\text{SiO}_2}{1.18 \text{Al}_2\text{O}_3 - \text{SiO}_2} \quad (\text{ for } \text{SiO}_2/\text{Al}_2\text{O}_3 < 1.18)$$

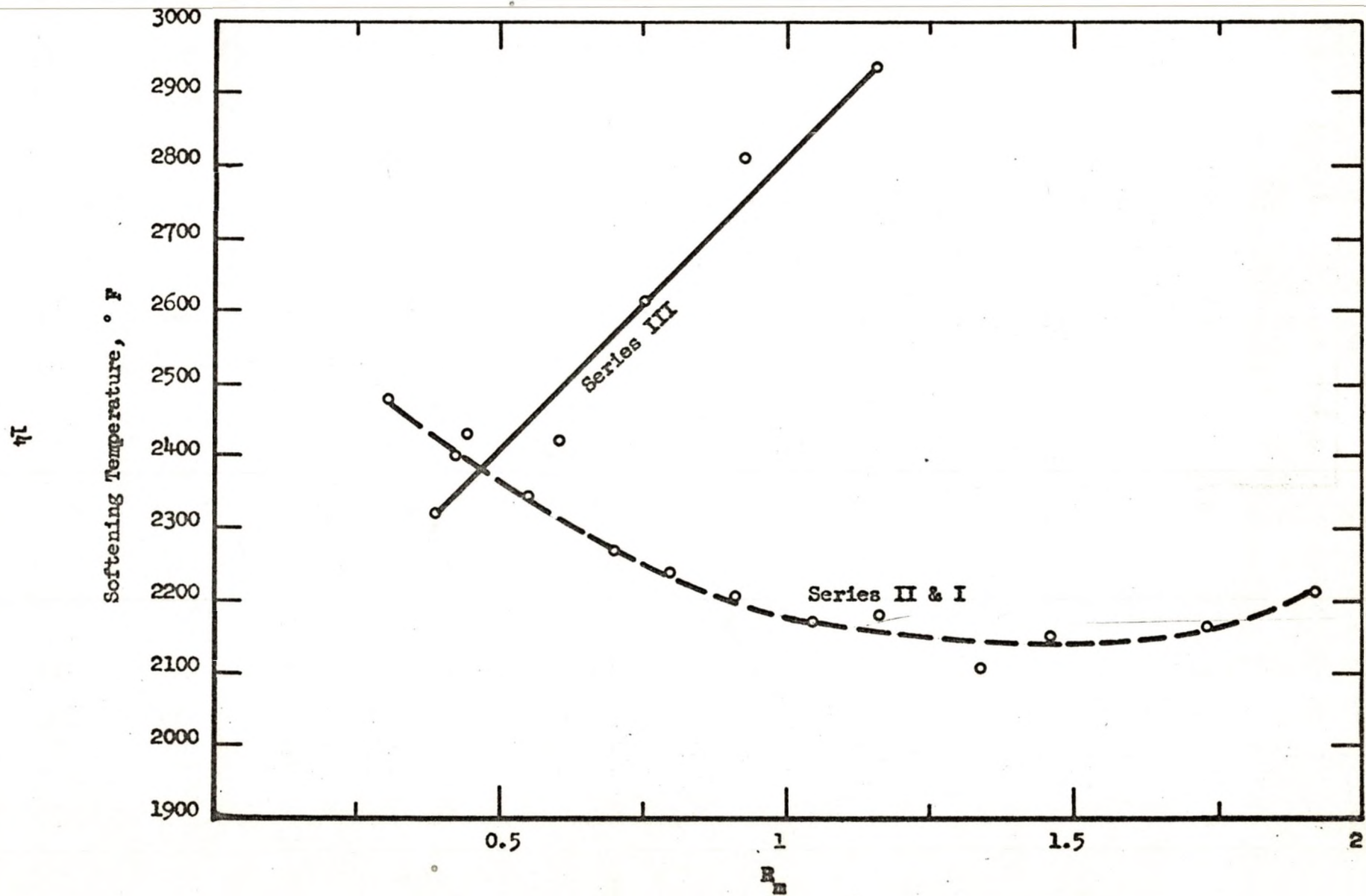


Figure 5:  $R_m$  vs. Softening Temperature.



TABLE V

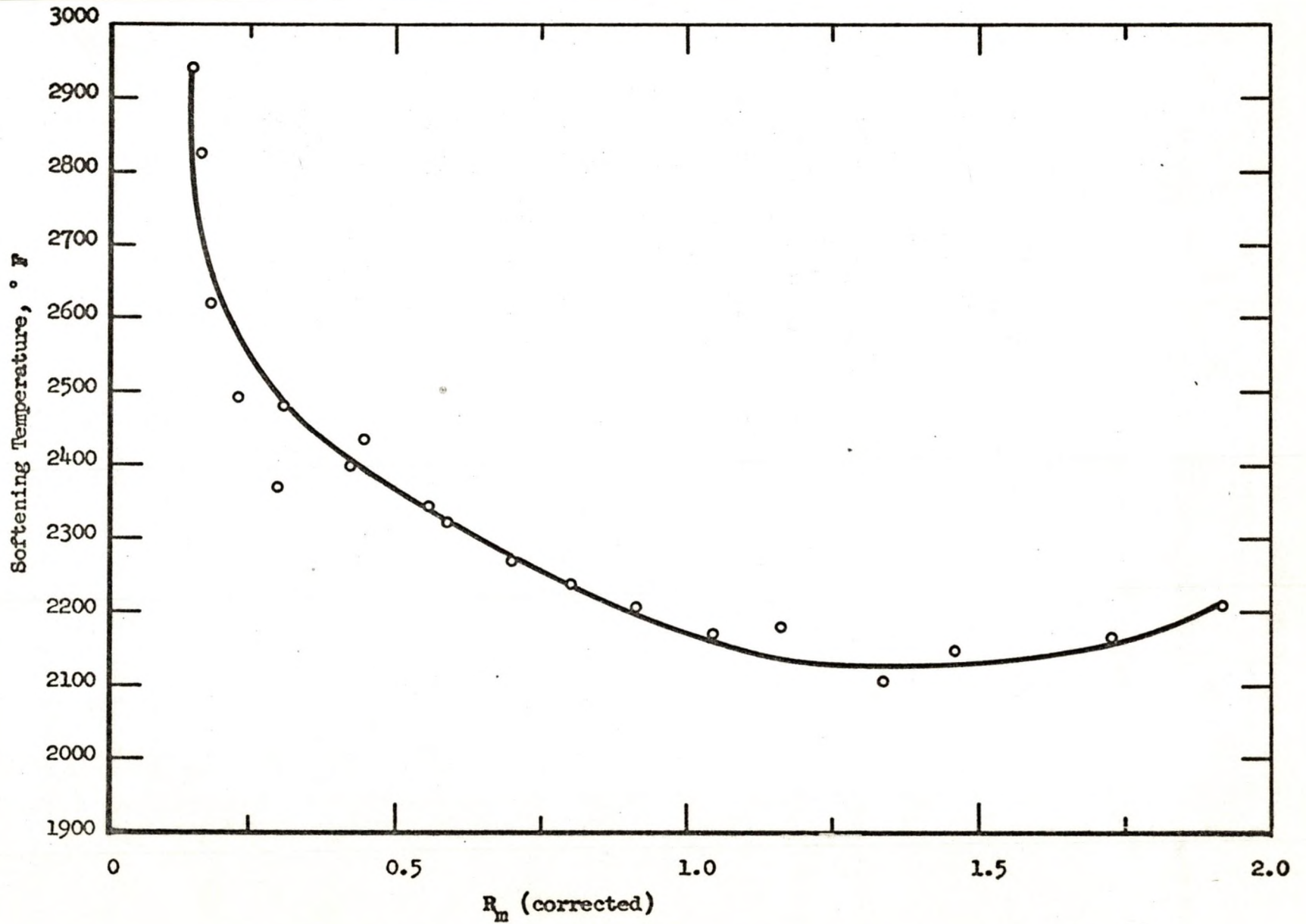
FUSION TEMPERATURES OF SYNTHETIC CUSTER  
ASH AND ADMIXTURES OF  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$

Sample	Initial Deformation Temperature ° F	Softening Temperature ° F	Fluid Temperature ° F
Original	2250	2480	2570
IA	2350	2400	2430
IB	2290	2340	2390
IC	2180	2270	2360
ID	2180	2210	2290
IE	2110	2180	-
IF	2090	2150	-
IG	2030	2220	2480
IIA	2340	2430	2450
IIC	2200	2240	2300
IID	2060	2170	2260
IIE	2010	2110	2230
IIF	2010	2160	2290
IIG	2030	2210	2310
IIIA	2210	2320	2430
IIIB	2210	2370	-
IIIC	2290	2420	-
IID	2430	2620	-
IIE	2600	2820	-
IIF	2650	2940	-
IIG	>2940	>2940	>2940

This factor is the  $\text{Al}_2\text{O}_3$  required to make the ratio 1.18 divided by the  $\text{Al}_2\text{O}_3$  present in excess of this amount. When the  $R_m$  index for Series III only was multiplied by this factor, a good correlation was obtained using all three series. This correlation is shown in Figure 6. No correlation exists when the factor is also used on Series I and II.

Figure 7 shows the points obtained from the samples tested in this project plotted on the correlation developed by the author in his Bachelor's thesis and subsequent work. They fall/very close to the curve, as would be expected, since Custer ash was used, and the admixtures were made in the same manner, in both cases, except that synthetic ashes were used instead of the natural ash in this case.

The Leitz Heating Microscope was used to determine the fusibility characteristics of a few selected samples of synthetic ashes. The

Figure 6:  $R_m$  vs. Softening Temperature



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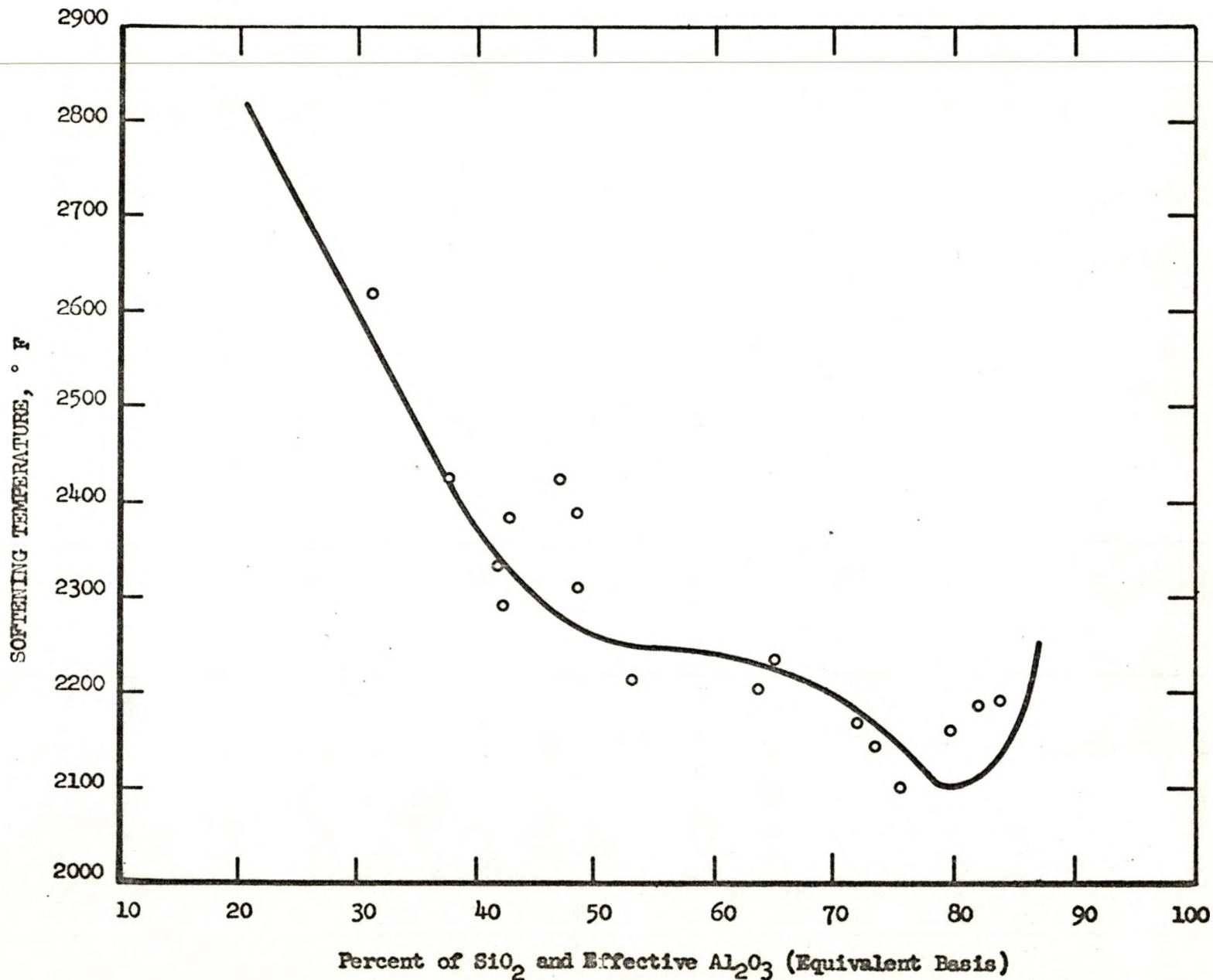


Figure 7: Effect of SiO<sub>2</sub> plus Al<sub>2</sub>O<sub>3</sub> on Ash Softening Temperature.

pictorial record of three ash fusion processes is shown in Figures 8, 9, and 10. Table VI gives the comparison of results obtained on the two types of equipment. In general, the same results are not obtained from the two pieces of equipment. These differences are probably caused by the dissimilar geometry of the samples and different atmospheric conditions in the furnaces. A mixture of 50% CO<sub>2</sub> and 50% CO was used as an atmosphere in the microscope.

TABLE VI  
COMPARISON OF FUSIBILITY CHARACTERISTICS OBTAINED ON  
THE LEITZ HEATED MICROSCOPE AND GAS FURNACE

Sample	Initial Deformation Temperature ° F		Softening Temperature ° F		Fluid Temperature ° F	
	1/	2/	1	2	1	2
	Natural Custer	2300	2320	2470	2500	2530
Synthetic Custer	2250	2320	2470	2480	2530	2600
IIG	2030	2170	2210	2210	2310	2370
IIIE	2600	2550	2820	2750	-	2930

1/ Obtained with gas furnace  
2/ Obtained with Leitz Microscope

The microscope is, in general, a better piece of equipment for experimental work. More precise control of the heating rate and atmosphere is possible, providing more precise duplication of results in addition to the permanent record of the process that it provides. However, the microscope is not in general use and is not accepted equipment for determination of fusion temperatures so that all data for general use must be obtained with the conventional gas fired furnace.

One very interesting phenomenon of the fusion process was noted using the microscope which was not apparent with the conventional furnace. This was the evolution of gas by the sample when it reached a partially melted state. This evolution of gas was accompanied by formation of large bubbles within the sample, making it expand to as much as double its previous size. The bubble would eventually break causing the sample to collapse. The reason for this gas evolution is not yet understood.



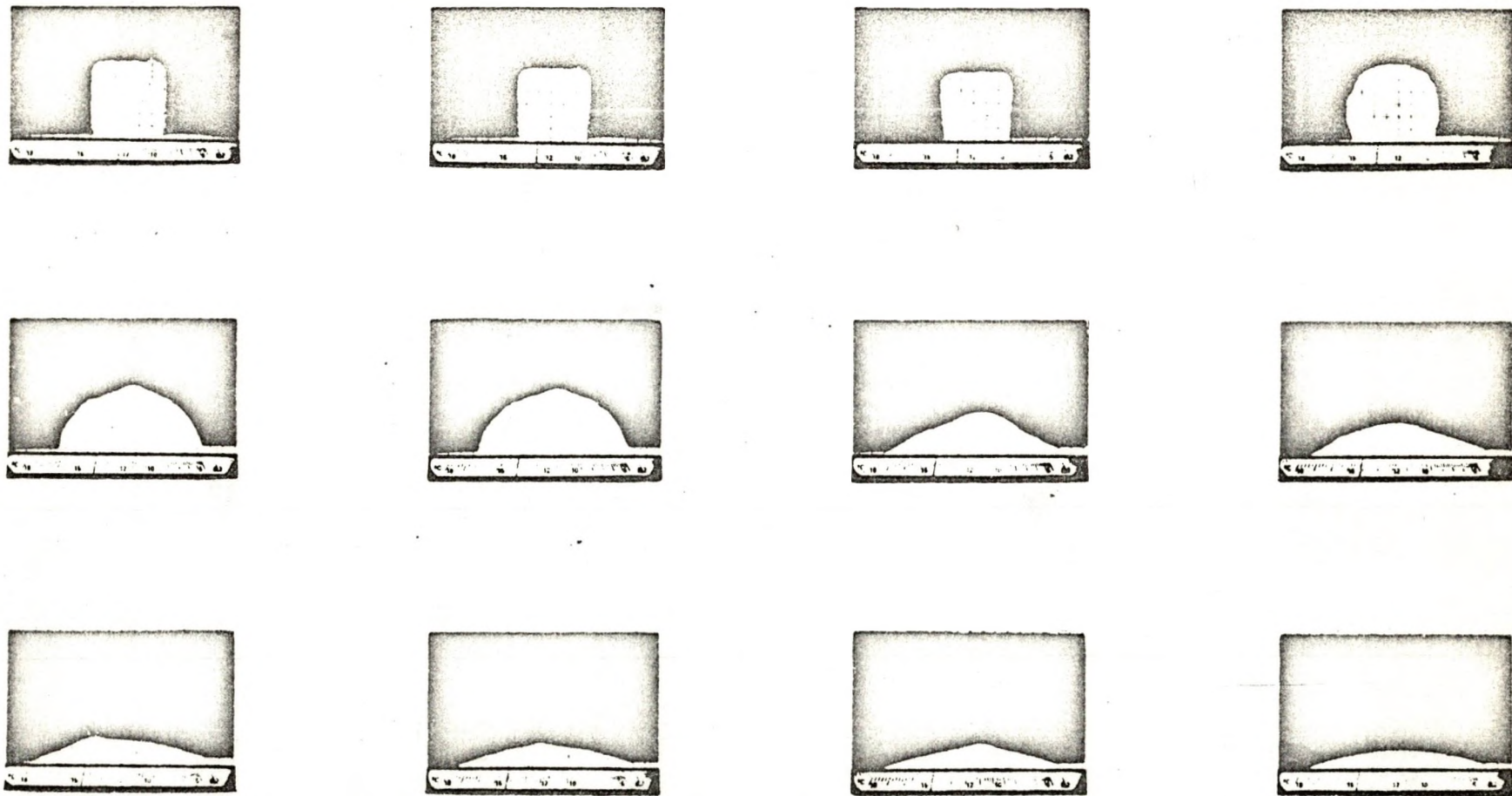


Figure 8.- Pictorial Record of Fusion of Synthetic Custer Ash

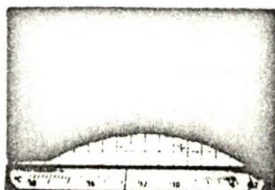
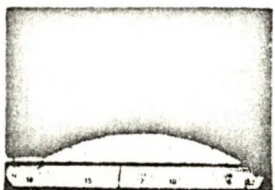
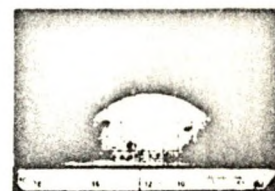
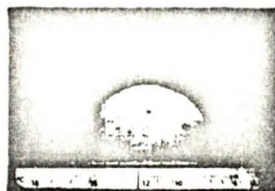
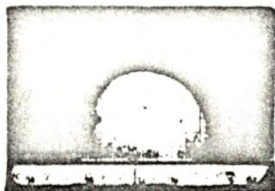
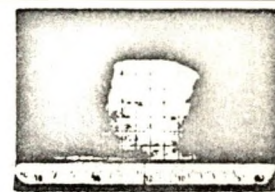
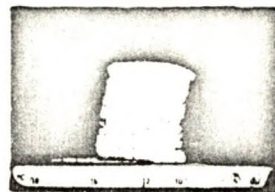
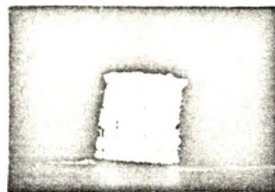
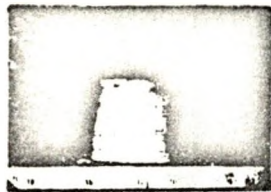


Figure 9.- Pictorial Record of Fusion of Sample IIG



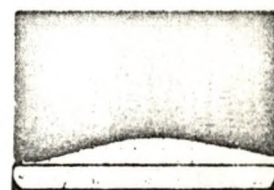
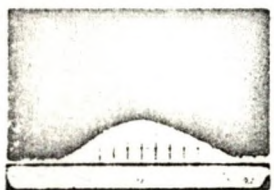
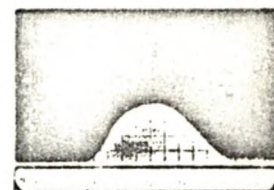
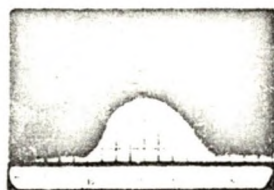
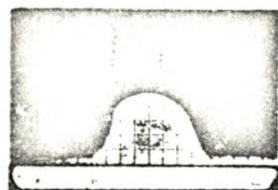
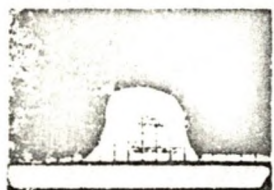
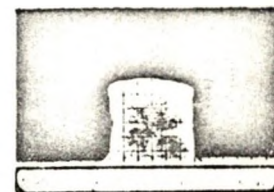
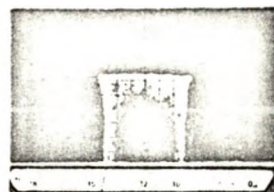
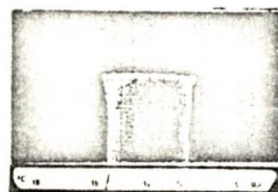
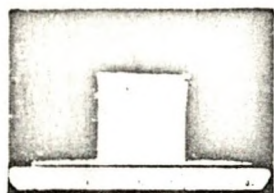


Figure 10.- Pictorial Record of Fusion of Sample III

## CHAPTER IV

### DISCUSSION OF RESULTS

The use of the correlations developed in this investigation is limited since they were developed using samples in which the ratios between all components except  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were constant. However, they provide a good indication of the effect of these two components on the fusibility characteristics of lignite ashes. This should not be construed to mean that they would affect all lignite ashes to produce data following identical curves but they should follow the same trend and produce the same shape curve somewhat displaced from those developed.

The value of the method for preparation of synthetic ash cannot be over-emphasized because it provides the means to make a complete statistical study of the effect of each component on fusion characteristics. This study would be a very extensive program and is beyond the scope of this project.

The spectrum of the synthetic ash after the specified heat treatment shows that all the  $\text{SiO}_2$  has combined with other oxides to form mineral type compounds. Thus, it would be expected to exhibit fusion characteristics similar to a natural ash. However, the discrepancies in the comparison of the natural and synthetic ash spectra indicate that the synthetic ash is not identical mineralogically to natural ash and therefore may not exhibit the same flow characteristics as determined by viscosity measurements.

## CHAPTER V

### SUMMARY

Fusibility characteristics of coal ash are highly significant factors in combustion and gasification of solid fuels. The complex nature and random distribution of the analyses of coal ashes cause prediction of fusion characteristics to be entirely empirical at the present time.

Present correlations of fusion temperatures with composition are generally unsatisfactory. Only one correlation previously developed produces predictions which agree with the majority of experimental data. This is a highly complex plot in three dimensions with the disadvantage that it applies to ashes from coals of higher rank than lignite.

No statistical study has ever been made of the effect of each oxide component on the fusion characteristics. This is undoubtedly due to the random distribution of the composition which will not readily lend itself to statistical analysis. The only solution to this problem appears to be the use of pure synthetic ash mixtures enabling systematic variations in composition.



Trial and error methods resulted in a process in which the synthetic ash was made from pure oxides and carbonates, the mixture of which was heat treated at  $2100 \pm 50^\circ$  F for two and one half hours in a mildly reducing atmosphere. The fusion temperatures of ten synthetic ashes prepared in the above manner show good agreement with those of the natural ash.

The correlation of softening temperatures with composition presented by the author in his Bachelor's thesis and subsequent work showed fairly good agreement with the results of this project. Also, a new correlation index of the molar ratio of  $\text{SiO}_2$  plus  $\text{Al}_2\text{O}_3$  to the remaining components, neglecting  $\text{SO}_3$ , was used giving excellent results.

The use of these correlations is limited. However, they would probably produce a characteristic trend when applied to ashes in general. There remains much work to be done in this field to develop methods for accurate prediction of fusion temperatures.

A Leitz Heating Microscope was obtained and used to determine the fusion temperatures of some selected samples. The temperature obtained with this equipment does not agree with that obtained using the conventional furnace. However, the microscope is much more sophisticated and gives results more precisely duplicated as well as a pictorial record of the fusion process. This equipment cannot be used in place of the conventional furnace, however, because it has not been accepted by ASTM as standard for ash fusion determinations.

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