



Silicon carbide synthesis using high-sulphur petroleum fluid coke and Montana silica
by Raymond Clayton Suiter

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
© Copyright by Raymond Clayton Suiter (1965)

Abstract:

This thesis is based on a study of the technical feasibility of synthesizing silicon carbide from high-sulfur petroleum fluid coke and Montana silica. A laboratory pilot-plant carbon resistance furnace was designed and constructed for this purpose.

Several possible reactions which might occur were studied thermodynamically to determine the theoretical feasibility of the completion at about 2100° C and any pressure. It was also found that losses in yield, due to the formation of silicon sulfides, were unlikely. The formation of the sulfides did not appear to be thermodynamically feasible, based on estimated thermodynamic data of fair reliability. Should these thermodynamic conclusions be in error, however, any sulfides formed would merely dissociate at temperatures above 1000°,C.

Both the high-temperature (alpha) and low temperature (beta) species of silicon carbide were synthesized from these materials, as substantiated by x-ray diffraction powder analysis. The maximum size crystals produced were about 0,2 millimeters on a side.

It was found that silicon carbide could best be produced when the resistance furnace was operated at a 1950-2100 watt power input at an optically observed temperature of about 1700°C and a current input not exceeding 440-450 amperes. This operation yielded a true temperature of about 2100°C in the reaction zone. Nitrogen purging was used to reduce the reaction zone oxygen content.

A maximum concentration of 55.7 per cent of an alpha-beta mixture of silicon carbide was obtained in the reacted mass, using the fluid coke as a carbon source and operating at optimum furnace conditions. The concentrations were compared with those obtainable by using pure graphite as a carbon source. Yields obtained using fluid coke appear to be about 90 per cent of those obtained by using graphite.

In a fixed reaction volume, the bulk volume per cent of the raw material ingredients affects the total yield. An increase in the bulk volume per cent of silica in the charge results in an increased yield of silicon carbide. It was found that the volume per cent of silica in the reaction charge could be varied from 40 to 55 per cent and this resulted in a silicon carbide concentration increase of about 20 per cent in the reacted mass.

SILICON CARBIDE SYNTHESIS USING HIGH-SULPHUR
PETROLEUM FLUID COKE AND MONTANA SILICA

by

RAYMOND CLAYTON SUITER

A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Approved:

Lloyd Bengtson
Head, Major Department

H. A. Sauer
Chairman, Examining Committee

F. Goering
Ass't. Dean, Graduate Division

MONTANA STATE COLLEGE
Bozeman, Montana

June, 1965

ACKNOWLEDGMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State College, and in particular Mr. H. A. Saner who directed this research. The author is indebted to Mr. Saner for his encouragement, advice, criticisms, and assistance which led to the successful completion of this project.

The author also wishes to acknowledge the Engineering Experiment Station of Montana State College for their financial support given this project. In addition, the author wishes to thank the Norton Company of Chippawa, Ontario for their advice, samples, and other valuable information. The help offered by The Exolon Company of Tonowanda, New York, in the form of analytical procedures, is also acknowledged with thanks..

TABLE OF CONTENTS

	Page
List of Tables	vi
List of Figures	vii
Abstract	ix
Introduction	1
What is Silicon Carbide?	1
Uses of Silicon Carbide	3
History of Silicon Carbide	3
Current Silicon Carbide Industry	6
Purpose of this Study	8
Research Objectives	11
Equipment and Experimental Procedure	12
Materials	12
Equipment	13
Operating Procedure	17
Analytical Procedure	18
Thermodynamic Feasibility Study	22
Discussion	22
Results of Calculations	28
Results and Discussion	31
Preparation of Raw Materials	31
Product Identification and Analysis	32
Preliminary Runs	36

TABLE OF CONTENTS (continued)

	Page
Optimization of Furnace Operating Conditions	41
Crystalline Product	44
Study of Bulk Density Effect	45
Comparison of Fluid Coke and Graphite	47
Conclusions	49
Recommendations for Further Work	51
Appendix	53
Least Squares Curve Fitting Calculations	54
Thermodynamic Estimation Techniques	56
Tables	55
Figures	69
Literature Cited	97

LIST OF TABLES

		Page
Table I	Least Squares Calculations Data	55
Table II	Thermodynamic Data Estimation Values	57
Table III	Uses of Silicon Carbide	58
Table IV	Inspection of Humble Oil Company Fluid Coke	61
Table V	Inspection of Silicon Dioxide from Pryor-Dryhead	62
Table VI	Thermodynamic Properties for Feasibility Study	63
Table VII	Percentage Conversions for the First Four Reactions Studied by Keller (16)	64
Table VIII	Interatomic Distances Based on Powder X-ray Diffraction Line Measurements	65
Table IX	Raw Material Particle Size Run Data	68

LIST OF FIGURES

	Page
Figure 1 Time-temperature Relation of Beta to Alpha Silicon Carbide (2)	69
Figure 2 Temperatures in Commercial Silicon Carbide Furnaces (27)	70
Figure 3 Schematic Drawing of Furnace	71
Figure 4 Picture of Furnace Equipment	72
Figure 5 Plot of Limiting Current Density vs. Carbon Resistor Diameter	73
Figure 6 Arrangement for Replacing Carbon Rods	74
Figure 7 Circuit Diagram of Apparatus	75
Figure 8 Carbon Boat Chamber and Sparger	76
Figure 9 Plot of ΔF_T vs. Temperature for Reactions (1.) through (4.)	77
Figure 10 Plot of ΔF_T vs. Temperature for Reactions (5.) and (6.)	78
Figure 11 Plot of Coke Particle Size vs. Bulk Density	79
Figure 12 Plot of Silica Particle Size vs. Bulk Density	80
Figure 13 Picture of X-ray Diffraction Patterns of Norton Co. Beta SiC and Sample from R-5	81
Figure 14 Picture of X-ray Diffraction Patterns of Norton Co. "green" Alpha SiC and Carborundum Co. "regular" Alpha SiC	82
Figure 15 Picture of X-ray Diffraction Patterns of Norton "regular" Alpha SiC and Samples from R-40	83
Figure 16 Photomicrographs of Typical SiC Crystals Produced	84

LIST OF FIGURES (continued)

	Page
Figure 17 Photomicrograph of Crystalline Chunk Produced in Run R-5	85
Figure 18 Photomicrograph of Separated Crystalline Material Produced in Run R-5	86
Figure 19 Photomicrograph of Dendritic Material Produced in Run R-10	87
Figure 20 Photomicrograph of "Glassy" Bubbles Formed in Pyrometer Sight-tube	88
Figure 21 Amorphous Material from Sight-tube and Shield	89
Figure 22 Transparent Needle-like Material from Sight-tube on Run R-20	90
Figure 23 Photomicrograph of Silicon Carbide Crystals Produced in Run R-26	91
Figure 24 Photomicrograph of Crystalline Mass Produced in Run R-36	92
Figure 25 Photomicrograph of Molten Silica Surrounding Coke Particles	93
Figure 26 Photomicrographs of "split-off" Partially Reacted Shell	94
Figure 27 Plot of Volume Per Cent Silica in Charge vs. Per Cent SiC Yield	95
Figure 28 Picture of X-ray Diffraction Pattern of Needle-like Crystalline Material from Sight-tube on Run R-20	96

ABSTRACT

This thesis is based on a study of the technical feasibility of synthesizing silicon carbide from high-sulfur petroleum fluid coke and Montana silica. A laboratory pilot-plant carbon resistance furnace was designed and constructed for this purpose.

Several possible reactions which might occur were studied thermodynamically to determine the theoretical feasibility of the completion at about 2100° C and any pressure. It was also found that losses in yield, due to the formation of silicon sulfides, were unlikely. The formation of the sulfides did not appear to be thermodynamically feasible, based on estimated thermodynamic data of fair reliability. Should these thermodynamic conclusions be in error, however, any sulfides formed would merely dissociate at temperatures above 1000°C.

Both the high-temperature (alpha) and low temperature (beta) species of silicon carbide were synthesized from these materials, as substantiated by x-ray diffraction powder analysis. The maximum size crystals produced were about 0.2 millimeters on a side.

It was found that silicon carbide could best be produced when the resistance furnace was operated at a 1950-2100 watt power input at an optically observed temperature of about 1700°C and a current input not exceeding 440-450 amperes. This operation yielded a true temperature of about 2100°C in the reaction zone. Nitrogen purging was used to reduce the reaction zone oxygen content.

A maximum concentration of 55.7 per cent of an alpha-beta mixture of silicon carbide was obtained in the reacted mass, using the fluid coke as a carbon source and operating at optimum furnace conditions. The concentrations were compared with those obtainable by using pure graphite as a carbon source. Yields obtained using fluid coke appear to be about 90 per cent of those obtained by using graphite.

In a fixed reaction volume, the bulk volume per cent of the raw material ingredients affects the total yield. An increase in the bulk volume per cent of silica in the charge results in an increased yield of silicon carbide. It was found that the volume per cent of silica in the reaction charge could be varied from 40 to 55 per cent and this resulted in a silicon carbide concentration increase of about 20 per cent in the reacted mass.

INTRODUCTION

What is Silicon Carbide?

Silicon carbide (SiC) is a crystalline substance varying in color from pale green or yellow to black depending primarily on the amount and type of impurities present. The compound exists in two crystallographic species and several sub-forms (2).

A low temperature species, or beta silicon carbide, was discovered in 1926 and has a cubic structure. For many years, this material was considered amorphous due to the lack of such methods as x-ray diffraction crystal examination. It is still considered microcrystalline and attempts to obtain quantities of very large crystals have been largely unsuccessful and the maximum size crystal is usually about 0.5 mm (2). Even crystals of this size rarely exhibit any developed crystal faces. Beta silicon carbide was formed at temperatures as low as 525°C by Baumann from silicon and carbon; however, in commercial furnaces it is believed that the material begins to form somewhere in the range of $1300^{\circ} - 1400^{\circ}\text{C}$. It is known to be stable up to approximately 2000°C , at which point there is a transition from the cubic to other forms (2, 15).

By and large, the major constituent of commercial processing is the high temperature species, alpha silicon carbide. This material occurs in at least ten different crystalline sub-forms, or modifications, which are very closely related. A discussion of these modifi-

cations is not related to this project and will not be presented. In general, alpha silicon carbide can merely be referred to as the commercial or hexagonal variety, although it occurs in both the hexagonal and rhombohedral classes. Alpha silicon carbide results from the beta transition and is then stable to about 2700°C. Figure 1 shows a plot taken from Baumann (2) showing time-temperature relationship of beta silicon carbide to alpha silicon carbide.

Silicon carbide is best known for its extreme hardness, being the first material to enter the range of hardness between corundum (Al_2O_3) and diamond or between 9 and 10 on Moh's hardness scale (25). The discovery of boron carbide necessitated a better scale of hardness between corundum and diamond. Knoop and his co-workers devised a diamond indentation method of measurement, whereby fused alumina measured 1635; silicon carbide 2000; boron carbide 2230; and diamond 8000-8500 (18). More accurate methods for measuring relative hardness values have also been developed and include abrasion tests and impact abrasion tests.

Silicon carbide, in addition to its extreme hardness, is very stable chemically. Very few chemicals attack it; however, air will oxidize it at high temperatures and it will dissociate completely at about 2700°C. The compound is thus a very desirable fabricating material in many systems and its high thermal conductivity (90 BTU/hr/ft.²/in./°F) deems it desirable for a multitude of refractory uses.

Uses of Silicon Carbide

Although best known for its abrasive and cutting qualities, silicon carbide has tremendous versatility. Table III shows a list of the major uses of silicon carbide as compiled by Butler (4). It is noted that the uses are broken down into six major divisions. There is every indication that this outstanding material will become even more diversified in the future. Many new applications are expected as methods for obtaining large quantities of ultra-pure material are developed.

History of Silicon Carbide

In our highly sophisticated and specialized era of space age science, it is hard to imagine a discovery, invention, and industry as being the net product of a single individual. However, this is precisely what happened in the development of silicon carbide.

Edward G. Acheson, the discoverer of silicon carbide was born in Washington, Pennsylvania in 1856. Mr. Acheson was among a school of "practical scientists" which evolved as a result of the era of American mechanization (24). After several years of practical and academic training (including study at Thomas Edison's famed Menlo Park Laboratory) in electricity and other areas, Mr. Acheson began to emerge as a skilled scientist, able administrator, and financial wizard. Finally, in the summer of 1891, after an already impressive period of accomplishments, Acheson made his famous discovery of silicon

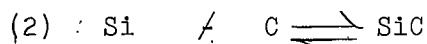
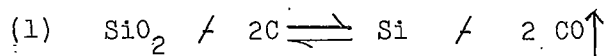
carbide (25). In a small iron bowl, Acheson sent an electric current from a carbon electrode through a mixture of clay and powdered coke to the iron container. It is interesting that he was attempting to form diamonds by dissolving carbon in molten clay (hoping the carbon molecules would rearrange to the crystalline form of diamond). The paradigms of the electrochemical field of Acheson's day, led him to believe that the attainment of diamonds was quite possible (19).

When Acheson first examined the results of his experiment, he saw little of interest. However, closer inspection of the carbon rod revealed small blue crystals which had formed on the end of the electrode. Very delighted, he felt that the crystals could only be a mixture of carbon and corundum, since they were obviously not diamonds. Thus, he named the new product "Carborundum", a trade name which exists today (25).

Acheson immediately recognized the possibilities of these hard crystals and, after enlarging his small furnace, he made enough product to take to the lapidaries in New York for examination. He sold his supply immediately and used the proceeds to buy his first good microscope with which to study his new product. After a few months of study, Acheson suspected that his crystals were actually silicon carbide. He further substantiated his suspicions by qualitative and crystallographic observations. On this basis, the reaction which had taken place was hypothesized as:

$$\text{SiO}_2 \quad \nearrow \quad 3\text{C} \longrightarrow \text{SiC} \quad \nearrow \quad 2\text{CO} \quad \uparrow$$

We now know that this reaction actually takes place in two steps, the second reaction being almost instantaneous, and the reactions beginning somewhere in the range of 1400° - 1500°C (27, 31).

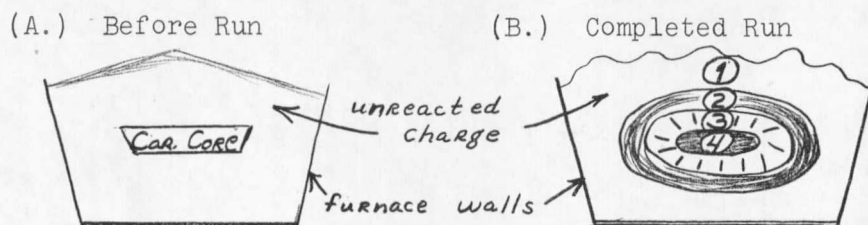


When Acheson discovered he had actually synthesized silicon carbide, he had the vision to organize the Carborundum Company. This firm, first started on September 21, 1891, is a leader in the electrochemical field today. The first manufacturing plant was built in Monongahela City, Pennsylvania and here Acheson started manufacturing grinding wheels. Silicon carbide thus began to replace the most popular current abrasive, ferro-silicon. The silicon carbide industry has been one of steady growth through expanded uses.

Unlike most minerals, silicon carbide was found in nature only after synthesis. In 1905, Henri Moissan (23) found that material in meteorites of the Canon Diablo area in Arizona was identical to electric furnace silicon carbide. Two other natural occurrences are reported in the literature. In 1958, beta silicon carbide was identified in Green River, Wyoming soda ash mines (26). Recently, a deposit of the hexagonal form was again reported in Bohemian volcanic outcroppings (1). In both cases, the deposits were not extensive. On this basis, the SiC manufacturing industry has had little competition from other sources.

Current Silicon Carbide Industry

The art of manufacturing silicon carbide has not departed radically from Acheson's method (21). The furnaces are larger and easier to load and unload; however, the principle of heating through an electrical resistance from within is still used (19, 28). The furnace consists of a trough built with removable side sections of refractory material and end structures through which large carbon electrodes enter the furnace (25). These electrodes are connected through the use of a granular core of carbon which acts as the power producing resistance. A high voltage is applied to the electrodes and current is passed through the carbon core, thus producing the necessary heat to carry out the reaction. The temperature of the central core increases as the reaction proceeds and the power requirements change, going from 1900°C after about an hour to a maximum of over 2400°C after about eighteen hours. From this point until the end of the total thirty-six hour run, the temperature drops off and stabilizes at about 2040°C (25). The power requirements increase due to the formation of semi-conducting silicon carbide. Figure 2. (27) represents R. R. Ridgway's discussion of how the temperature in various furnace zones changes throughout the run (19). These zones may be depicted as follows:



An explanation of these zones is as follows:

- (A.) Zone (1) contains unreacted material which did not reach synthesis temperatures.
- (B.) Zone (2) contains partially reacted material, or "firesand" (a low temperature form of silicon carbide) which must be recharged to the furnace.
- (C.) Zone (3) contains silicon carbide which is processed into sized material.
- (D.) Zone (4) contains graphite which has either formed as a result of graphitizing the granular carbon core or has resulted when silicon carbide formed, became too hot, and then dissociated leaving graphite. This material is used for the core material in future runs.

The raw materials of course are mainly sand (SiO_2) and carbon, in the weight ratio of 60% : 40% respectively. Sawdust is also added to promote porosity in the bed, allowing for the circulation of reacting vapors. Salt (NaCl) is also added to remove metal impurities as volatile chlorides.

Recent changes in core composition and geometry had improved the overall efficiency of the furnaces. (21). In addition, the physical and chemical properties of the product have been improved by varying the mix composition and furnace operating conditions. However, as yet, no methods of controlling the purity and crystal size and shape have been

reported. The material is still made in a batch-type operation, although several attempts have been made to devise a continuously operating furnace.

The U. S. Bureau of Mines reports (25) that, since 1946, the annual tonnage of silicon carbide produced in the U. S. and Canada has increased from approximately 60,00 short tons to a 1960 production rate of over 130,000 short tons. The amount and value of this production, in general, reflects business conditions, due to the large number of industries using the product. The industry has not overexpanded and there appears to be room for both incremental increases in production as well as for new limited capital investments.

Purpose of this Study

Montana's economy has traditionally depended on the agricultural conditions in the state and the nation. The cattle and farming industry ranks first in Montana, with tourism and recreation expanding steadily. This situation prevails mainly because of Montana's geographical location, which restricts local industry with necessarily high plant-to-market freight costs. Based on the decline in the employment which has been taking place in the agriculture in Montana for many years, concerned Montanans have been trying to build tourism as well as supplement the state's economy with the development of industry. Among these is the manufacturing of specialized, high value per unit cost, products. Silicon carbide falls into this category. The

market price of grained silicon carbide varies from about \$0.20 to \$0.80 per pound, depending on size, purity, package, etc. This would, more than likely, make freight costs to reach markets a significant but not a major cost. These factors, along with the known availability of carbon and silicon dioxide in Montana, provided the necessary incentive for undertaking this study to investigate silicon carbide production from Montana raw materials.

Carbon exists as a by-product of petroleum refining at the Humble Oil and Refining Company plant east of Billings. A fluid coking operation at the refinery to obtain additional gasoline was installed in 1955. Since that time, attempts to find market outlets for the by-product fluid coke have been only partially successful. A significant amount of the material is currently being sold for metallurgical purposes, however it appears that a further upgrading of the product would be desirable and also that a 7-8 year stockpile remains for disposal. A silicon carbide plant in the area would dispose of a small amount of the coke, in addition to upgrading it to a significantly higher valued product.

In addition to a large supply of carbon, southern Montana also contains extensive deposits of high-purity silica. The availability of this material further enhances the idea of a local manufacturing plant. Selling either of these materials outside of the state provides only a marginal incentive. Upgrading both would certainly be desirable.

Finally, one of the major costs in the manufacture of silicon carbide is electrical power. Current construction of Yellowtail Dam near Hardin, Montana, which is 60 miles southeast of Billings, has indicated that an abundant supply of competitive electrical power will be available in the near future.

In summary, a silicon carbide plant in Montana could significantly stimulate the area's economy, provide jobs, and provide an investment opportunity. The overall incentive exists due to the availability of an abundant supply of carbon, high-purity silicon dioxide sand, and electrical power.

RESEARCH OBJECTIVES

The primary objectives of this project were as follows:

- A. Predict the thermodynamic feasibility of producing silicon carbide from high-sulfur, petroleum fluid coke available in Montana and Montana silica by studying the thermodynamics of reactions which might possibly be involved.
- B. Determine whether or not silicon carbide could be synthesized from the materials in question on a laboratory scale.
- C. Optimize the operating conditions necessary for producing the silicon carbide in a small laboratory pilot furnace.
- D. Determine the relationship between yields of silicon carbide obtainable using the fluid coke and using conventional high-purity carbon, such as graphite. Determine any other apparent differences between the two products.
- E. Determine whether or not a relationship exists between the particle size and/or bulk density of these raw materials and the yields obtainable.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

Materials

Petroleum Fluid Coke

Table IV. lists the typical properties of Humble petroleum fluid coke (33). Also included in this table are inspections made on the material by the author. It will be noted that the sulfur content of the material runs approximately 6 per cent, accounting for much of the market limitation.

Graphite

For those runs in which graphite was used as a raw material instead of fluid coke, National Carbon Company, grade CS, graphite was ground to the desired particle size. This material consists of graphitized petroleum coke and a graphitized pitch binder. Ash content runs less than 0.5 per cent.

Silica

The silica used in this study consisted of a fine quartz sand obtained in the Pryor-Dryhead area of southern Montana. The Montana Bureau of Mines and Geology examined the material with the following conclusions: (20)

"The material is fine white quartz grains with no other minerals present. The material is not radio-active. The material may be used for silica refractory brick for lining furnaces providing the deposit is large enough and the

material is of high purity."

The author has analyzed this material quantitatively and found it to run in the range of 99.0-99.8 per cent SiO_2 . Table V.

Equipment

Economic considerations dictated the type of experimental equipment which was used in this study. Very sophisticated graphite-tube furnaces are available commercially, similar to those described by Gartland (10) and with even more sophisticated design features. It was felt that these type of furnaces were financially out-of-reach for this study. In addition, a limited power supply was available which in turn placed a restriction on the type and size of resistor which could be used. A DC motor-generator was available as a power source with a maximum output of 500 amperes at 6 volts.

On this basis, a simple carbon-rod resistance furnace was constructed as shown by the schematic diagram in Figure 3 and an actual picture of the apparatus in Figure 4. The critical point in the design of this apparatus was the sizing of the resistor. As reported by National Carbon Company (14), carbon-rod resistors less than two inches in diameter are limited by surface evaporation. Depending on the temperature of the surroundings, those rods with diameters larger than two inches are limited either by surface evaporation or by interior temperature considerations which would cause the resistor to explode because

of rapid sublimation of the graphite. The power supply available and the desired temperature set the size of the carbon resistor used.

If the correlation between limiting current density and diameter of carbon resistors in Figure 5 is observed (14), it will be seen that for a given furnace temperature the limiting current density in the rod is set. Above this current density, and at the given temperature, the surface evaporation of the rod becomes considerable, due to the rod surface temperature exceeding 2200°C. Therefore, if the desired furnace temperature is taken as 2050°C, or at the line-out temperature of the core in a commercial furnace (25), the following limiting current densities and limiting currents prevail for different size rods (see Figure 5):

<u>Rod Size</u>	<u>Crosssectional Area</u>	<u>Limiting Current Density</u>	<u>Limiting Current</u>
1/2 inch	0.1963 in ²	2300 amp/in ²	452
9/16 "	0.2485 "	2160 "	537
5/8 "	0.3068 "	2120 "	652
3/4 "	0.4418 "	1875 "	830

It may be seen from these values that a 1/2 inch diameter rod is the maximum size which can be used with the given power supply. Although it is not desirable to exceed the maximum current density, it is desirable to approach it as closely as possible to obtain maximum temperatures. Any rod larger than 1/2 inch in diameter, required more current than was available with the power source available.

It was found that the size of the rod was the most important consideration. Two grades of rods were used:

(A.) "National grade AUC graphite

(B.) Ultra Carbon Corporation, UF-4-S graphite.

The UF-4-S rods were found to be denser than the AUC rods and theoretically should have oxidized slower at the same temperature. This may have been true in a few cases; however, inconsistencies in the UF-4-S rods overshadowed any advantages due to the higher densities. As a result, it was concluded that the two grades of resistors were essentially equal for use in this furnace.

The carbon resistor was imbedded in two cylindrical copper blocks, two inches in diameter. The holes in these blocks were machined $1/64$ of an inch oversize and the rod was then imbedded in the hole and bonded with acid-core solder. The rods had to be replaced quite frequently and the jig arrangement shown in Figure 6 was used for this operation. This resistor-electrode arrangement was then bolted to $1/4 \times 2$ inch copper bus-bar leads, which in turn were connected to the DC motor-generator.

The resistor was then inclosed in the furnace wall structure made of Transite.¹ Any openings adjacent to the rod were sealed during the runs to prevent oxidation of the resistor. In addition, the furnace

1. Trade name, Johns-Manville Corporation.

was provided with nitrogen purging connections, as shown in Figure 3. The copper blocks, or electrodes, were provided with water cooling-coils, for holding the temperature of the copper within reasonable limits.

The amperage was measured by the use of a shunt arrangement and a DC ammeter. Power measurements could then be made by including a DC voltmeter in the circuit. A circuit diagram of the apparatus is shown in Figure 7.

Optical temperature measurements were made by providing the furnace with a carbon observation sight-tube. This tube was constructed of National Carbon Company, 3/4 inch I.D., schedule B, carbon pipe. The outer opening of the tube was fitted with a clear fused quartz window.¹ The tube fittings were sealed with carbon paste² and the tube was purged during the runs with nitrogen. Temperature measurements were made with a "Pyro" optical pyrometer, model 84, made by The Pyrometer Instrument Company. The pyrometer was provided with a neutral filter allowing for temperature measurements in the two ranges, 1000° - 1800°C and 1800° - 3250°C.

Immediately beneath the carbon rod, a removable reaction chamber was constructed. This chamber consisted of a graphite semi-cylindrical

1. Manufactured by Thermal American Fused Quartz Co., Montville, N.J.
2. Cement Grade C-9, National Carbon Company

boat, plugged on either end with solid graphite. The boat rested in a solid frame of graphite which in turn rested on a graphite nitrogen sparger in the bottom of the furnace. This arrangement is shown in Figure 8.

Operating Procedure

It was concluded that a new rod should be used for each run to insure consistency in the run conditions. The first step in each run, therefore, was the installation of a new rod. Each rod was cut $7 \frac{9}{16}$ inches long, allowing for $1/16$ inch clearance on either end. The rods were bonded to the copper electrodes with acid core solder, as previously explained.

The entire jig arrangement was then bolted into place in the furnace casing. The slots in the casing holding the rod were then closed with fitted Transite slides and the entire furnace casing was sealed with carbon paste. The portions of the rod protruding from either end of the furnace were coated with a ceramic cement to prevent oxidation.¹ Next, the pyrometer sight-tube was inserted in the furnace and also sealed with paste. Finally, the carbon boat, or reaction chamber, was placed in the furnace containing a weighed charge. The furnace was filled with petroleum coke insulation and, after a two hour nitrogen purge period, was ready for the run.

1. "Sauereisen" Cement No. 6 Powder, Sauereisen Cements Co., Pittsburgh, Pennsylvania.

The run included a period of initial low-power heating to dry and harden the carbon paste and check-out the system. At the end of this period (about 20 minutes), the input was increased to the full desired power and held for approximately 3 hours. Three hours was chosen as a run length, in an attempt to insure complete equilibrium. Since time was not a studied run variable, this procedure was merely intended to allow the reactions to proceed as far as possible, under a given set of power conditions. During the run, the power was assiduously controlled and the temperature, amperage, voltage, and generator input voltage were recorded at approximately thirty-minute intervals.

On the completion of the run, the furnace was allowed to cool overnight. The insulation and reaction chamber were then removed and the product collected for examination.

Analytical Procedure

On removal of the reaction chamber from the furnace, the material within was first examined microscopically for crystal formation and other phenomena. The product material was then ground to approximately 200 mesh with a Plattner¹ tool steel mortar and pestle. The following analyses were then performed:

X-Ray Diffraction Observations

The powder collected was, first of all, used for x-ray

1. Trade-Name, Chemical Rubber Co., Catalog No. 13-4825.

diffraction powder analysis methods. For this work, an x-ray tube with a copper target was used and the exposure time for Kodak KK film was approximately 7 hours. The powder was mounted in a standard powder camera on a glass rod by covering the end of the small glass rod with mineral grease and dipping the rod in the powder sample.

Quantitative Analysis

Product samples were analyzed quantitatively according a procedure published for the Abrasive Grain Association by the Exolon Company of Tonawanda, New York (5). The procedure, as slightly modified by the author, was used as follows:

"Silicon Carbide Determined by Fusion with Potassium Bisulphate."

Weigh out 1 gram of the sample, which has been ground to approximately 200 mesh into a platinum crucible and add approximately 10 grams of potassium bisulphate. Place a cover on the crucible and contents and fuse at a very low heat over a Bunsen burner. Be very careful that the fusion contents do not boil over and that the cover is slightly open. After a few minutes increase the heat gradually and swirl the fusion contents a few times in order to bring any adhering particles of the sample on the sides of the crucible in contact with the flux. When the fusion is quiet, remove

from the burner and swirl around so a thin film is deposited on the sides of the crucible. When cool, place crucible, contents, and cover into a 400 milliliter beaker containing about 200 cc of H_2O and 20 cc of 1:1 H_2SO_4 (volume ratio). When the contents have all leached from the crucible, remove it by washing with small jets of water. Filter the contents in the beaker through a No. 42 filter paper and wash with hot water. Place the filter paper and wash with hot water. Place the filter paper and contents into a tared platinum crucible and ignite in a muffle furnace at $800^{\circ}C$. After the paper has been burnt off, remove the crucible from the furnace and cool. Then add about 5 drops of 1:1 H_2SO_4 ; 10 cc of HF (48%); and 5 cc of 1:1 HNO_3 ; digest on a hot plate slowly, keeping the crucible almost completely covered. Take the contents down to H_2SO_4 fumes and repeat the acid treatment two or three times. Finally, after the last dehydration, remove all the H_2SO_4 by heating over a bunsen burner, being very careful not to lose any of the contents of the crucible. Place the crucible and contents into the muffle furnace at $800^{\circ}C$ for 15 to 20 minutes. Remove the crucible from the furnace and place in a dessicator to cool. After the crucible has cooled, weigh it and subtract the weight of the empty crucible from the weight of the crucible and contents.

Multiply the weight by 100 to obtain the per cent SiC.

Example:

Weight of crucible and contents 40.0529

Weight of crucible 39.0843

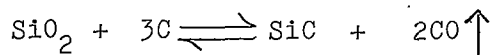
Weight of residue 0.9686

Per cent SiC = $0.9686 \times 100 = 96.86\%$

THERMODYNAMIC FEASIBILITY STUDY

Discussion

The thermodynamic feasibility of silicon carbide formation has been discussed repeatedly in the literature. The first extensive study was made by Ruff (27) and his co-workers who concluded that the overall reaction



begins above 1500°C and is complete at 1800°C, to beta silica carbide. Other related reactions have also been studied thermodynamically, by theoretical and experimental means and, since Ruff's study many reports of such studies have been made.

A thermodynamic discussion reveals nothing about the rates of the considered reactions; however, by placing limits on the extent to which reactions may proceed, important criteria can be established for observing the experimental work. Actually, even in a small laboratory furnace, such as that used in this study, true thermodynamic equilibrium does not exist. However, steady state is usually approached and the thermodynamic calculations are valuable in preliminary determinations of whether or not experimental work is even worthwhile.

On this basis, several reactions were studied thermodynamically for the author, by a Montana State College graduate student (16), to obtain some criteria for what might possibly happen when the raw materials in question were studied experimentally.

The reactions studied were:

1. Silicon Dioxide + Carbon $\rightleftharpoons$ Silicon Carbide + Carbon Monoxide
 $\text{SiO}_2(\text{g}) + 3\text{C}(\text{s}) \rightleftharpoons \text{SiC}(\text{s}) + 2\text{CO}(\text{g})$
2. Silicon Dioxide + Carbon $\rightleftharpoons$ Silicon + Carbon Monoxide
 $\text{SiO}_2(\text{g}) + 2\text{C}(\text{s}) \rightleftharpoons \text{Si}(\text{g}) + 2\text{CO}(\text{g})$
3. Silicon + Carbon Monoxide $\rightleftharpoons$ Silicon Dioxide + Silicon Carbide
 $3\text{Si}(\text{g}) + 2\text{CO}(\text{g}) \rightleftharpoons \text{SiO}_2(\text{g}) + 2\text{SiC}(\text{s})$
4. Silicon Carbide $\rightleftharpoons$ Silicon + Carbon
 $\text{SiC}(\text{s}) \rightleftharpoons \text{Si}(\text{g}) + \text{C}(\text{s})$
5. Silicon Dioxide + Sulfur $\rightleftharpoons$ Silicon Sulfide + Sulfur Dioxide
 $\text{SiO}_2(\text{g}) + \text{S}_2(\text{g}) \rightleftharpoons \text{SiS}(\text{g}) + \text{SO}_2(\text{g})$
6. Silicon Dioxide + Sulfur $\rightleftharpoons$ Silicon Disulfide + Sulfur Dioxide
 $\text{SiO}_2(\text{g}) + 3/2 \text{S}_2(\text{g}) \rightleftharpoons \text{SiS}_2(\text{g}) + \text{SO}_2(\text{g})$

Many other reactions could have been studied. These six reactions were chosen because they were considered basic to the study and because the silicon sulfides were the only sulfur compounds which could be formed which would be even reasonably stable in part of the temperature range being considered. The first four of these reactions have been studied by various researchers (27, 2, 9, 8). The fifth and sixth reactions listed above were studied to determine the thermodynamic possibilities of the high amount of sulfur in the fluid coke to be used.

Although the thermodynamic data for silicon carbide studies have been somewhat refined in recent years, the thermodynamic conclusions have remained essentially the same. It is felt that the thermodynamic data used in this study is the most accurate available.

Several researchers have hypothesized a vapor-vapor reaction between silicon and carbon (2,4). This is probably not a very good theoretical assumption, since the vapor pressure of elemental carbon at the reaction temperature range (1500°-2400°C) does certainly not seem sufficient to provide concentrations necessary for crystal formation. This fact is substantiated by the fact that calculated measurements of the heat of formation of silicon carbide (8) are not in close agreement with experimental measurements (27, 13). It is probably more reasonable to believe that a vapor-solid reaction takes place; however, this introduces cumbersome thermodynamic factors. Therefore, most treatments of the subject are quite obscure. In this study, an assumption was made that carbon and silicon carbide exist as solids and that their activity values are unity. This is probably not completely justified theoretically since unit activity cannot be confirmed for pure solids (7, 29, 12). However, it is felt that this approach is valid based on the data available and the fact that results from this approach do compare favorably with experimental results (27).

The above reactions were studied theoretically at the following conditions:

<u>Temperatures, °C</u>	<u>Pressures, atm.</u>
0	0.5
250	1.0
500	2.0
750	5.0
1000	

<u>Temperatures, °C</u>	<u>Pressures, atm.</u>
1250	
1500	
1750	
2000	
2250	
2500	

The heats of reaction and changes in entropy were calculated for the six reactions. Then using the expression

$$T_{\text{Neutral Equilibrium}} = \frac{\Delta H_R \text{ at } 298^\circ\text{K}}{\Delta S_R \text{ at } 298^\circ\text{K}}$$

where,

$$\text{Heat of Formation} = \Delta H_{R298} = \sum n \Delta H^\circ_{298} (\text{Products}) - \sum n \Delta H^\circ_{298} (\text{Reactants})$$

$$\text{Entropy Change} = \Delta S_{R298} = \sum n \Delta S^\circ_{298} (\text{Products}) - \sum n \Delta S^\circ_{298} (\text{Reactants})$$

the temperatures of neutral equilibrium were calculated. This indicates the favorability of the various reactions as the temperature changes. As ΔF_T becomes negative, the reaction becomes more favorable.

The next phase of the thermodynamic study involved calculating the percentage conversion for each reaction of each temperature and pressure. The standard free energy is given by

$$\Delta F^\circ_{298} = \Delta H_{R298} - (298)\Delta S_{R298}$$

and, for the temperature range considered, the heat capacities of the materials can be assumed to remain constant. Therefore, at temperatures

other than normal,

$$\Delta F_T \approx \Delta H_{R298} - (T) \Delta S_{R298}$$

Also, by considering the chemical equilibrium of each reaction, it can be stated that

$$\Delta F_T = -RT \ln K_{eq} \text{ (Smith \& Van Ness - (29))}$$

where

$$\begin{aligned} R &= \text{Universal Gas Law Constant} \\ K_{eq} &= \text{Equilibrium Constant of the Reaction}^1. \end{aligned}$$

and

$$K_{eq} = [e]^{-\frac{\Delta F_T}{RT}}$$

Then, the concept of activity coefficient can be defined by deriving the following equation from the Berthollet equation of state (29):

$$\ln \gamma = \frac{9 P_c T_c}{128 P_c T} \left(1 - 6 \frac{T_c^2}{T^2} \right)$$

where

$$\begin{aligned} \gamma &= \text{activity coefficient (fugacity/pressure)} \\ P &= \text{Pressure} \\ P_c &= \text{critical pressure} \\ T &= \text{Temperature} \\ T_c &= \text{critical temperature} \end{aligned}$$

Using this concept, the values of activity coefficient and activity constant can be calculated. The activity constant is given by the defini-

tion:

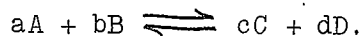
$$K_Y = \frac{(\gamma_C)^c (\gamma_D)^d}{(\gamma_A)^a (\gamma_B)^b}$$

1. Based on the typical reaction $aA + bB \longrightarrow cC + dD$

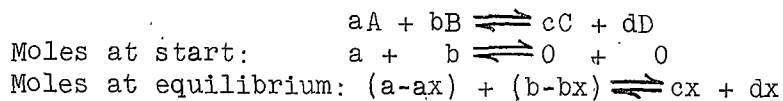
where
$$K_{eq} = \frac{(a')_A^a (a')_B^b}{(a')_C^c (a')_D^d}$$

and a' = activity of material or fugacity ratio.

which is based on the typical reaction



Next, the total number of moles of each reactant and product may be represented as follows:



where,

x = conversion to given products

$a+b+cx+dx-ax-bx$ = total number of moles present at equilibrium.

It may also be stated, from Le Chatelier's Principle (12), that

$$K_N = \frac{K_{eq}}{K_P^{\Delta n}} = \frac{N_C^c N_D^d}{N_A^a N_B^b} \quad (1)$$

where,

$$\Delta n = (c + d) - (a + b) \quad (\text{gaseous reactants})$$

N = mole ratio of each reactant at equilibrium

Thus,

$$K_N = \frac{\left[\frac{cx}{a+b+cx+dx-ax-bx} \right]^c \left[\frac{dx}{a+b+cx+dx-ax-bx} \right]^d}{\left[\frac{a-ax}{a+b+cx+dx-ax-bx} \right]^a \left[\frac{b-bx}{a+b+cx+dx-ax-bx} \right]^b} \quad (2)$$

Therefore, by equating (1) and (2), the conversion (x) for each specific case can be calculated, based on a knowledge of:

1. The temperature, pressure, and critical constants
2. The calculated activity coefficients.
3. The change in number of moles for the given reaction.

Results of Calculations

Table VI lists the thermodynamic data used for the calculations in this study. The data was obtained from various sources, as listed in this Table.

In general, the effect of temperature on each reaction is shown in Figures 9 and 10 (16). Reactions (3.) and (4.) compare very favorably with results reported by Baumann (2). The plots show the effect of temperature on the favorability (negative free energy of formation) of each reaction. It may be seen that, up to approximately 2100°C, the formation of silicon carbide is favorable in reactions (1.), (3.), and (4.). The formation of silicon is favorable in reaction (2.). Above this temperature, only the third reaction becomes unfavorable and the silicon carbide formed in this reaction reverts to silicon, which would then react to form silicon carbide by another route. The fifth and sixth reactions, as depicted by Figure 10 are realistically unfavorable. Neither reaction shows a degree of thermodynamic feasibility, within the realm of realistic temperatures. Should either of these materials form, however, they would decompose, due to their high-temperature instability.

The secondary portion of this thermodynamic study pointed out several factors which have allowed for the following conclusions, based on the first four reactions:

(A.) The optimum theoretical temperature for the production

of silicon carbide is approximately 2100°C , considering the interdependence of all four reactions. Neglecting reaction (3.), the production of silicon carbide merely becomes more favorable as temperature increases.

(B.) Pressure affects each reaction markedly; however, the overall effect is negligible. Hence, any pressure would yield approximately the same percentage conversion at 2100°C .

(C.) The maximum conversion at the optimum temperature would be approximately 90 per cent.

Table VII (16) shows the tabulated values of per cent conversion for the first four reactions, at the various conditions.

The study of reaction five and six, merely points to a general trend in the thermodynamic feasibility of these two reactions. It would be very desirable to confirm these results by obtaining the sulfide thermodynamic properties experimentally and repeating the study. However, in general, it is felt that two conclusions may be drawn:

(A.) Neither silicon monosulfide nor silicon disulfide would form, in the temperature range considered.

The only loss in silicon carbide yield which would probably occur when using the high-sulfur fluid coke as a carbon source, would be attributable to the

coke not being pure carbon. The starting weight of the coke would contain sulfur and other volatile matter. This loss would merely be a result of driving off the sulfur and volatile matter and would not affect the amount of silica present for reaction.

(B.) If, due to the lack of reliable thermodynamic data, the above conclusion is not valid and the sulfides were formed, they would immediately dissociate at the temperatures used in silicon carbide manufacture. The sulfides are known to be unstable above 1000°C.

RESULTS AND DISCUSSION

Preparation of Raw Materials

In all of the runs, the raw material weight ratio of silica to coke was the same. This was set at 60 per cent silica and 40 per cent coke, or at 3.0 : 2.0. Theoretically, this puts the carbon in slight excess; however, the 3.0 : 2.0 ratio is commonly reported as being used in the commercial operations, and was therefore chosen (19, 28). In a few of the preliminary runs, lampblack was used as a carbon source and also in this weight ratio.

In a fixed volume, the volume per cent of each ingredient changes as their individual bulk densities change. For those runs where the effect of bulk density changes was studied, the silica and carbon ingredients were screened to a pre-determined particle size and weighed out in the ratio of 3.0 : 2.0. In this way, the volume per cent of the ingredients was changed without changing the weight percentages. Figures 11 and 12, show how the bulk densities of the fluid coke and the silica change with particle size. These plots were used to determine the proper raw material particle sizes to obtain the different volume per cent blends. The values of bulk density for each of the particle sizes were determined by the use of a Eimer and Amend bulk density measuring apparatus, which yields very consistent data. It is comprised of a feed funnel and a series of glass baffles to ensure free-fall packing. The material being tested leaves the last baffle and spills into a known volume. When full, this container is

merely leveled and weighed.

Other than sizing, the raw materials were not processed at all. They were weighed out, mixed, and charged to the furnace, as explained in the operating procedure.

Product Identification and Analysis

The identification of silicon carbide in the top of the reaction zone was comparatively easy. Any considerable amount of crystalline material in the top of the reaction chamber, could hardly be expected to be anything but silicon carbide. Microscopic observation was used extensively in this project to determine the necessity of further analysis. Several pictures of magnified crystals are shown in the appendix and will be mentioned individually later. The maximum size crystals obtained were approximately 0.2 millimeters on a side. A picture of such crystals is shown in Figure 16. It is impossible to ascertain the crystalline type or species of the crystals by observation, due to the small size of the crystals. The limited size of the crystals is understandable, based on the type of reaction chamber used in the furnace. It has been felt by some that the formation of the large alpha silicon carbide crystals in a commercial furnace involves the vaporization of crystals in the inner zone of the charge and the recrystallization of larger crystals in the adjacent cooler zones (19). The vapor of silicon carbide or its dissociation products supposedly supplies the material for large crystal growth. The point of controversy here is to

whether or not decomposition, vaporization, or both occur; however, it is known that when silicon vapors pass over hot carbon, or a mixture of hot carbon and silica, crystal growth occurs (4). In the apparatus used in this study, the geometry of the reaction chamber was not such as to expect free flow of silicon or silicon carbide vapors to any great extent. Therefore any crystals found would be expectedly small and mechanisms would be localized.

In addition to micrographic inspection of the crystals formed, x-ray diffraction comparisons were used. As standards, samples of commercial product were obtained as follows:

- (1.) Beta Silicon Carbide
(Norton Company)
- (2.) Alpha Silicon Carbide (green)
(Norton Company)
- (3.) Alpha Silicon Carbide (regular)
(Norton Company)
- (4.) Alpha Silicon Carbide (regular)
(Carborundum Company)

X-Ray powder patterns were taken of each of these samples and are shown in Figures 13, 14, and 15. These patterns were used as a method of comparing product obtained in this study to commercial product.

It will be noted by observing the powder patterns of these four samples that the lines common to beta silicon carbide are also common to alpha silicon carbide. This makes it very difficult to attempt quantitative determinations of the two crystalline species on the basis of x-ray diffraction. Baumann has used the method of comparative

amplitudes of lines common to alpha and beta to those of alpha alone (2). This method could have been used on the samples analyzed in this study, however, the results would have been indicative only of the relative amounts of alpha and beta silicon carbide in the powder sample and not in the total product. This is true, due to the fact that the total charge did not achieve steady state conditions. There was a gradation of the product in the boat from crystalline silicon carbide to unreacted material. The powder pattern samples were chosen from only the crystalline material to give consistent and distinct patterns. This, of course, eliminated the possibility of obtaining a sample which was representative of the total product. Therefore, quantitative x-ray diffraction measurements would not suffice in this study. Quantitative measurements were made by using the analytical procedure mentioned earlier on the total product.

The x-ray studies were very valuable from a qualitative standpoint however (3,17). The results were effectively pointed out the presence of silicon carbide, and further, the presence of alpha silicon carbide. A visual inspection of the x-ray diffraction patterns in Figures 13 through 15 points out the similarities between the standard samples and the various samples of product made in this study. Qualitative determinations were made of every sample obtained; however, not all of these patterns are included. Only the more important patterns have been included as will be explained later. It will suffice to say that silicon

carbide was revealed in all of the other runs and with the exception of run R-5, alpha silicon carbide was always present.

In addition to visual inspection of the powder patterns, it was possible to calculate the interplanar distances corresponding to the lines in the diffraction patterns by the use of Bragg's Law (17), which states that

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta} \quad (1)$$

where,

λ = Wavelength of x-rays.

d = Distance between successive identical planes of atoms in the crystal.

θ = Angle between the incident x-ray beam and the atomic planes.

n = Any Whole number determined by the order of the reflection.

In discussing x-ray reflection, it is customary to set "n" equal to 1, and consider the higher order reflection as being first-order reflections from another atomic plane. This standardizes the identification of the recorded reflections.

Thus, equation (1) becomes

$$d = \lambda / 2 \sin \theta \quad (2)$$

In this study a standardized "powder camera" was used in which the circumference was machined to make π radians, or 180 degrees, equivalent to 180 millimeters. In this way, the distances between the corresponding arcs on either side of the unreflected x-ray beam gave a

direct measurement of 4θ (and indirectly, θ), in degrees. Then using equation (2), the interatomic distances were measured. These values are shown in Table VIII. The values obtained from product synthesized in this study were not only compared with those from the standard samples, but with standard values provided by the American Society for Testing Materials (6). This comparison is also shown in Table VIII.

Finally, the product obtained was analyzed quantitatively by the procedure mentioned earlier. The results of these measurements are shown in the appendix.

Preliminary Runs

It was pointed out in the discussion concerning the equipment used in this study, that empirical correlations were used to size the heating element for the furnace. Once complete, however, the limitations of the furnace had to be checked. The initial furnace runs were performed with this thought in mind.

Due to financial limitations, it was initially felt that high-temperature measurements would have to be bypassed. To get a rough idea of the furnace capabilities a few runs were made by packing lampblack around the carbon resistor, inserting a chromel-alumel thermocouple into the lampblack and adjacent to the rod, and recording the temperature and time for various amperages (power input). It was found that the response of the furnace was very rapid. Runs were made at 140, 260, and 325

ampere inputs. Although the thermocouple burned out at approximately 1400°C, extrapolation of time-temperature plots indicated that an amperage of approximately 350 would yield temperatures approaching 2000°C.

Another approach was then taken to establish a current-temperature relationship as well. A small carbon boat was placed in the furnace adjacent to the rod. In five separate compartments of the boat the following chemicals were placed:

	<u>Melting Pt.</u>	<u>Metal Melt. Pt.</u>	<u>Metal Boil. Pt.</u>	<u>Carbide</u>
BaSO ₄	1580°C	850°C	1140°C	-
BaO	1923°	850°	1140°	-
Al ₂ O ₃	2025°	660°	2450°	decomp. 1400°C
NiO	2090°	1455°	2900°	-
CaO	2580°	840°	1240°	decomp. 450°C

The object here was to investigate the outcome of heating these chemicals and correlate the results with their physical properties. The furnace was heated at about 300 amperes input for two hours. In all but the NiO compartment, nothing remained of the chemical. This indicated evaporation of the chemical or its reduced product metal, or decomposition of a resulting carbide. In the NiO compartment, pure nickel remained. This confirmed reduction of the metal oxides and that 1455°C was exceeded in the boat. A similar run was made using chromium metal in the boat. In this run, at an amperage of 270, what appeared to be chromium carbide was produced in fused masses. The melting point of the

chromium carbides is approximately 1665°C . The result was reasonably consistent with that of the other chemical tests; however, it was concluded that, if temperature was to be measured, a more accurate method was desirable and that only power input should be used to correlate the temperature.

With these results in mind, a Pyro optical pyrometer was ordered. In the meantime, a DC voltmeter was installed and a few constant power runs were made. Indicative of these runs is run R-5. In this run an average power input of 1600 watts was used for approximately one hour. The run produced a fine crust on top of the boat chamber (see Figure 8) of agglomerated crystals. These crystals were very small (appeared to be about 0.1 mm on a side). Microscopic observations of samples of the R-5 crystals are shown in Figures 17 and 18. The crystals were observed by x-ray powder analysis to be micro-crystalline beta silicon carbide, see Figure 13 and Table VIII. Quantitative analysis of the powder sample found it to contain 37.7 per cent silicon carbide.

The production of this material was very encouraging and proved that silicon carbide could be synthesized from the raw materials in question.

The next phase of the project was to attempt to measure the temperature of the reaction zone using the pyrometer. A sighting arrangement was constructed, as shown in Figures 3 and 4 and a few

"dry runs" were made to check out the pyrometer at the lower temperatures, by comparison with thermocouple measurements. Up to about 1000°, the measurements were quite close with the pyrometer reading a little below the thermocouple. It was decided to proceed with the synthesis runs and attempt to attain finer control with the pyrometer.

As a preliminary comparison between the coke and a purer source of carbon, a run was then made using No. 15 Columbian Lampblack as a carbon source. After a slow temperature build-up, the the furnace was held at a power input of approximately 1500 watts for only twenty minutes. The maximum optical temperature reading was 1200°C. It was necessary to shut down, due to combustion of the lampblack insulating bed. This was primarily due to entrained oxygen igniting the lampblack, however, some volatiles were observed leaving the bed. Apparently carbon monoxide was produced from entrained oxygen, or partially from silica reduction. Surprisingly enough, the reaction chamber contained some silicon carbide crystals. A photomicrograph of some of the dendritic crystalline material produced in this run, is shown in Figure 19. The fact that this material was produced at an apparent temperature reading of 1200°C indicated that the pyrometer was reading low for two reasons:

- (a.) It was not felt that silicon carbide synthesis would start under these conditions at 1200°C. Some oxygen was present and the temperature was just too low for the solid-vapor reaction.

(b.) The optical temperature measurements were of the rod, which was even hotter than the charge.

It was felt that, if possible, a correction factor should be determined for the temperature measurements.

At this point, it was also felt that nitrogen purging would eliminate bed combustion and help prevent carbon rod oxidation. Therefore, the furnace was equipped with the purging arrangement shown in Figures 3 and 4.

To further substantiate the fact that the furnace temperature was higher than the observed readings, transparent bubbles were collecting in the pyrometer sight-tube during the runs, see Figure 20. In addition, transparent needles and frosty-looking materials were found on the carbon shield which covered the end of the sight-tube, see Figure 21. X-ray diffraction analysis of this material indicated it to be amorphous (undoubtedly silica). On this basis; and by observing the silica in the boat after each run, it was felt that the furnace temperatures achieved were high enough to melt the silica and also produce sufficient vapors for the reaction even though the pyrometer indicated differently. In fact, in one of the successive runs, material collected from the sight-tube actually appeared to be a form of silicon carbide similar to the Wurtzite form pictured by Merz (22), see Figure 22. X-ray diffraction of a sample of this material (Table VIII & Figure 28.), weakly substantiates the presence of Wurtzite, however, quantitative

analysis of this material indicated only a trace amount of carbide. In addition, it is difficult to conceive of the material being formed at the temperatures which would have been prevalent in the sight-tube. The amount of material formed was insignificant; however, its apparent existence and that of amorphous silica in the sight-tube indicated that reaction temperatures were being achieved.

It was then decided to optimize the furnace operating conditions to obtain maximum yields of silicon carbide.

Optimization of Furnace Operating Conditions

Optimization of the furnace operating conditions was fixed from the upper side by the maximum amperage input consideration, due to the surface evaporation limitations of the carbon rod. It was mentioned earlier, that a 1/2 inch diameter resistor was used to allow maximum temperature without surface evaporation, for the power source available. With this size resistor, it was pointed out that the calculated limiting current was approximately 450 amperes. This estimated current limitation turned out to be quite accurate. In several of the preliminary runs this limitation was exceeded and the rods were completely destroyed by surface evaporation. To make matters worse, of course, any surface evaporation decreased the rod diameter, increased the resistance, and lowered the allowable current even further. Therefore, the optimum current input was also experimentally set at 450 amperes.

In addition to this current value, the optimum power was also determined. Several runs were made in an effort to produce, consistently, clearly defined crystals such as those shown in Figures 16, 23, and 24. It was not necessary to optimize by yield analysis, as the range of power input for significant crystal production was found to be quite limited. The optimum power input range determined was 1950 to 2100 watts (not to exceed 440-450 amperes). Power inputs much above this range usually meant that the limiting current density had been exceeded and that the rod was deteriorating. Much below this range, very few crystals would be formed. This latter fact could be easily determined by microscopic observation. Figure 25 shows a photomicrograph of material, taken from the charge boat, which had not been sufficiently hot for the reaction to proceed. These photomicrographs also help substantiate the type of physical mechanism which occurs preceding the reaction. The silica melts, surround the carbon particles, and the reaction proceed at the liquid-solid interface. These pictures parallel those obtained by Baumann through high-temperature microscopy (2). This type of material prevailed in the carbon boat, up to power inputs approaching 1900 watts. Above 1900 watts, microcrystalline material formed on the coke particles with a few salient crystals protruding from the mass. Also at this point, shells of partially reacted material began to "split-off" from the major coke particles, see Figure 26. This very interesting phenomena might possibly enhance a commercial operation, depending on the true mechanism of the reaction.

Above 2000 watts, the top portion of the charge, and much of the under-portion, became highly crystalline and the resulting reacted mass contained approximately 50 per cent silicon carbide.

At the above amperage and power input the observed temperature was 1675° - 1750°C . Due to the surface evaporation correlations and the existence of the resultant product, it was known that the true rod temperature must be about 2200°C and the top of the charge about 2000° - 2100°C . These temperatures appeared to be maximum for the furnace and the correction factor for the optical pyrometer readings is apparently about 1.25. Actually, the rod and charge temperatures may have slightly exceeded 2200°C and 2100°C respectively, in these runs, for two reasons:

(A.) Rod evaporation was slightly noticeable, although the limiting current density was not exceeded.

This would tend to indicate ambient temperatures above 2000° - 2100°C , which would cause rod evaporation at amperages below 440-450.

(B.) As seen in Table VII, alpha silicon carbide was produced, although to a limited extent. It has been reported by some researchers (2), that the transition from the beta to alpha form will not occur below 2200°C .

At any rate, these temperature speculations are very close and, if anything, are conservatively on the low side.

The nitrogen purge rate was set at 1.0 SCFH¹ through the main sparger (see Figure 8) and 0.3 SCFH through the sight-tube. These rates were established by experience to provide a slow, steady bleeding through the insulating bed and to keep the sight-tube free of interfering vapors.

As mentioned earlier, the run time was arbitrarily set at 3 hours, at full power, to insure equilibrium conditions. Therefore, summarizing the optimum operating conditions for the production of silicon carbide crystals, with an attempt to achieve alpha silicon carbide, the following prevails:

Power Input:	1950 - 2100 watts
Amperage:	Not exceed 440 - 450 amperes
Temperature:	Observed - 1675° - 1750°C (Rod) Estimated - 2200°C (Rod) 2000° - 2100°C (Top of Charge)
N ₂ Purge Rate:	1.0 SCFH (Sparger) 0.3 SCFH (Sight-tube)
Run Time:	3 hours at full power

Crystalline Product

The maximum (concentration of) silicon carbide in the reacted mass

1. Standard Cubic Feet per Hour

obtainable by using the fluid coke and silica raw materials was 55.2 per cent. A discussion of the raw material preparation leading to this yield will be presented later. As already mentioned, product was obtained which definitely shows evidence of the presence of alpha silicon carbide. The total product appears to be a mixture of alpha and beta silicon carbide, with the relative amounts undetermined. The presence of alpha silicon carbide has been indicated by x-ray diffraction powder analysis. Observing Table VIII, it may be seen that the strongest lines representing the interatomic distances prevalent in both the alpha and beta forms, were present in the product. In addition, line numbers 19, 25, 28, 31, 32, 34, 38, and 43 indicate interatomic distances prevalent to the alpha form but not the beta form.

Unfortunately, the crystals obtained were not of sufficient size to examine by any x-ray method, other than powder analysis. The maximum size crystal obtained appears to be about 0.2 millimeters on a side.

Study of Bulk Density Effect

During the preliminary runs, very little consideration was given to the particle size of the raw materials. Runs were made using the fluid coke and silica in their received conditions. Runs were also made using finely ground material. There appeared to be some difference in the results achieved and it was decided that particle size might possibly play an important part in reaction efficiency. Two theories were

hypothesized:

- (A.) Very small silica particles would possibly mean more individual particles of silica could attach themselves to the coke particles, as the fusion of the silica progressed. This would mean better contact between the two materials, thus maximizing the conversion.
- (B.) Secondly, the liquid silica-solid carbon contact could theoretically be maximized by minimizing the volume per cent. of coke present in the reaction boat. Assuming most, or all, of the silica would be melting, this arrangement would mean the smaller volume of coke would be easier to engulf in liquid silica. This would also maximize contact.

It was felt that the second theory was the more logical of the two; however, both theories were tested with the same set of runs.

To accomplish the minimization of the volume per cent of coke in the boat, bulk density data had to be obtained. Plots of the bulk density versus average particle diameter, for both the coke and silica, are shown in Figures 11 and 12. It was explained earlier how the bulk density measurements were made. By choosing various bulk density values for the two raw materials and then finding the corresponding particle size from these plots, the volume percentages were set at several levels, *

maintaining a constant weight ratio of the ingredients. Measured bulk densities of the blends compared favorably with those obtained by assuming weighted averages of the two ingredients. Runs were then made using these special raw material blends at the optimum furnace operating conditions. The product obtained in each case was analyzed to determine the per cent of silicon carbide. A summary of the results is shown in Table IX. The reacted mass silicon carbide concentration for each of these runs is plotted against the volume per cent silica in the charge, in Figure 27.

There were several sources for error introduction in this particle size study, including a probable error of $\pm(5 - 10)$ per cent in the analytical procedure. However, Figure 27 definitely shows that, for this furnace operation, a correlation exists between the bulk volume percentages of the raw material mixture and the concentration of silicon carbide in the product obtained. By using the method of least squares, as shown in the Appendix, the best straight line was drawn through the data points.

There is no apparent correlation between the silica particle size and the resulting concentrations of silicon carbide.

Comparison of Fluid Coke and Graphite

Recognizing the fact that the furnace used in this project was not capable of duplicating commercial furnace conditions, it was felt

that a good measure of the potential of the fluid coke could be attained by a comparison with pure graphite as a carbon source. Three runs were made whereby the carbon boat chamber was partitioned and silica-coke and silica-graphite mixtures were placed on either side of the partition. The raw material particle sizes of the two ingredients were the same in each run. The following results prevailed:

<u>Run No.</u>	<u>Per Cent SiC in Reacted Mass</u>	
	<u>Coke Charge</u>	<u>Graphite Charge</u>
R-34	26.7	29.2
R-35	38.7	43.3
R-40	55.2	59.3

In Run R-40, the optimum volume per cent blend was used in both the coke and the graphite mixtures. Run R-34 was a short run, due to a forced shutdown; however, a good comparison was still obtained.

On the basis of these runs, the yields of silicon carbide from coke appear to be about 90 per cent of those obtainable from graphite. Some of this loss in yield could probably be attributed to unreacted or unremoved sulfur and volatile matter.

CONCLUSIONS

The primary objective of this research was to determine the technical feasibility of producing silicon carbide from high-sulfur petroleum fluid coke and Montana silica. Considering the results of this study, it appears that commercial production of silicon carbide from these two raw materials is a definite possibility providing confirmation of this feasibility is provided from an economic and market feasibility standpoint.

It is possible to synthesize silicon carbide in the small laboratory furnace used in this research. A mixture of beta and alpha silicon carbide is obtainable if the furnace is operated at a 1950 - 2100 watt power input and a limiting current of 440 - 450 amperes is not exceeded. The maximum concentrations of silicon carbide obtainable from the above ingredients in this furnace appear to be in the range of 40 - 50 per cent of the reacted mass. In the furnace used, crystals approximately 0.2 millimeters on a side can be produced.

If the quantitative results are compared the yields obtained by using coke as a carbon source are approximately 90 per cent of those obtained by using graphite as a carbon source. This comparison is based on comparing the resulting concentrations of silicon carbide in the reacted mass left from the two raw material combinations. In a commercial operation these lower yields would undoubtedly be offset by a reduced price in the source of carbon.

In a fixed reaction volume the bulk volume per cent of the ingredients affects the conversion. An increase in the bulk volume per cent of silica in the charge will result in a corresponding increase in the silicon carbide yield. Based on the ingredients used in this research, the bulk volume per cent of silica in the charge can be varied easily from about 40 to 55 per cent. This variation increased the concentration of silicon carbide in the reacted mass by approximately 20 per cent.

RECOMMENDATIONS FOR FURTHER WORK

Additional pilot-plant data should be obtained before a commercial attempt is made to produce silicon carbide from these raw materials.

Almost imperative is the purchase of a graphite-tube furnace for this additional research. With this type of pilot-plant there would be several advantages.

- (A.) Complete isolation of the raw material ingredients from any foreign material. This would result in refined yield data and would then allow for refinement of the particle size correlations.
- (B.) The atmosphere could be controlled as could the reaction pressure. This would make thermodynamic studies feasible.
- (C.) Optical temperature measurements would be easier to obtain and their accuracy should be enhanced.

With this type of furnace it is felt that several studies could be made. The literature is very lacking in certain critical information:

- (A.) The reaction mechanism is essentially unknown. A critical, although difficult, study would be an investigation of this mechanism from mass transfer, heat transfer, and thermodynamic considerations.
- (B.) A study of the reaction kinetics of the basic synthesis reactions and several side reactions would be desirable.

- (C.) Utilization of the off-gases in a commercial furnace has not been effectively achieved. A study related to this problem would be interesting.
- (D.) It is felt that the source of carbon used in this research might possibly have some inherent reaction advantages over conventional carbon sources based on such factors as: Particle size, particle shape, porosity, fluidizing properties, etc. An investigation of this area would be desirable.

Several attempts have been made aimed at achieving a continuous furnace for this process. Success in this area would, more than likely, revolutionize the industry. It is felt that additional research along these lines might prove to be quite fruitful.

Basic to all of these suggested studies would be the use of more refined analytical tools. Further use of the quantitative x-ray procedures is urged as is the investigation of other analytical tools.

-53-

APPENDIX

LEAST SQUARES CURVE FITTING CALCULATIONS

Assuming that the correlation between volume per cent silica in the charge and the yield of silicon carbide could only be a linear relationship, it can be said that

$$y = a + bx$$

where,

y = Per cent silicon carbide yield

x = Volume per cent of silica in the charge.

and that this straight line can be fitted to n data points (x_1, y_1) , (x_2, y_2) , ..., (x_n, y_n) . By following the least-square criterion which states that the parameters a and b should be chosen so as to make the sum of the squares of the deviations $(y_i - a - bx_i)^2$ as small as possible, the following equations are arrived at (34):

$$na + b \sum_{i=1}^n x_i = \sum_{i=1}^n y_i \quad (1)$$

and

$$a \sum_{i=1}^n x_i + b \sum_{i=1}^n x_i^2 = \sum_{i=1}^n x_i y_i \quad (2)$$

Using these two equations, a and b can be calculated easily.

Table I shows the treatment of the data in this study.

Table I. Treatment of Volume Per Cent Run Data by Least Squares Method

$\underline{x_i}$	$\underline{y_i}$	$\underline{x_i^2}$	$\underline{x_i y_i}$
41.9	30.5	1,756	1,278
48.3	42.1	2,333	2,033
48.5	36.0	2,352	1,746
51.0	48.5	2,601	2,474
52.8	45.7	2,788	2,413
52.8	39.0	2,788	2,059
54.3	42.5	2,948	2,308
55.0	49.1	3,025	2,701
$\underline{55.0}$	$\underline{55.2}$	$\underline{3,025}$	$\underline{3,036}$
$\sum x_i = 459.6$	$\sum y_i = 388.6$	$\sum x_i^2 = 23,616$	$\sum x_i y_i = 20,048$

Then, using equations (1) and (2), the following parameters were calculated:

$$b = 1.40$$

$$a = -28.3$$

Therefore,

$$y = -28.3 + 1.40x$$

This equation is the basis of the plot shown in Figure 27.

THERMODYNAMIC DATA ESTIMATION TECHNIQUES

Most of the thermodynamic data used in this thesis was available in the literature. Some critical pressure data was estimated by comparison to similar compounds. Keller (16) used the method of "parachor" for estimating critical pressure data. In this method,

$$V_c = (0.377 [P] + 11.0)^{1.25}$$

where

V_c = Critical volume of the material

$[P]$ = Parachor of the material

Then, if critical temperatures are obtainable and

$$P_c = \frac{20.8 T_c}{V_c - 8}$$

the critical pressures can be calculated.

The heat of formation for silicon disulfide is reported in the literature (30). Using this value as a standard, the heat of formation of the monosulfide was obtained by comparisons with other metallic mono- and disulfides, see Table II below.

In a similar manner, the entropies for both silicon monosulfide and silicon disulfide were obtained by comparing with Group IV-A oxides and sulfides, as shown in Table II.

Table II. Thermodynamic Data Estimation Values

<u>Metallic Sulfide Compounds</u>		<u>Heat of Formation Change</u>	
FeS	→ FeS ₂	-19.80	
PtS	→ PtS ₂	- 7.0	
MoS ₂	→ MoS ₃	- 5.7	
		avg. -10.9	
<u>Group IVA Compounds</u>		<u>Absolute Entropy Change</u>	
CO ₂	→ CS ₂	$\frac{0}{2} \rightarrow \frac{S}{2}$	$\frac{0}{2} \rightarrow \frac{S}{2}$
SnO ₂	→ SnS	+9.54	+11.1
PbO ₂	→ PbS		+ 3.5
		Avg. +9.54	+ 7.3

On this basis, the necessary heat of formation and entropy data was estimated. Experimental data would definitely be more reliable; however, no such data was obtainable.

Table III.

Uses of Silicon Carbide (4)

Uses of Loose SiC Grain

Abrasive:	Lapping and polishing Wire sawing of stone Abrasive blasting Non-slip additive for concrete
Metallurgical:	For deoxidation of steels and reducing agent in alloy steel and ferroalloy manufacture.
Chemical:	For chlorination to produce silicon tetrachloride, made into silicones, silicon metal, ethyl silicate, and fine silica.
Electrical:	Lightning arresters

Uses of Coated SiC Abrasives

Abrasive:	Auto body undercoat sanding Glass edging Leather grinding and finishing Floor sanding Stone grinding and polishing Grinding soft nonferrous metals and alloys; also cast iron Finish-grinding glass-reinforced resins
-----------	--

Bonded SiC Uses

Wheels:	Tungsten carbide rough-grinding Grinding and cutting glass, gems, marble, ceramics, stone Grinding cast iron and hard cast alloys Wood pulp grinding; leather, rubber, and plastic grinding Aluminum, copper, brass, bronze grinding
Sticks and stones:	Cast iron cylinder honing Sharpening stones

Table III (continued)

Nonslip uses: Stair treads and floor inserts

Refractory Uses for SiC wares

Silicate bond: Kiln furniture (tiles, posts, saggars)
 Muffles, hearths, skid rails
 Retorts and condensers for zinc distillations
 Heat recuperator tubes and core-busters
 Wear and erosion-resistant parts
 Boiler settings

Silicon nitride bond: Rocket motor nozzles and
 combustion chambers
 Brazing jigs
 Containers, pump parts, protection
 tubes and allied parts for molten
 aluminum and zinc
 Acid burner tips and spray nozzles

Silicon bond: Heating elements
 Thermocouple protection tubes
 Nuclear fuel elements (possibility)

Carbon bond: Graphite-silicon carbide crucibles

Potential Uses for dense, impervious SiC ware

Valves and piping for corrosive materials
Pumps and related parts for handling
 molten alumina
Sandblast nozzles
Rocket nozzles
Fuel elements and structural members in
 gas-cooled nuclear reactors
Thermocouple protection tubes
Heat exchangers

Predicted areas for increased SiC consumption

Chemical: Rapid growth as raw material for silicon
 tetrachloride production, ending up as
 silicon metal and as fine silica

Table III. (continued)

	Piping, valving out of self-bonded silicon carbide
Metallurgical:	Marked upswing as addition to ferro-silicon furnaces to increase production Continued growth in briquette use in iron foundry practice. Possibly new source of silicon metal by thermal dissociation
Electrical:	Transistor and rectifier use at elevated temperatures, if necessary purity is achieved Electroluminescent powder for low intensity area lighting Increased use of nonlinear resistor
Nuclear energy:	Fuel element for sheaths or fuel carriers for high-temperature reactors.

Table IV. Inspection of Humble Oil Company Petroleum Fluid Coke (33)

Sieve Analysis

Cumulative, % Retained				Non-cumulative*, % Retained			
<u>on:</u>	10m	----	2	<u>on:</u>	12m	----	4.2
	20	----	5		20	----	3.9
	48	----	11		40	----	6.4
	60	----	20		50	----	37.6
	80	----	44		70	----	29.2
	100	----	65		100	----	10.0
	150	----	88		200	----	6.4
	200	----	95		325	----	1.2
Through	200	----	5	Through	325	----	1.1

Particle Density, g/cc

1.3

Bulk Density, lb/ft.³

61.0

Bulk Density, lb/ft.³ *

55.9*

Calorific Value, Btu/lb. (ASTM D-271) 14,100

Proximate Analysis, wt. % (ASTM D-271)

Moisture	0.3
Volatile Matter	6.0
Fixed Carbon	93.4
Ash	0.3

Ultimate Analysis, wt. % (ASTM D-271)

Carbon	90.0
Hydrogen	2.0
Sulfur	6.0

Metals, (wt. % on coke)

Nickel	0.013
Vanadium	0.034
Iron	less than 0.01
Calcium	less than 0.01
Silicon	less than 0.005
Titanium	less than 0.001
Sodium	less than 0.02

* Author's data

Table V. Inspection of Silicon Dioxide from Pryor-Dryhead Area

Non-cumulative, % retained on:

12 mesh	----	0.1
20	----	0.1
40	----	0.5
50	----	1.1
70	----	74.7
100	----	4.8
200	----	16.0
325	----	2.0
Through 325	----	0.7

Bulk density, lb/ft.³ 86.8

Table VI. Thermodynamic Properties for Feasibility Study

<u>Compound</u>	ΔH°_{f-298} <u>(Kcal/mole)</u>	S°_{298} <u>(E.U./mole)</u>	T_c <u>(°K)</u>	P_c <u>(atm)</u>
Carbon (c)	0	1.361 (30)	-	-
Carbon Monoxide (CO)	- 27.42 (11)	47.301 (30)	134 (16)	34.6 (16)
Silicon (Si)	0	4.47 (11)	8,940 (16)	182.0 (16)
Silicon Carbide (SiC)	- 26.7 (30)	3.935 (30)	-	-
Silicon Dioxide (SiO ₂)	-205.4 (30)	10.0 (30)	10,680 (16)	95.5 (16)
Silicon Disulfide (SiS ₂)	- 34.7 (11)	19.5*	11,050 (16)	58.1 (16)
Silicon Sulfide (SiS)	- 23.8*	17.3*	5,360 (16)	87.0 (16)
Sulfur (S ₂)	+ 29.86 (11)	54.41 (11)	1,313 (16)	242.0 (16)
Sulfur Dioxide (SO ₂)	- 70.96 (11)	59.24 (11)	430 (16)	77.7 (16)

* Estimated data

Table VII. Percentage Conversions for the First Four Reactions Studied by Keller (16)

Temperature (°C)	Pressure (atm)	Reaction (1.)	Reaction (2.)	Reaction (3.)	Reaction (4.)
0	0.5	0	0	100	0
250		0	0	100	0
500		0	0	100	0
750		0	0	100	0
1000		52	0	100	0
1250		81	17	99	1
1500		94	63	57	3
1750		99	92	26	10
2000		100	98	17	15
2250		100	100	2	19
2500		100	100	0	23
0	1.0	0	0	100	0
250		0	0	100	0
500		0	0	100	0
750		0	0	100	0
1000		1	0	100	0
1250		42	8	100	0
1500		77	49	100	0
1750		99	82	84	1.5
2000		100	96	45	12
2250		100	100	31	14
2500		100	100	12	17
0	2.0	0	0	100	0
250		0	0	100	0
500		0	0	100	0
750		0	0	100	0
1000		0	0	100	0
1250		26	1	100	0
1500		71	32	100	0
1750		92	73	100	1
2000		100	93	62	8
2250		100	100	49	11
2500		100	100	25	16
0	5.0	0	0	100	0
250		0	0	100	0
500		0	0	100	0
750		0	0	100	0
1000		0	0	100	0
1250		3	0	100	0
1500		47	11	100	0
1750		81	51	100	0
2000		99	81	81	1.2
2250		100	95	71	1.8
2500		100	100	51	7

Table VIII. Interatomic distances Based on Powder X-ray Diffraction Line Measurements

	Norton Co. Beta-SiC (Commercial)	A.S.T.M. Standard Beta-SiC	Sample from Boat from R-5	Norton Co. Alpha-SiC (Green)
Line (No.)	d(Å) I*	d(Å) I	d(Å) I	d(Å) I
(1)			4.14 VW	
(2)			3.47 VW	
(3)				
(4)				
(5)	3.39 VW			
(6)				
(7)	*Approximate intensity: very strong,			3.28 VW
(8)	strong, weak, very weak			
(9)				
(10)				
(11)	2.78 VW			
(12)				2.66 W
(13)	2.64 VW			
(14)				2.62 S
(15)	2.55 S		2.55 W	2.55 S
(16)				
(17)	2.50 VS	2.51 S	2.49 VW	2.50 VS
(18)				2.38 W
(19)				2.34 S
(20)				
(21)	2.19 W		2.18 W	2.18 W
(22)	2.16 VW			
(23)				
(24)				
(25)	(Doublets could be due to splitting of			2.00 W
(26)	small angle reflections, owing to the			
(27)	beam passing around the specimen and			
(28)	not through the center.)			1.68 VW
(29)				
(30)				1.59 VW
(31)			1.55 VW	
(32)		1.54 S	1.54 W	1.55 S
(33)	1.44 S			
(34)				1.42 W
(35)				
(36)				1.33 VW
(37)	1.31 S	1.31 W	1.31 S	1.32 VS
(38)				1.29 W
(39)	1.26 W		1.26 VW	1.26 W
(40)				1.22 VW
(41)				
(42)				
(43)				1.14 VW

Table VIII. (Continued)

Line (No.)	Norton Co. Alpha-SiC (Regular)		Carborundum Co. Alpha-SiC (Regular)		A.S.T.M. Standard Alpha-SiC		Sample from Coke Produced SiC from R-40	
	d(A)	I	d(A)	I	d(A)	I	d(A)	I
(1)							4.15	W
(2)							3.72	VW
(3)							3.48	S
(4)								
(5)								
(6)	3.32	VW					3.37	S
(7)								
(8)							3.15	VW
(9)							2.89	S
(10)							2.83	VS
(11)							2.78	VW
(12)	2.66	W	2.66	W			2.66	W
(13)					2.63	S		
(14)	2.61	S	2.60	S				
(15)	2.55	S	2.55	S			2.55	VS
(16)								
(17)	2.51	VS	2.49	VS	2.51	VS	2.50	VS
(18)	2.39	W	2.39	VW				
(19)	2.34	S	2.34	S			2.35	W
(20)								
(21)	2.18	W	2.18	W			2.18	S
(22)							2.13	VW
(23)	2.08	VW						
(24)	2.02	VW					2.04	W
(25)	2.00	VW	2.00	VW			2.01	S
(26)	1.83	VW						
(27)	1.70	VW					1.72	VW
(28)	1.68	W	1.68	VW				
(29)	1.61	W					1.65	W
(30)	1.60	VW						
(31)	1.55	VW	1.55	VW			1.56	W
(32)	1.54	VS	1.54	S	1.54	W	1.54	VS
(33)	1.44	VW						
(34)	1.42	S	1.42	W			1.43	W
(35)	1.40	VW						
(36)	1.32	W	1.33	VW				
(37)	1.31	VS	1.31	S			1.32	VS
(38)	1.29	W	1.29	W			1.28	W
(39)	1.26	W	1.26	W			1.26	W
(40)	1.22	VW	1.22	W			1.23	VW
(41)	1.14	VW						
(42)							1.17	W
(43)	1.14	VW	1.14	VW			1.17	W

Table VIII. (Continued)

Line (No.)	Sample from Graphite Produced SiC from R-40		Sample of Crystal from sight-tube from R-20		A.S.T.M. Standard SiO ₂ -Quartz	
	<u>d(Å)</u>	<u>I</u>	<u>d(Å)</u>	<u>I</u>	<u>d(Å)</u>	<u>I</u>
(1)	4.15	W			4.26	W
(2)	3.71	VW				
(3)						
(4)	3.41	VW				
(5)						
(6)	3.33	VS			3.34	VS
(7)						
(8)	3.16	VW				
(9)	2.90	S				
(10)	2.83	VS				
(11)						
(12)	2.66	W				
(13)						
(14)						
(15)	2.56	S				
(16)			2.52	W		
(17)	2.50	VS	2.48	W		
(18)			2.37	W		
(19)	2.35	W				
(20)			2.32	W		
(21)	2.19	W	2.18	W		
(22)	2.15	VW	2.14	W		
(23)						
(24)	2.04	W	2.02	W		
(25)	2.01	S				
(26)			1.86	VW	1.82	VW
(27)	1.72	VW	1.77	VW		
(28)	1.68	W	1.66	VW		
(29)	1.64	S	1.62	VW		
(30)						
(31)	1.56	VW				
(32)	1.54	VS	1.54	W		
(33)						
(34)	1.42	W	1.42	VW		
(35)			1.39	VW		
(36)			1.32	VW		
(37)	1.31	VS				
(38)	1.28	S				
(39)	1.26	W				
(40)	1.23	W	1.23	VW		
(41)			1.20	VW		
(42)	1.16	S	1.17	VW		
(43)	1.12	VW				

Table IX. Raw Material Particle Size Run Data

<u>Run No.</u>	<u>Vol. % SiO₂</u>	<u>SiO₂ Bulk (g/cc)</u>	<u>SiO₂ Davg. (inches)</u>	<u>Vol. % Coke</u>	<u>Coke Bulk (g/cc)</u>	<u>Coke Davg. (inches)</u>	<u>Yield -% SiC</u>
R-27	41.9	1.400	0.0089	58.1	0.673	0.0494	30.5
R-25	48.3	1.400	0.0089	51.7	0.870	0.0134	42.1
R-38	48.5	0.700	0.0012	51.5	0.440	0.0012	36.0
R-43	51.0	1.225	0.0023	49.0	0.869	0.0140	48.5
R-41	52.8	1.105	0.0124	47.2	0.824	0.0071	45.7
R-42	52.8	1.105	0.0124	47.2	0.824	0.0071	39.0
R-39	54.3	1.093	0.0140	45.7	0.869	0.0140	42.5
R-36	55.0	1.054	0.0246	45.0	0.867	0.0124	49.1
R-40	55.0	1.054	0.0246	45.0	0.867	0.0124	55.2

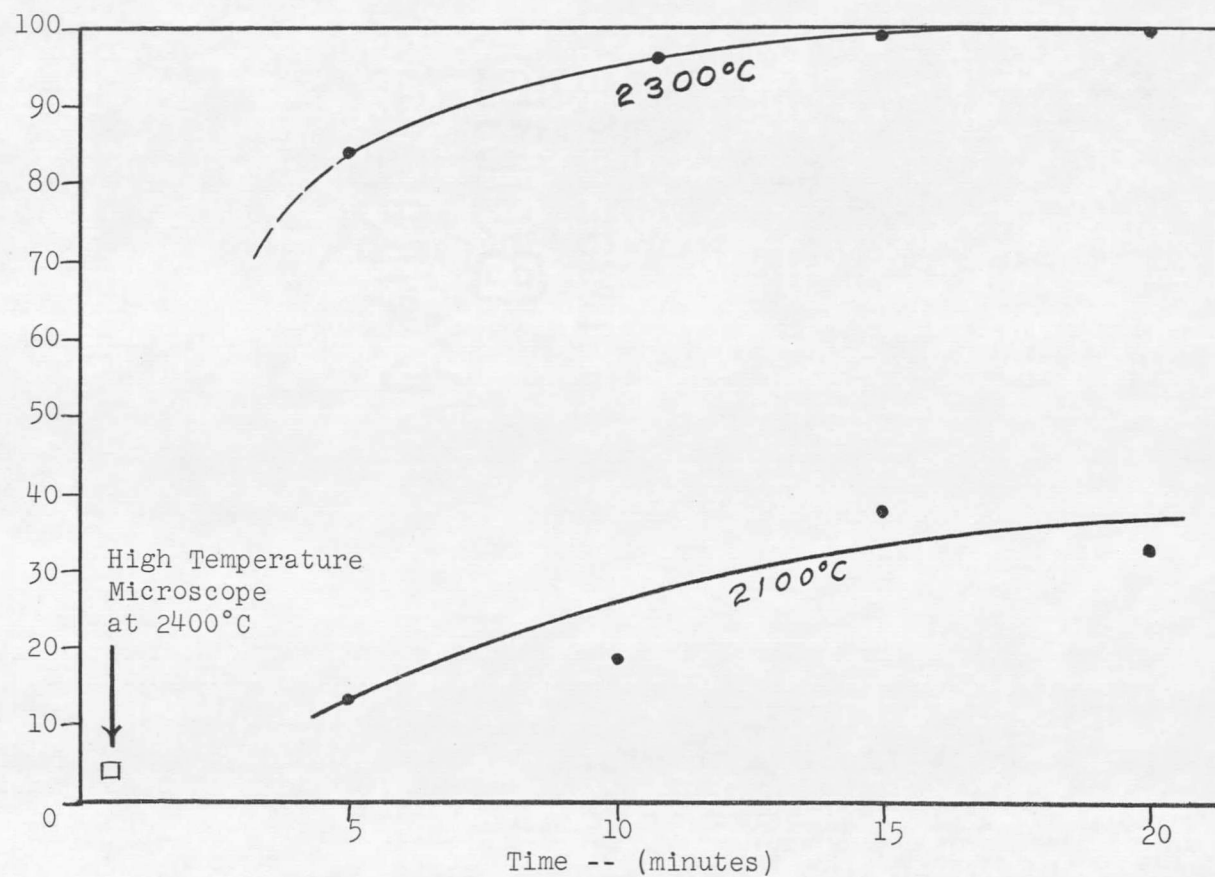


Figure 1. Time-temperature Relation of Beta to Alpha Silicon Carbide (2)

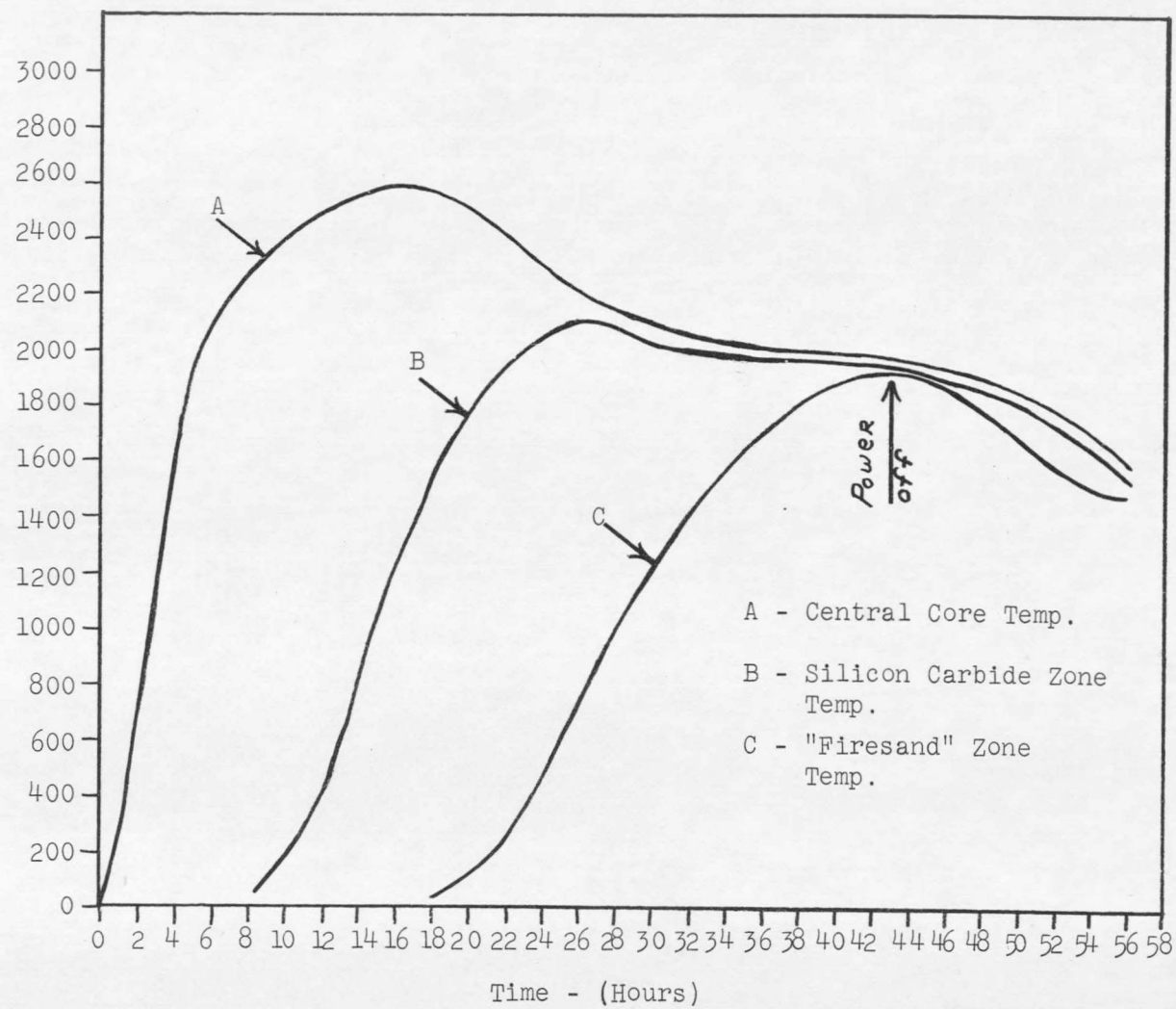


Figure 2. Temperatures in Commercial Silicon Carbide Furnaces (27)

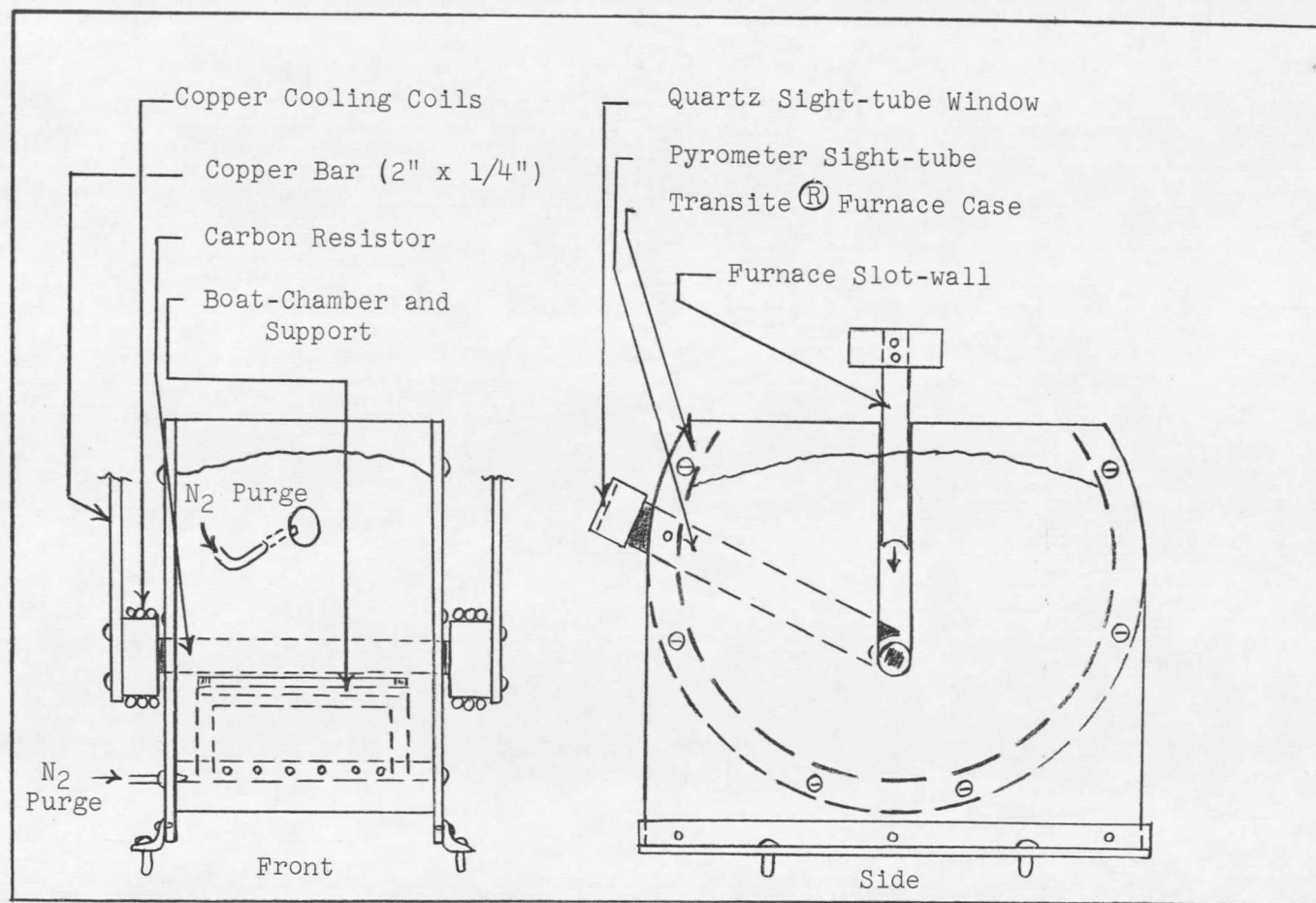


Figure 3. Schematic Drawing of Furnace

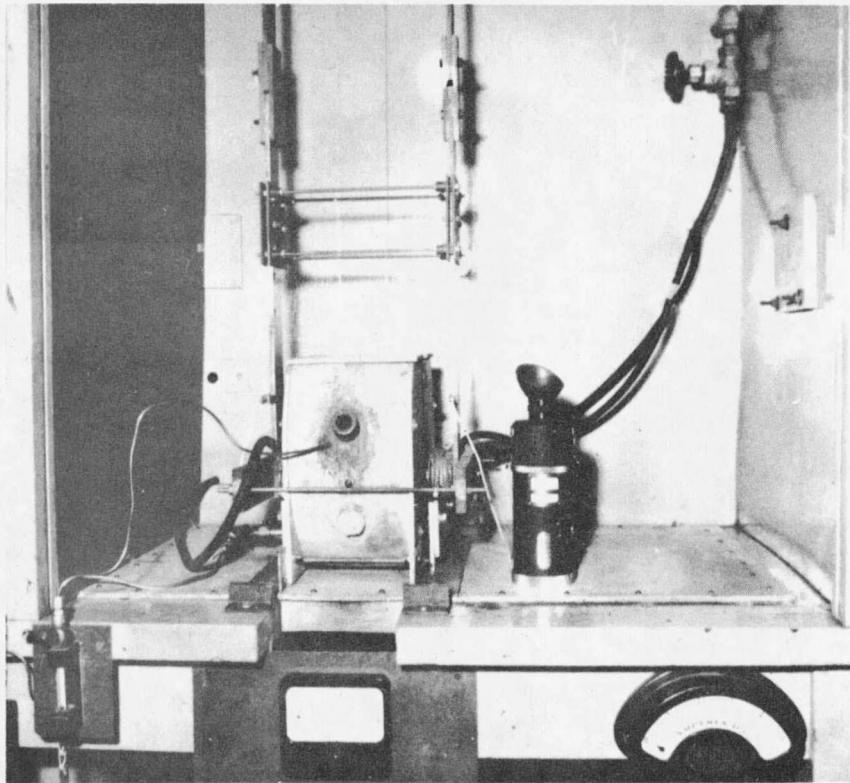


Figure 4 picture of Furnace Equipment

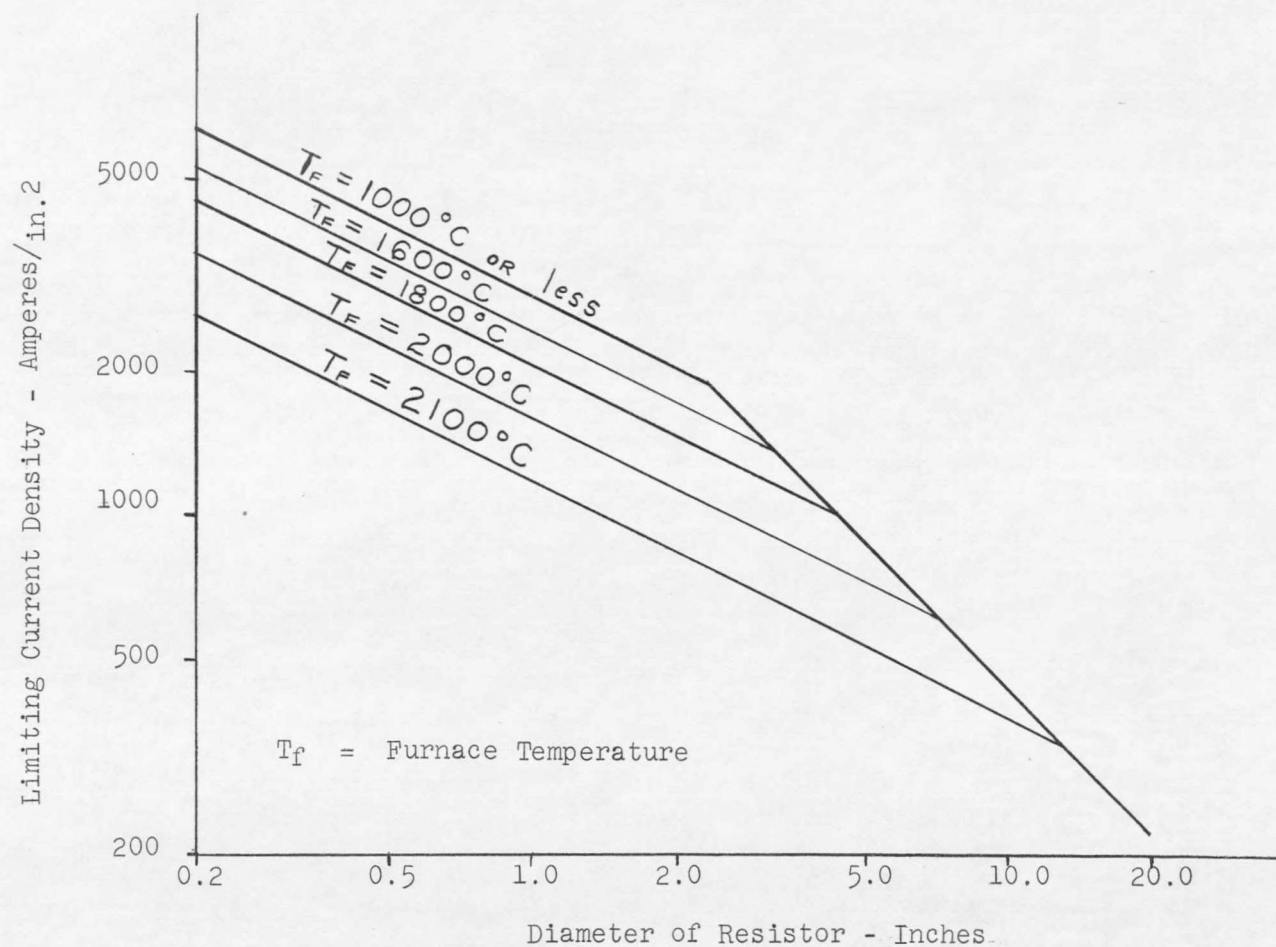


Figure 5. Plot of Limiting Current Density vs. Carbon Resistor Diameter

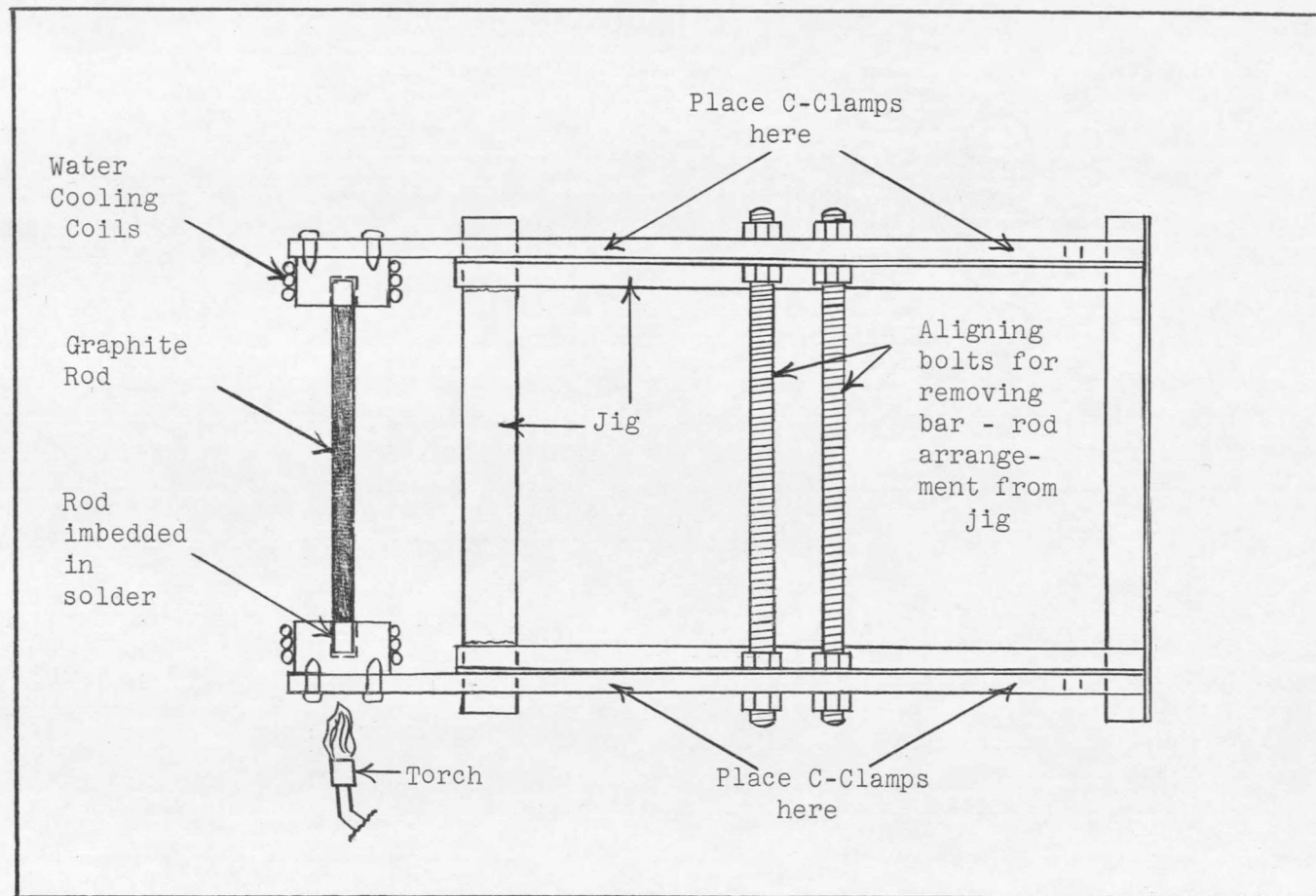


Figure 6. Arrangement for Replacing Carbon Rods

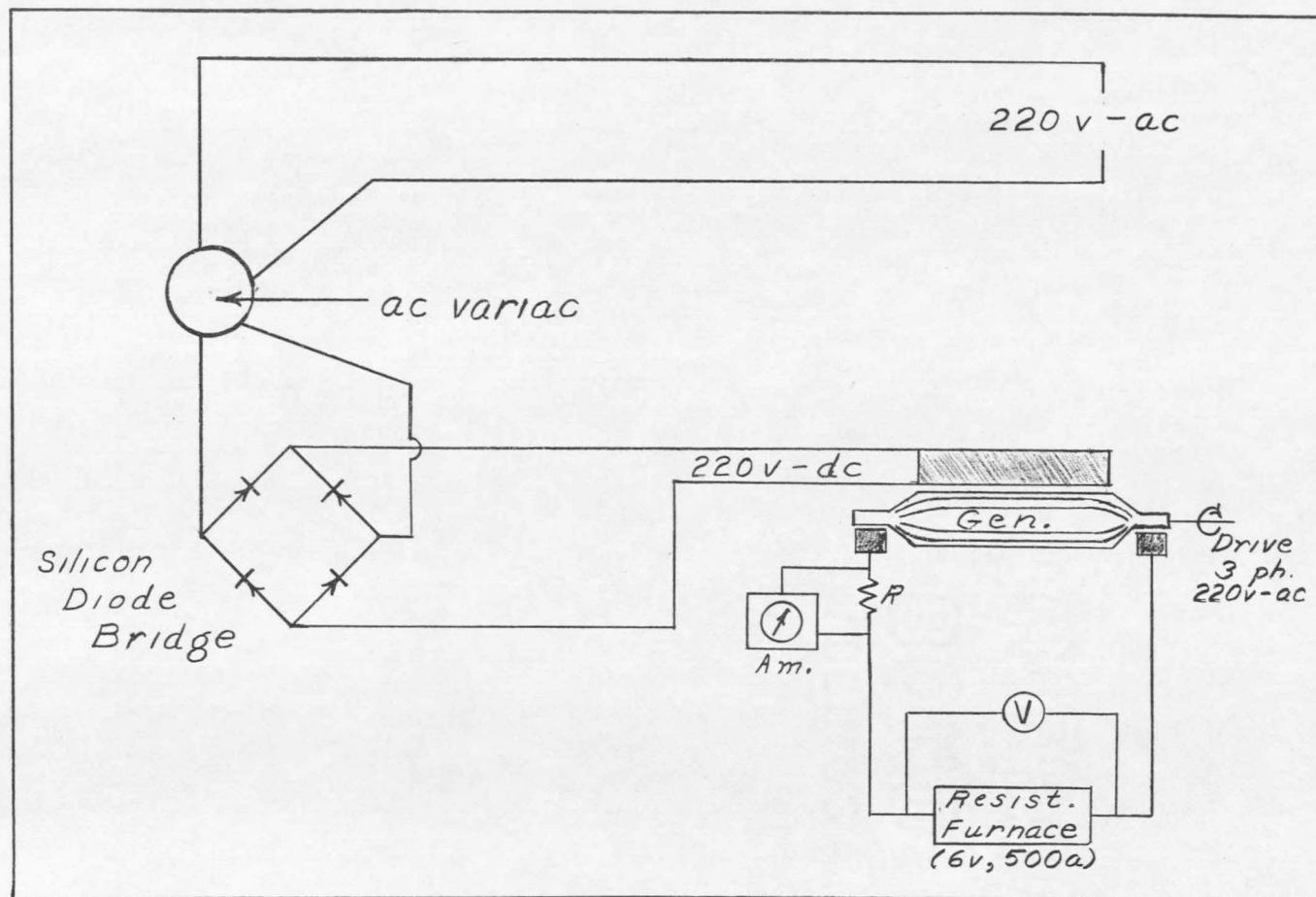


Figure 7. Circuit Diagram of Apparatus

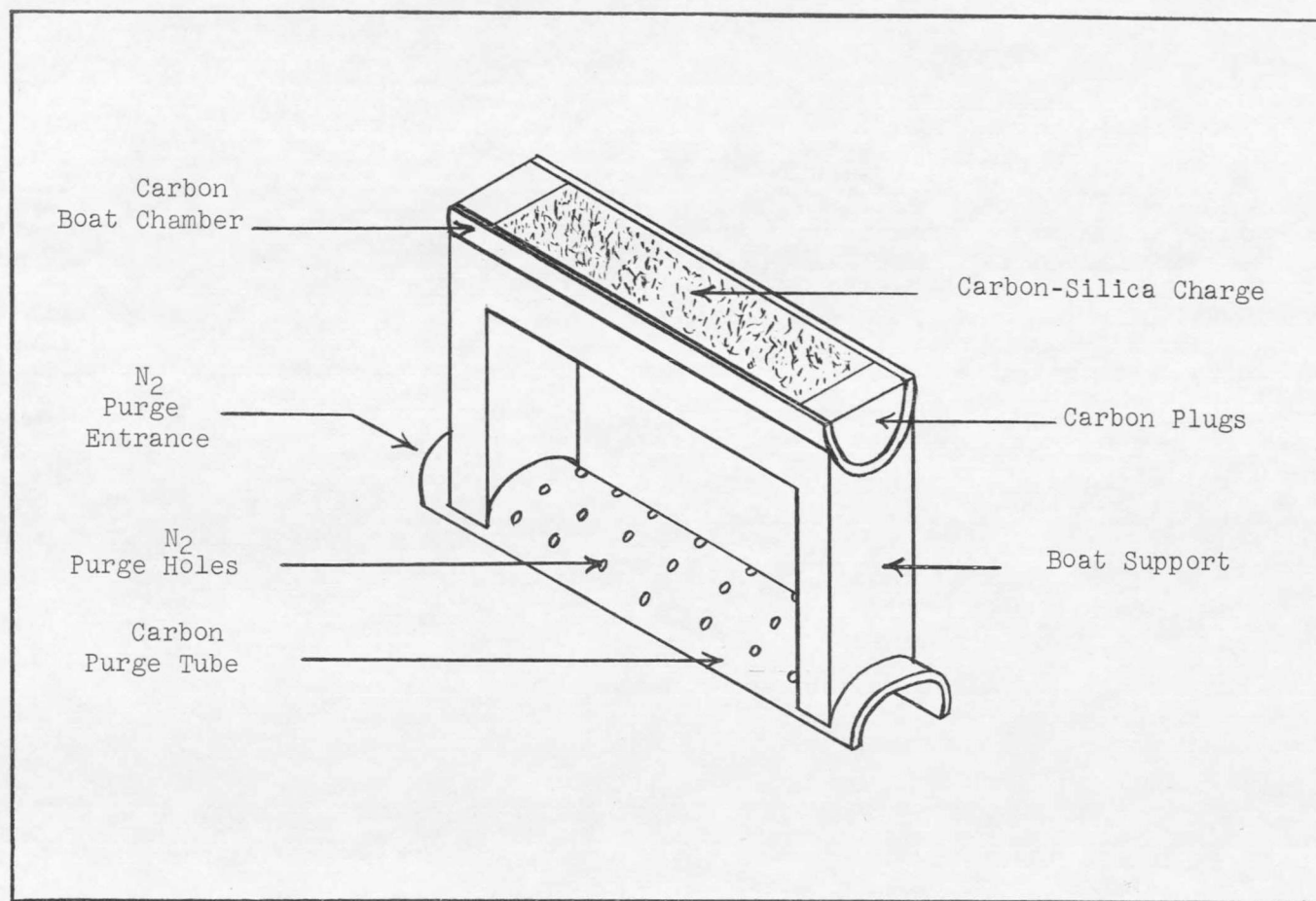


Figure 8. Carbon Boat-Chamber and N_2 Purge Sparger

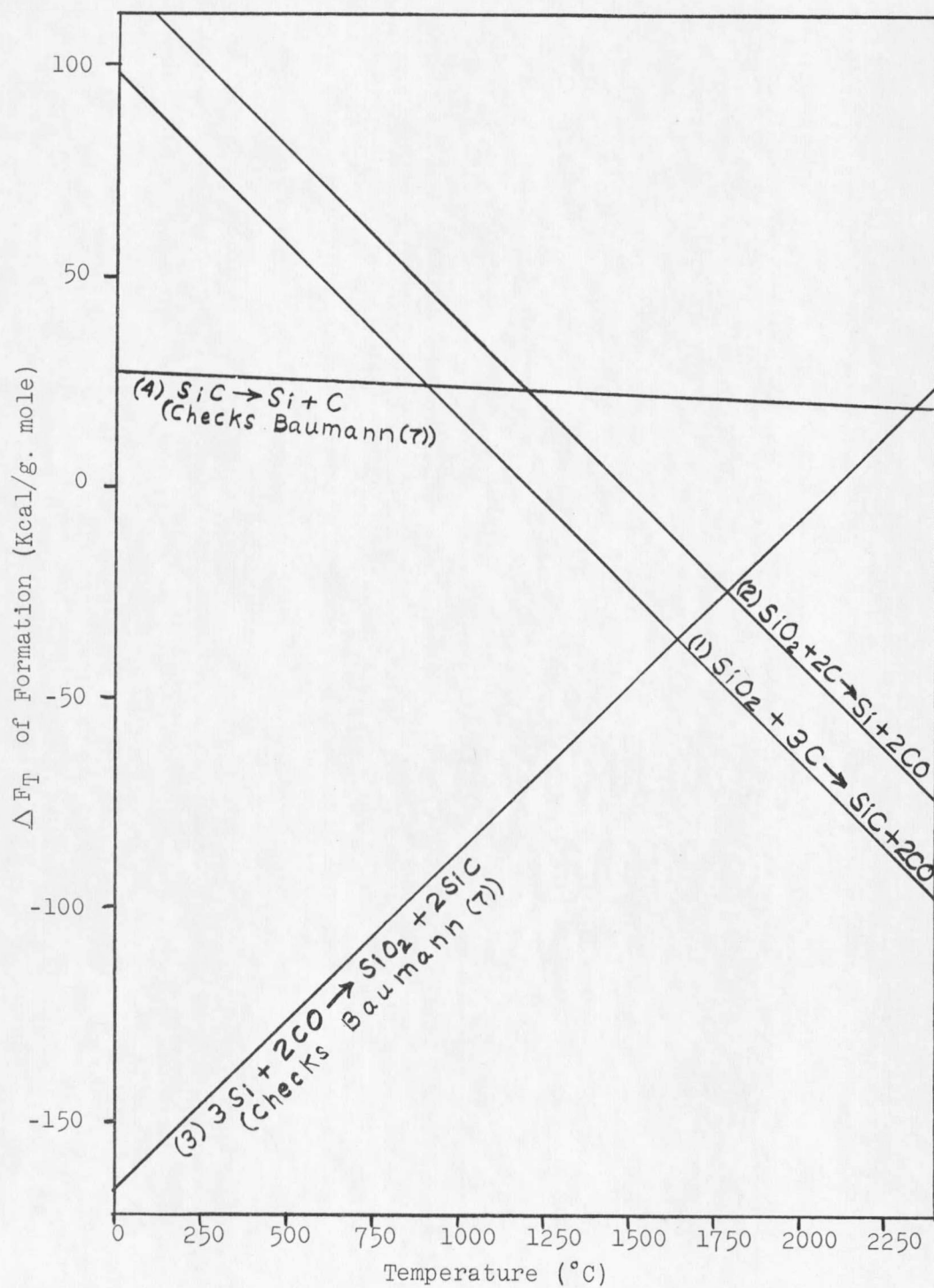


Figure 9. Plot of ΔF_T vs. Temperature for Reactions (1.) through (4.)

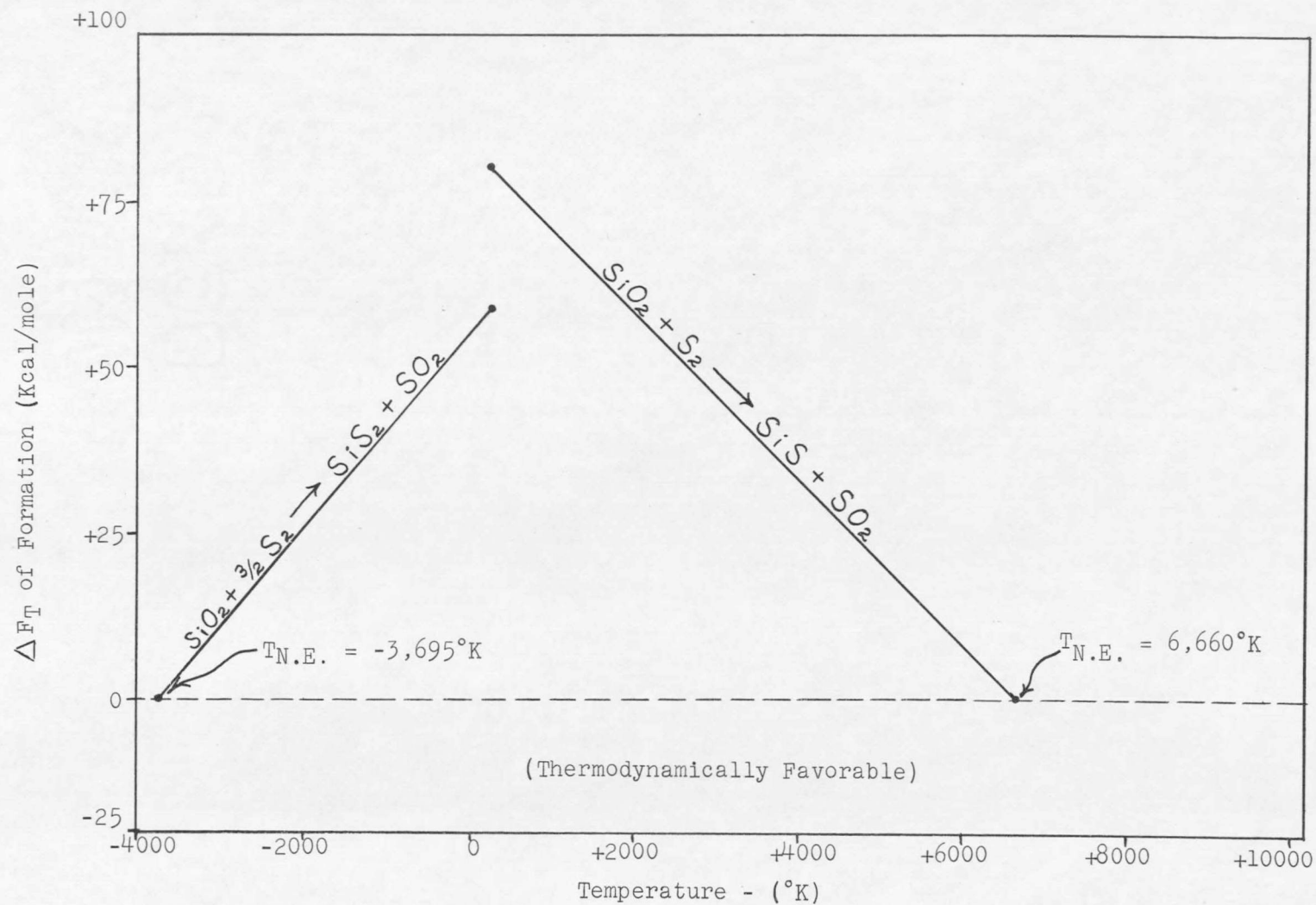


Figure 10. Plot of ΔF_T vs. Temperature for Reactions (5.) and (6.)

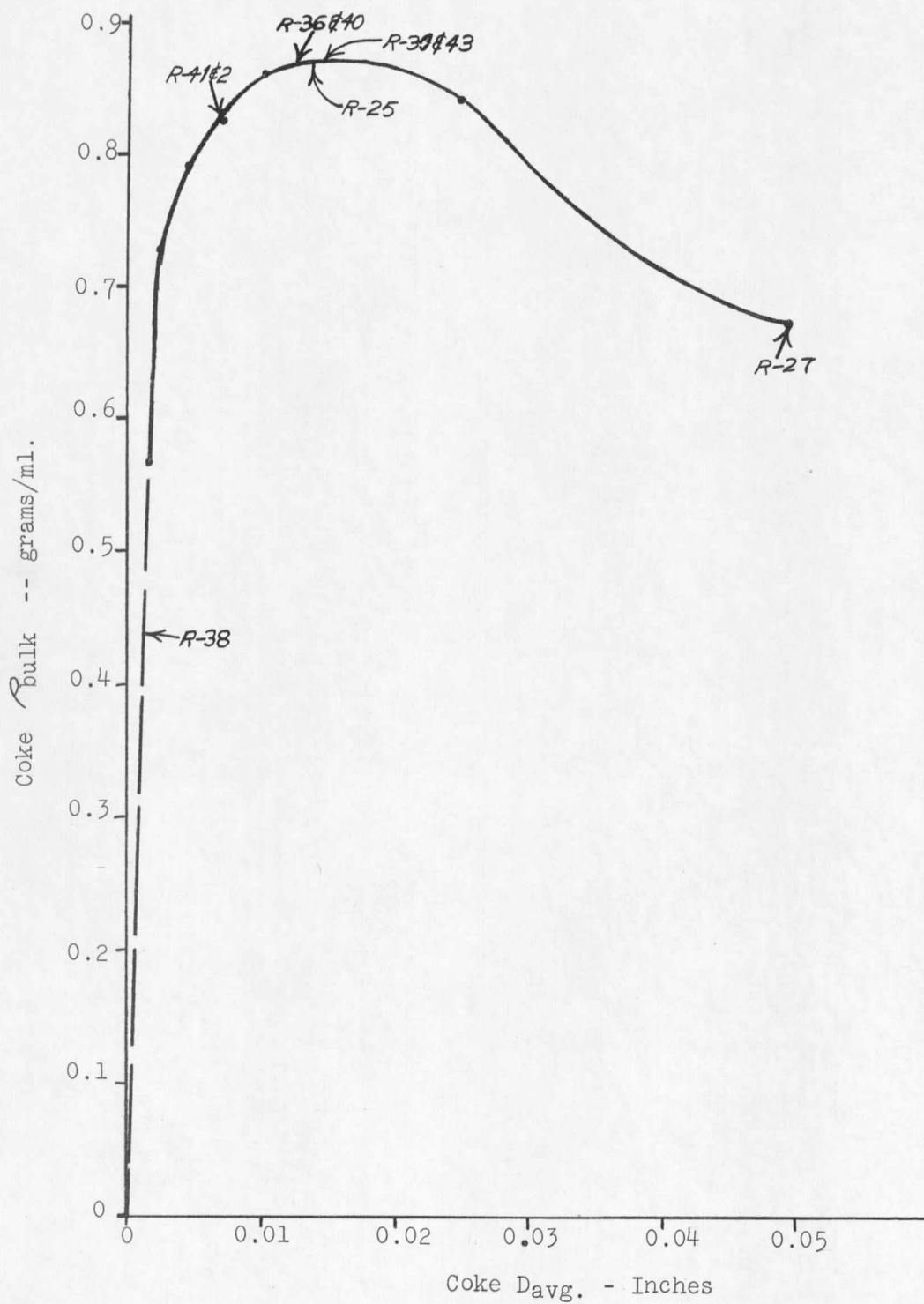


Figure 11. Plot of Coke Particle Size vs. Bulk Density

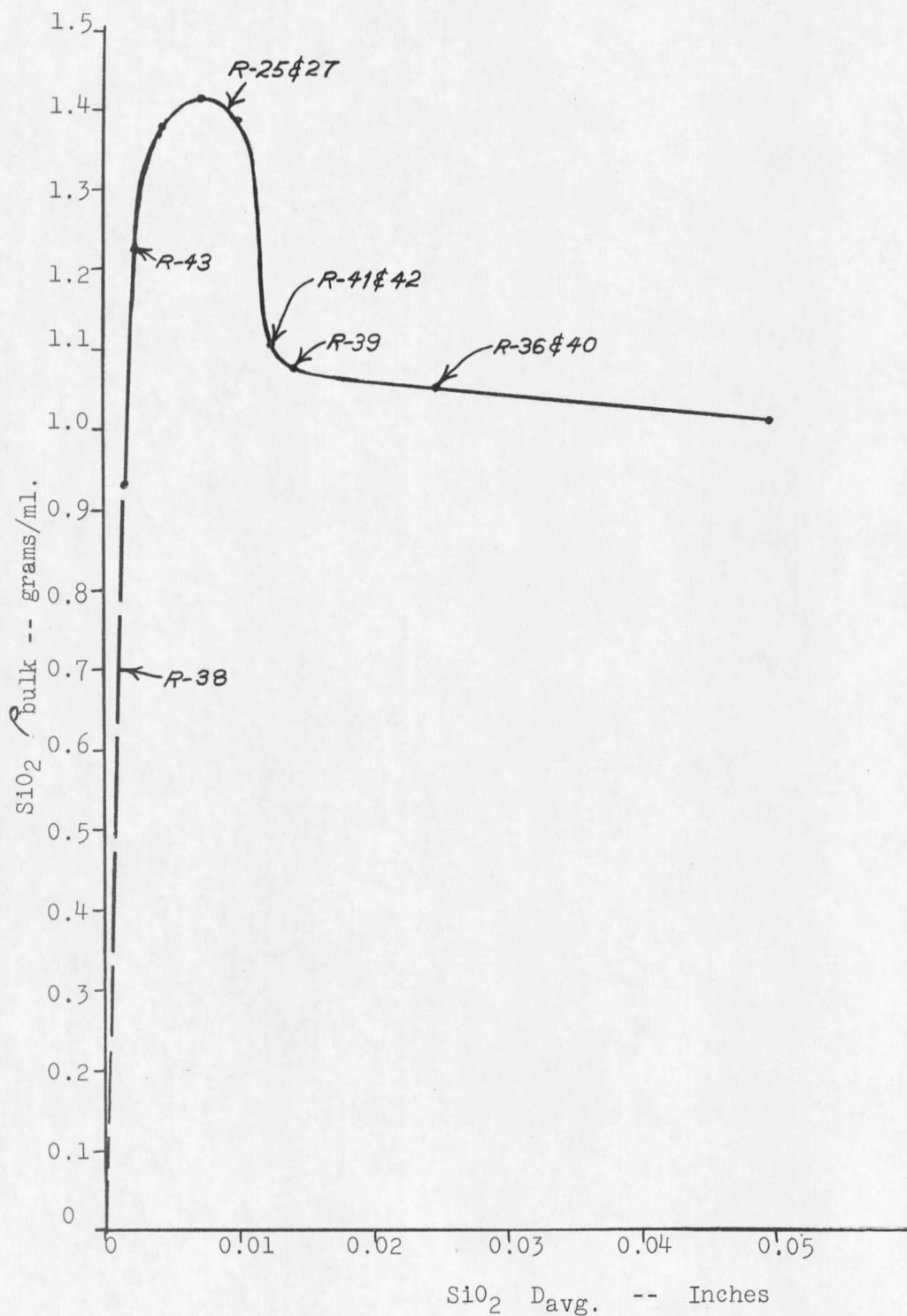
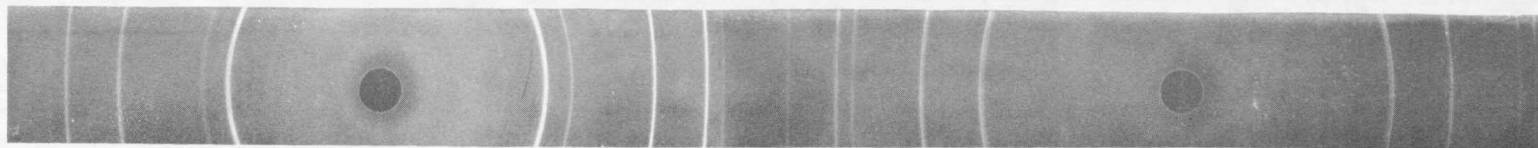
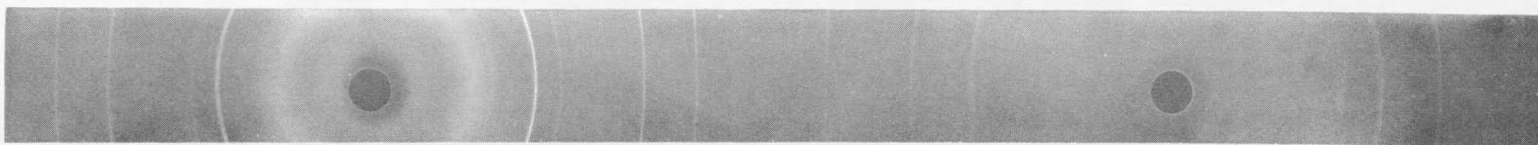


Figure 12, Plot of Silica Particle Size vs. Bulk Density

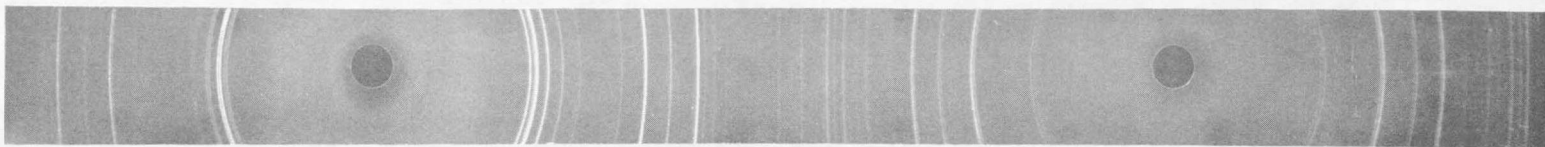


(a) Norton Beta Silicon Carbide

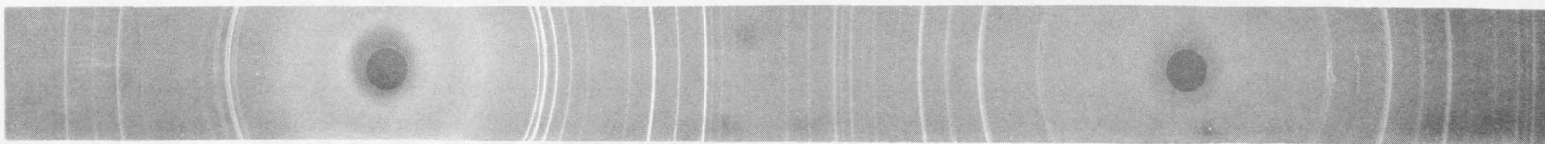


(b) R-5 Crystals

Figure 13 X-ray Diffraction Patterns of Norton Co.
Beta SiC and Sample from R-5 Crystals

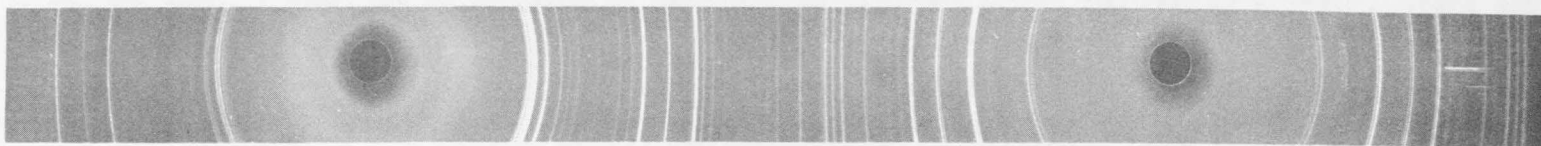


(a) Norton Co. Green Alpha Silicon Carbide

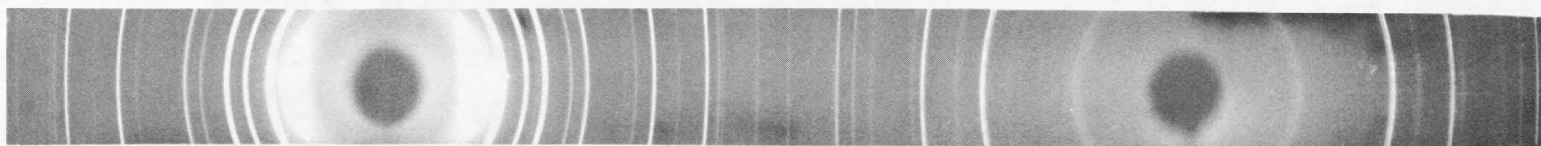


(b) Carborundum Co. Regular Alpha Silicon Carbide

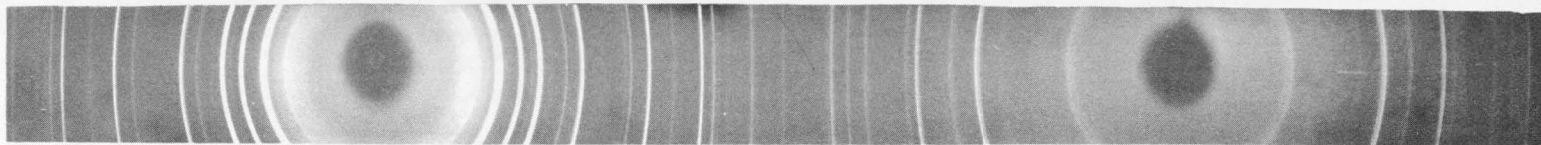
Figure 14 X-ray Diffraction Patterns of Norton Co. Green
Alpha SiC and Carborundum Co. Regular Alpha SiC



(a) Norton Co. Regular Alpha Silicon Carbide

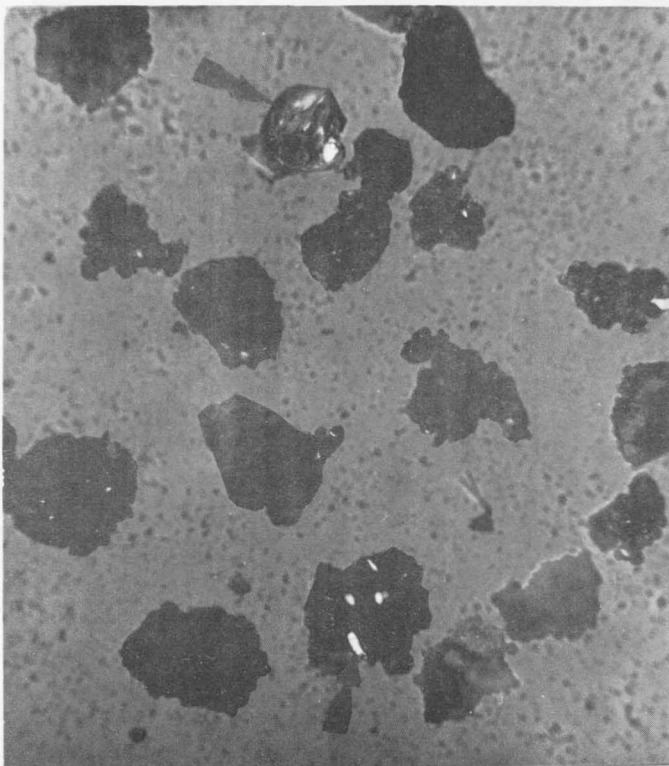


(b) Sample of Coke Produced SiC from R-40

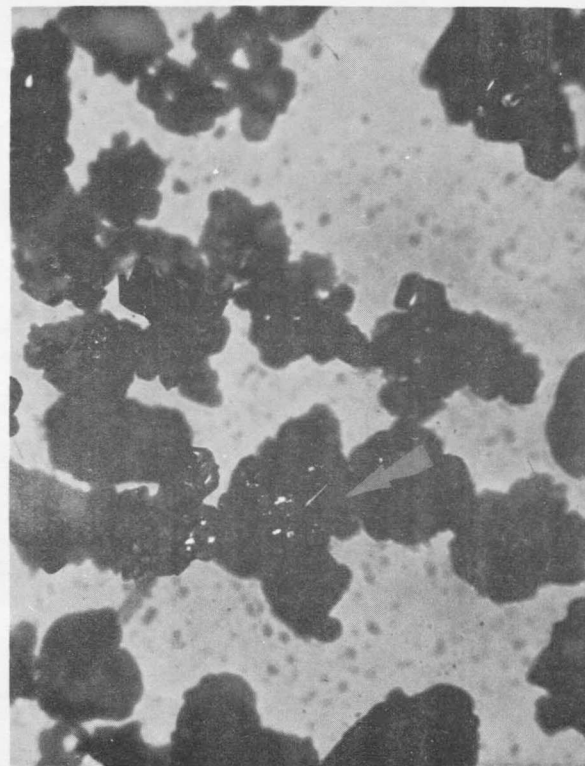


(c) Sample of Graphite Produced SiC from R-40

Figure 15 X-ray Diffraction Patterns of Norton Regular Alpha SiC and Samples from R-40



(a) Green and Black Crystals



(b) Predominantly Black Crystals

Figure 16 Photomicrographs of Typical SiC
Crystals Produced

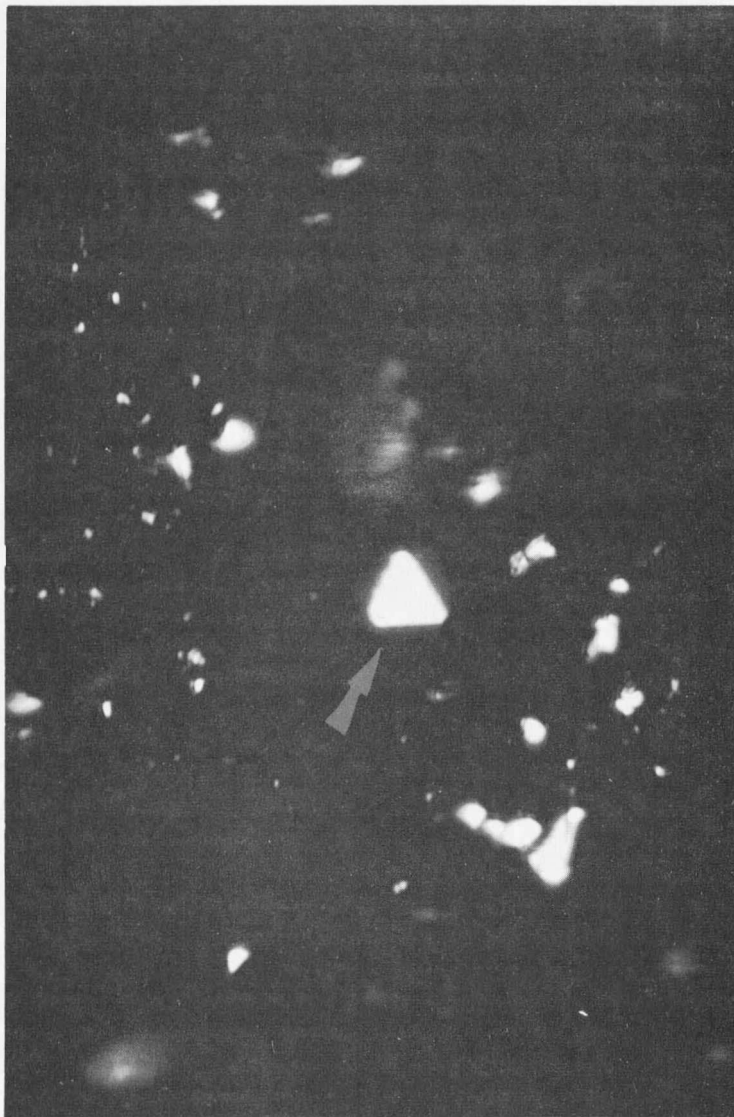


Figure 17 Photomicrograph of Crystalline Chunk
Produced in Run R-5

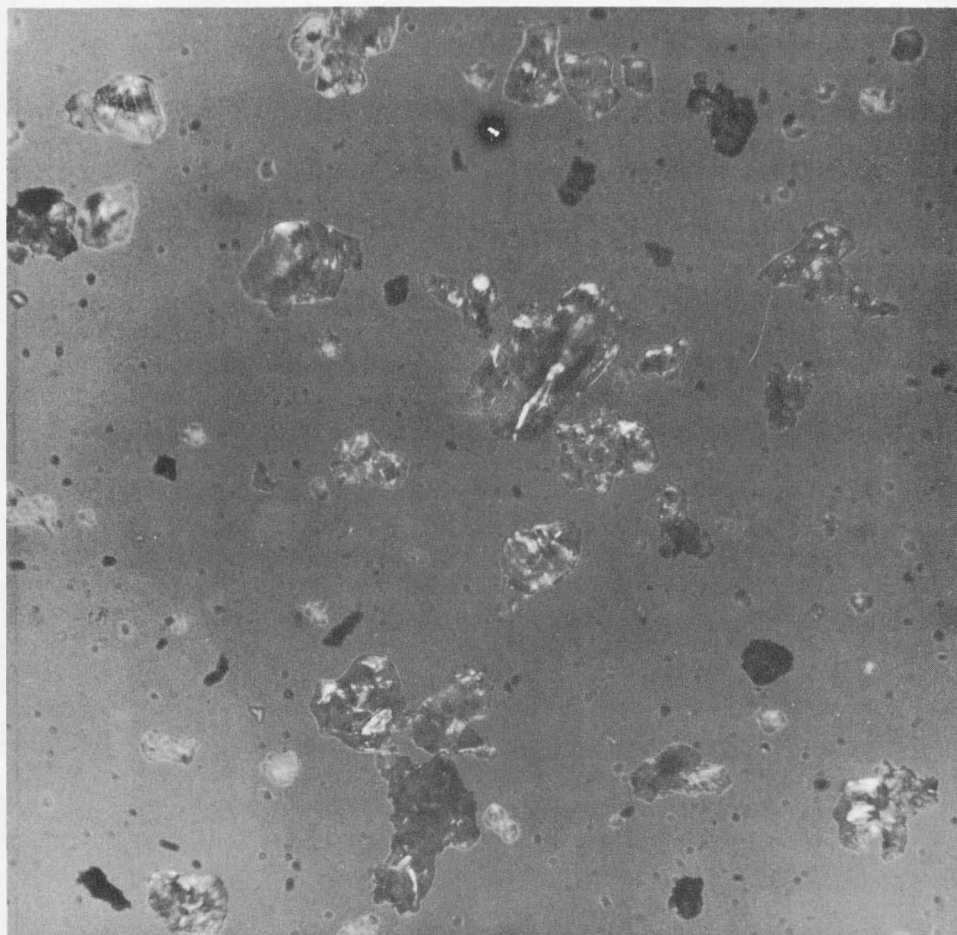


Figure 18 Photomicrograph of Separated Crystalline
Material Produced in Run R-5

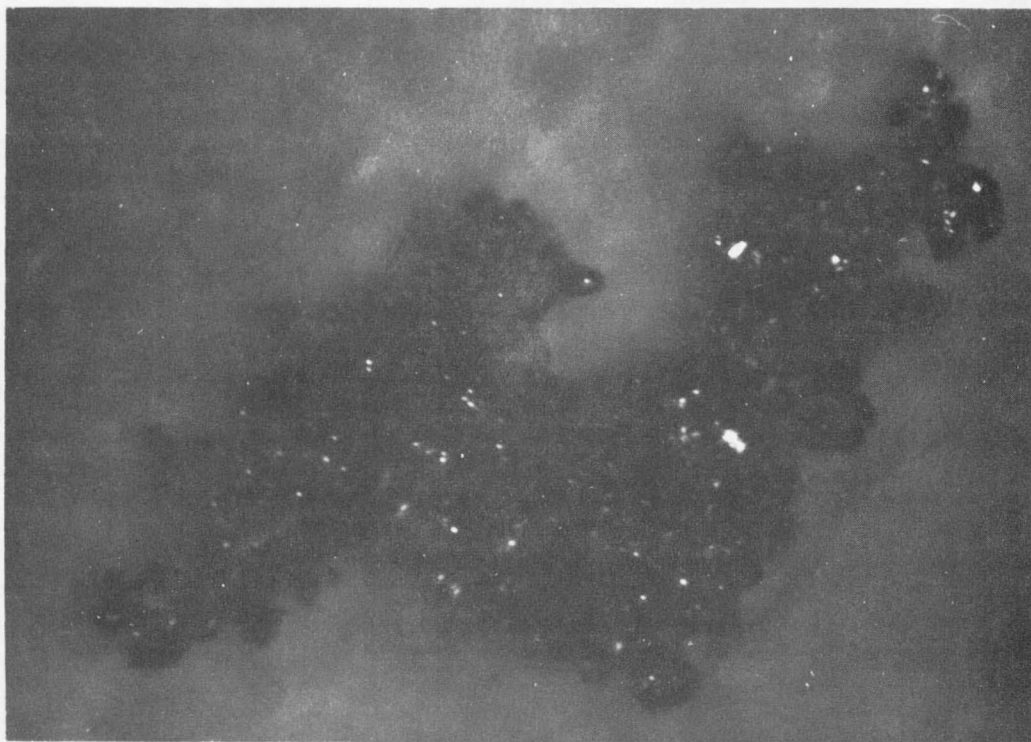


Figure 19 Photomicrograph of Dendritic Material
Produced in Run R-10

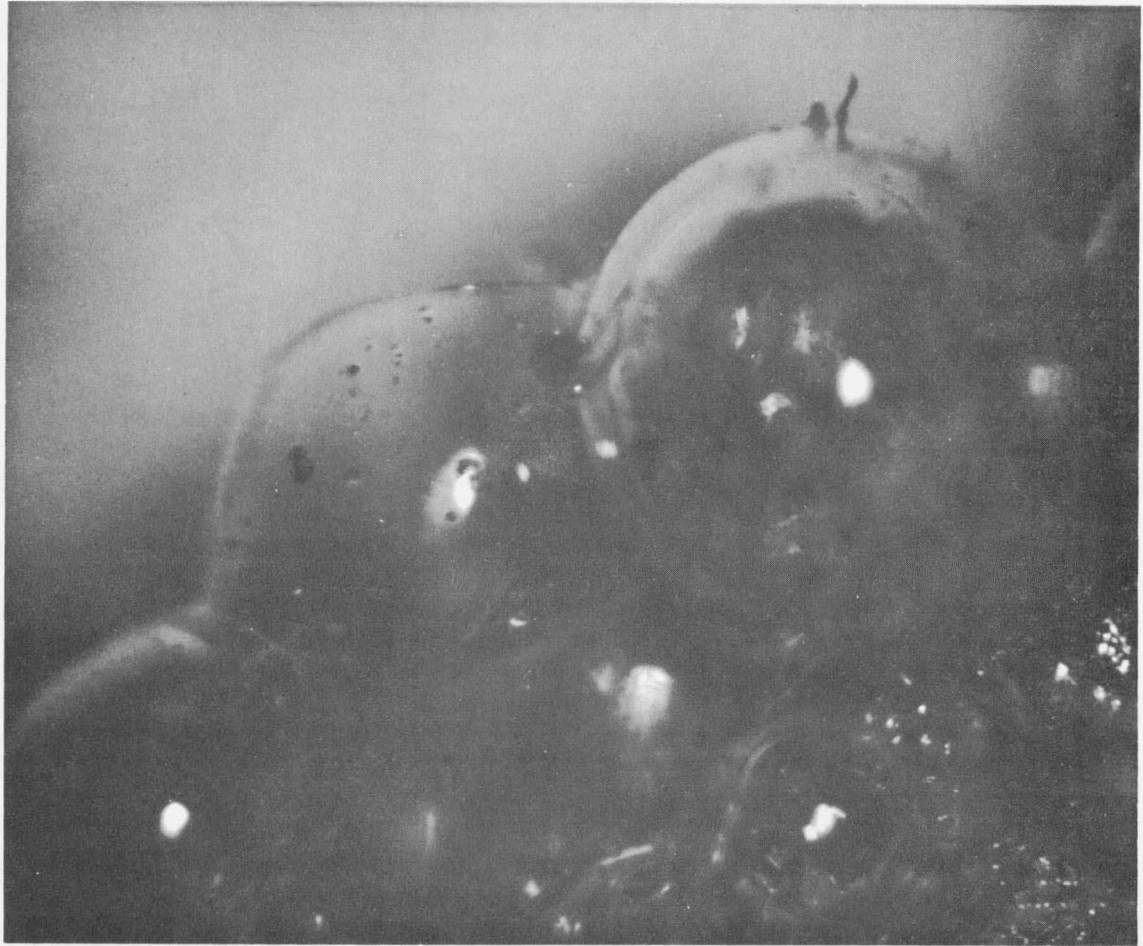
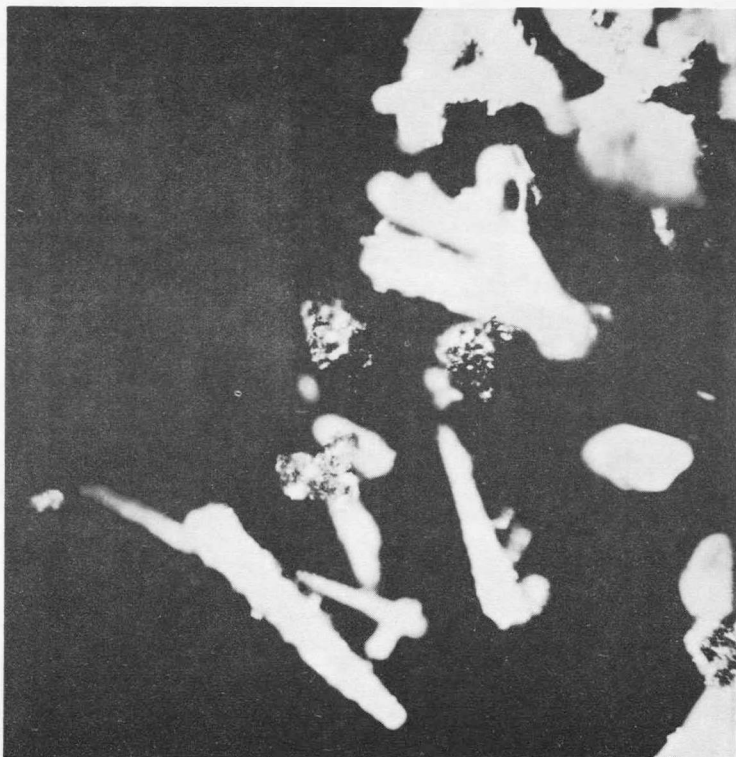
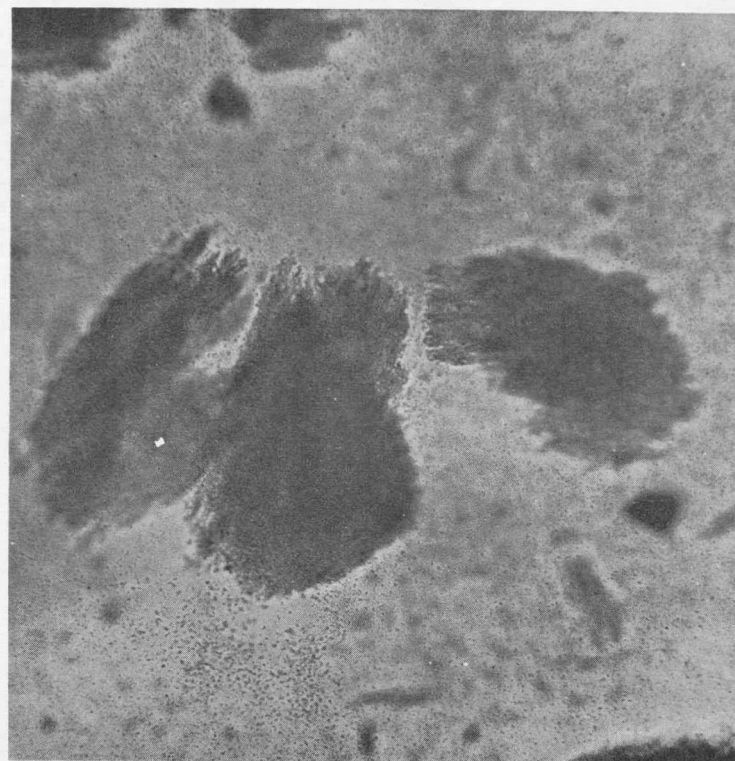


Figure 20 Photomicrograph of Glassy Bubbles
Formed in Pyrometer Sight-tube

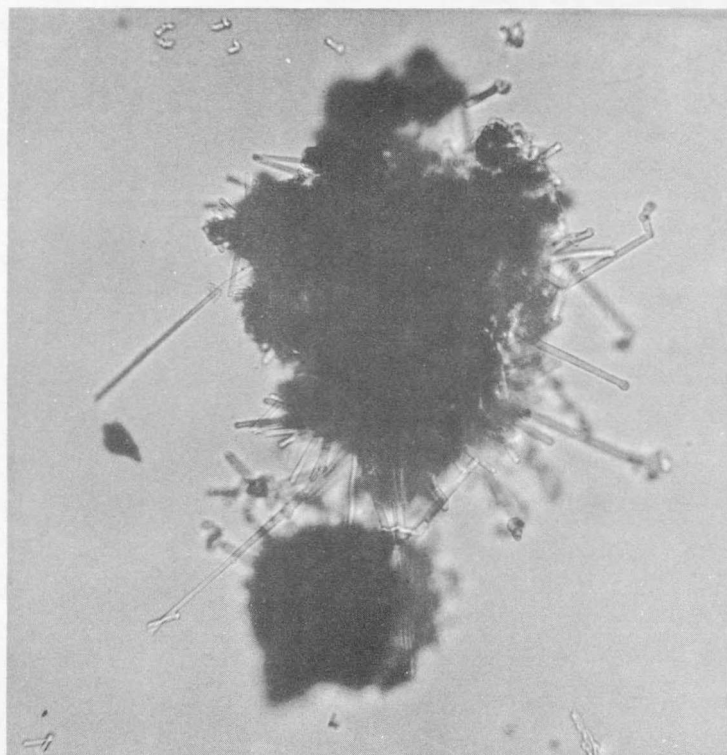


(a) Needles from tube



(b) Collected from shield

Figure 21 Amorphous Material from Sight-tube and Shield



(a) Growth on Coke Surface



(b) Single Growths

Figure 22 Transparent Needle-like Material
from Sight-tube on Run R-20

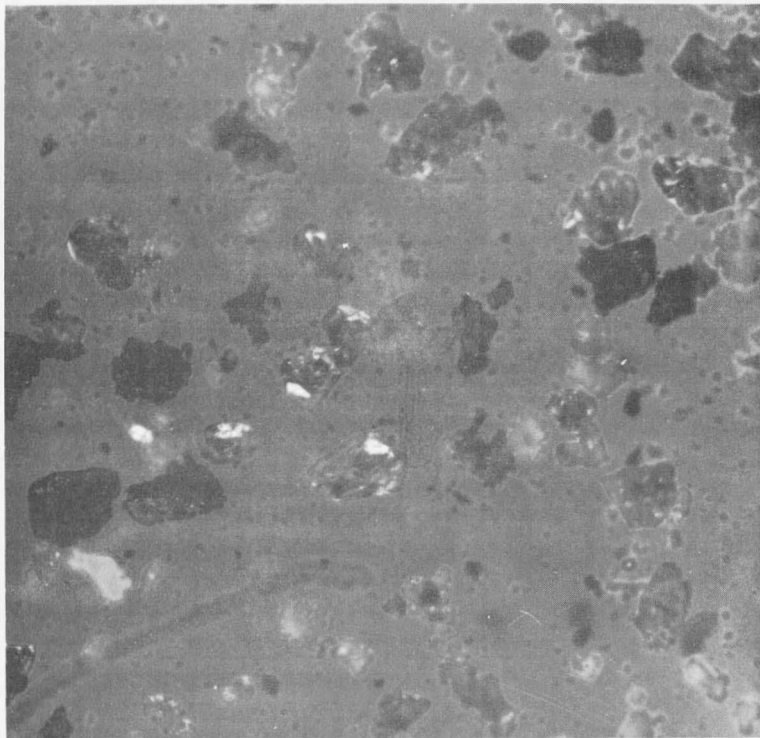


Figure 23 Photomicrograph of Silicon Carbide Crystals
Produced in Run R-26

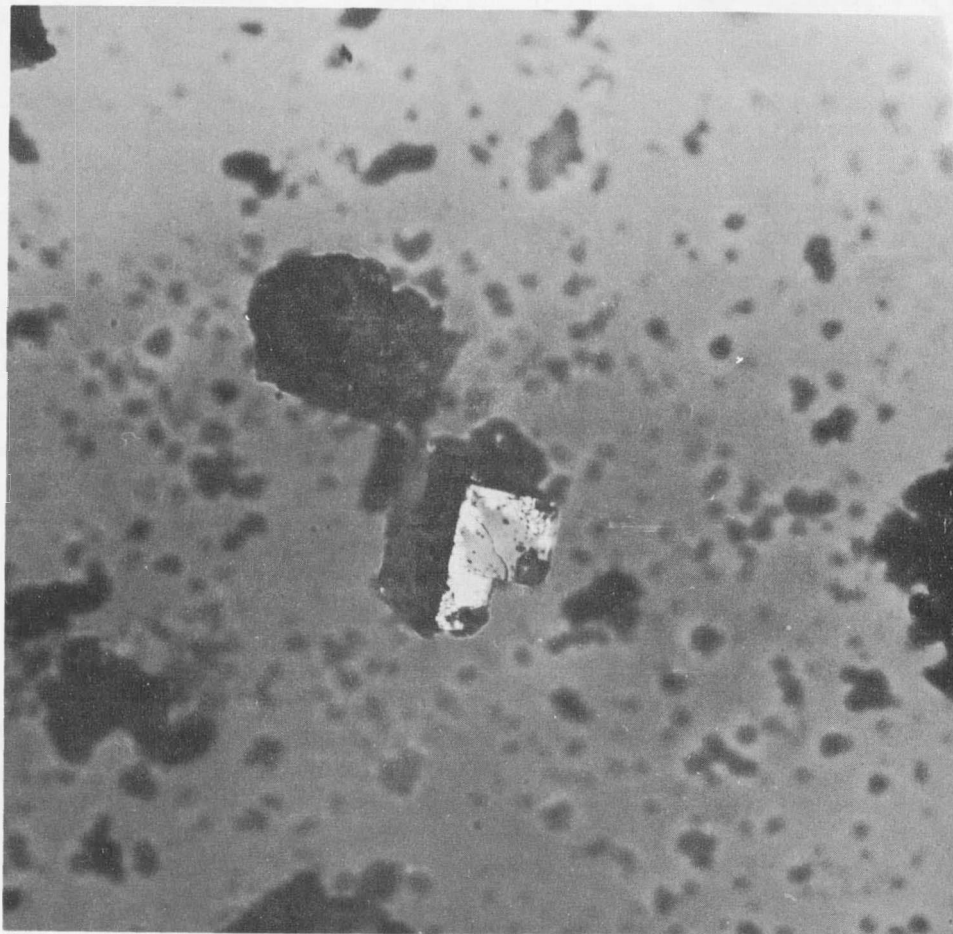


Figure 24 Photomicrograph of Crystalline Mass
Produced in Run R-36

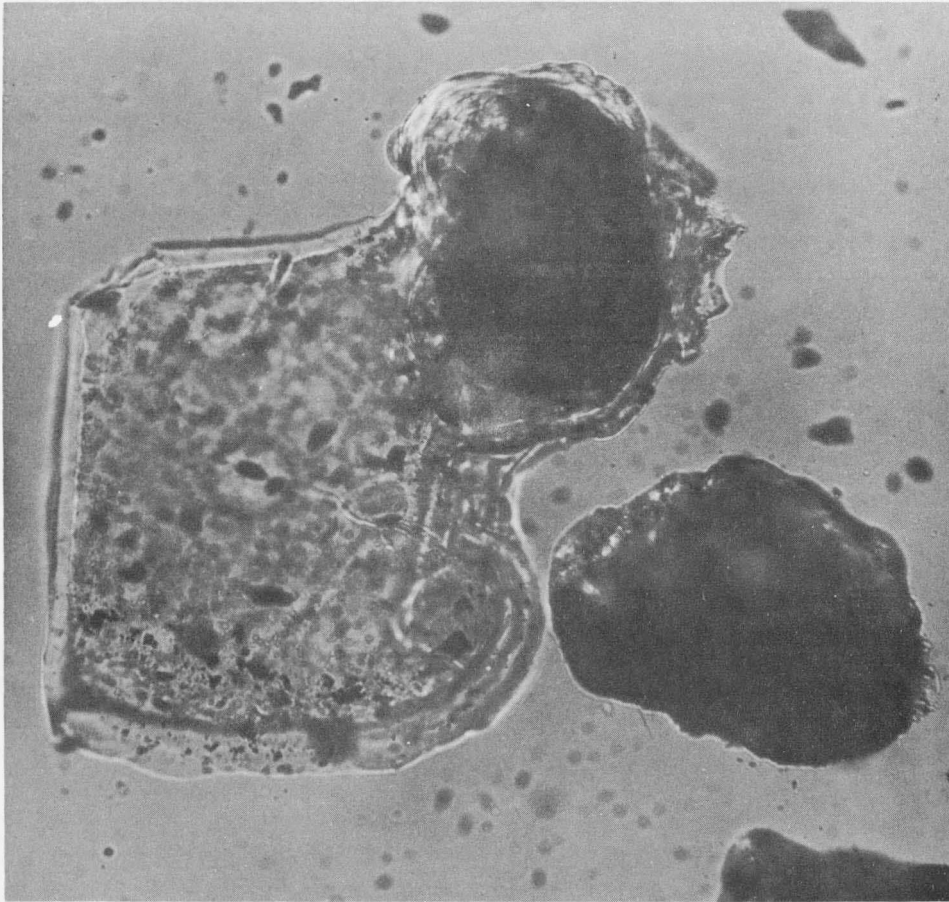
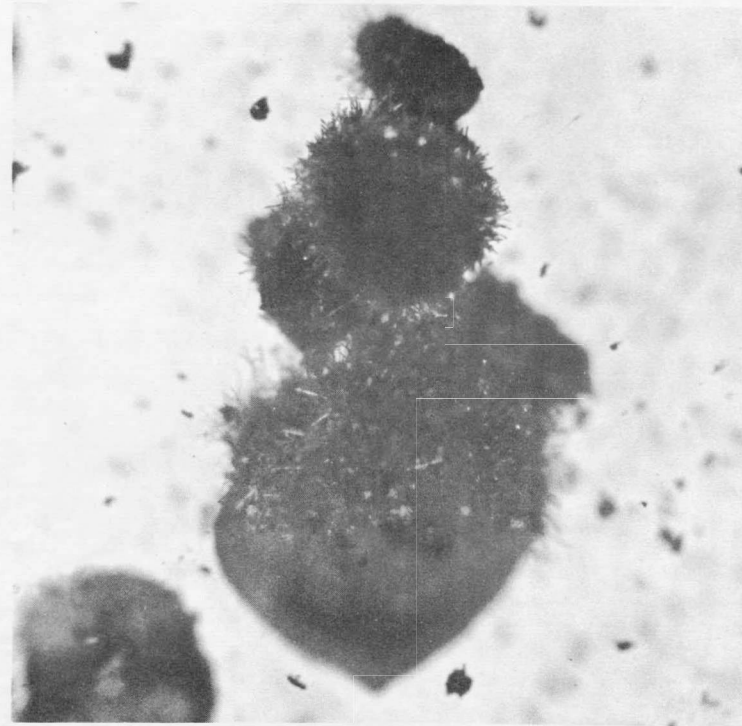
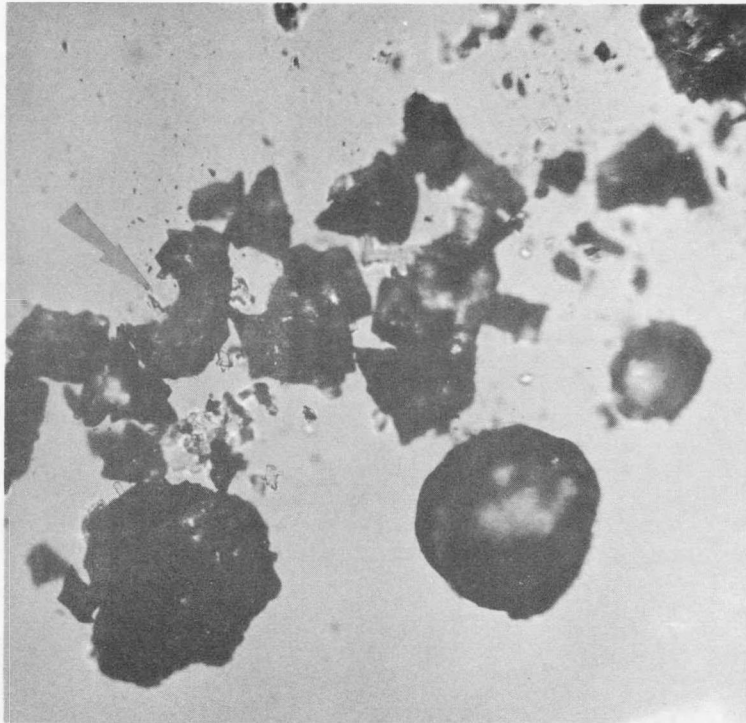


Figure 25 Photomicrograph of Molten Silica
Surrounding Coke Particles



--94--

Figure 26 Photomicrographs of Split-off Partially Reacted Shell

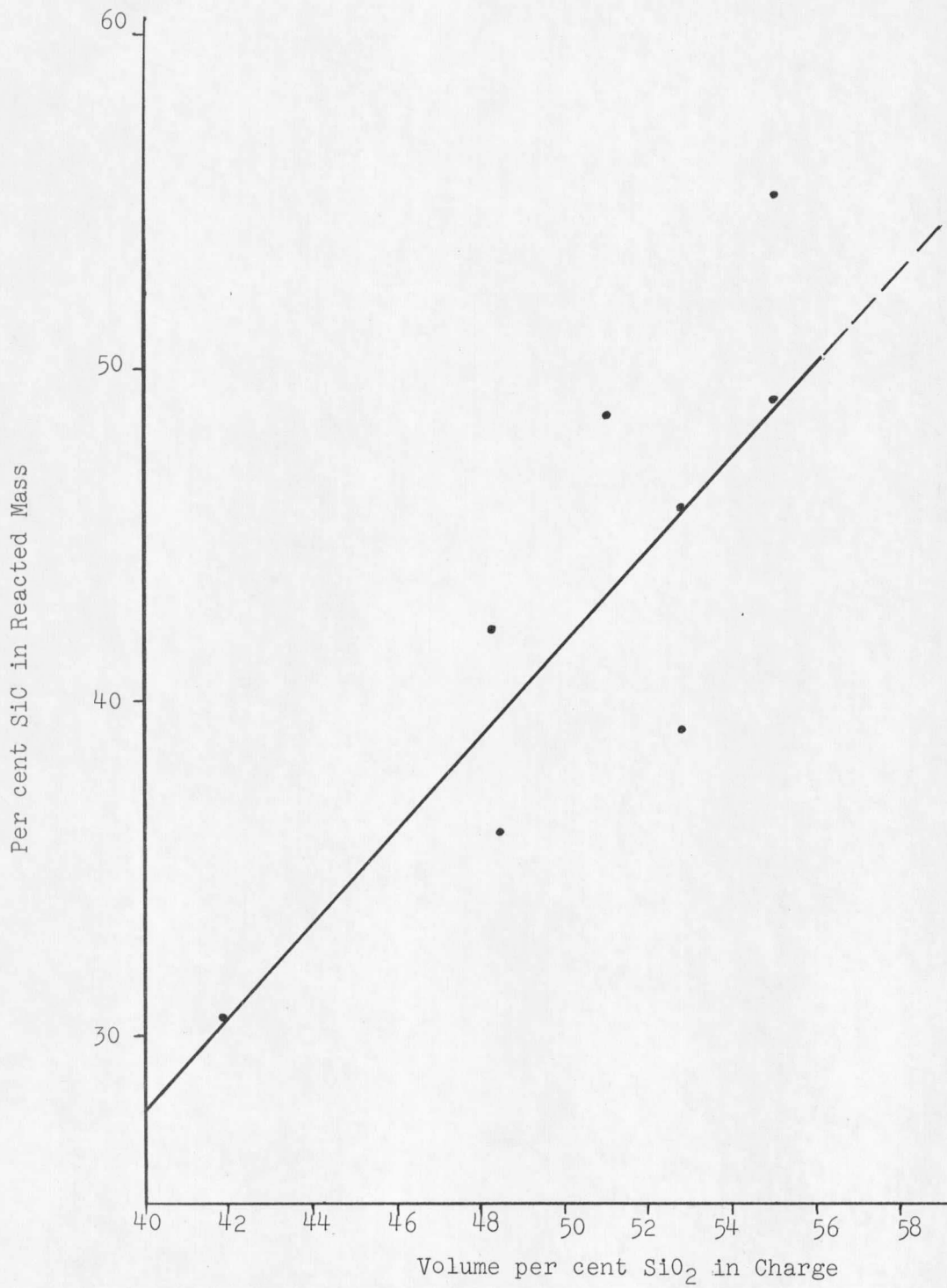


Figure 27. Volume Per Cent SiO₂ in Charge vs. Per Cent SiC in the Reacted Mass



--96--

Figure 28 Picture of X-ray Diffraction Pattern of
Needle-like Crystalline Material from Sight-tube on Run R-20

LITERATURE CITED

- (1) Bauer, J.; Fiala, J.; Hrichova, R.; "Natural Alpha SiC"; American Mineralogist; Vol. 48, 1963, pp 620-34.
- (2) Baumann, H. N. Jr.; "The Relationship of Alpha and Beta SiC"; Electrochem. Soc.; Vol. 99, 1952, pp 109-14.
- (3) Bunn, C. W.; Chemical Crystallography; Oxford University Press; 1946.
- (4) Butler, G. M.; "The Past and Future of SiC"; J. Electro-chem. Soc.; Vol. 104, 1947.
- (5) "Chemical Analysis of Silicon Carbide"; Exolon Co. Report for the Abrasive Grain Ass'n.; Feb. 26, 1947.
- (6) Cumulative Alphabetical and Grouped Numerical Index of X-ray Diffraction Data; American Society for Testing Materials; 1955.
- (7) Denbigh, K.; The Principles of Chemical Equilibrium; Cambridge University Press, 1st Ed.; 1955.
- (8) Drowart, J.; DeMaria, G.; Thermodynamic Study of Silicon Carbide Using a Mass Spectrometer; Conference on Silicon Carbide, April 2-3, 1959, Pergamon Press, New York, 1960.
- (9) Finlay, G. R.; "Calculated Energy Requirements of Electric Furnace Products"; Chemistry in Canada; Vol. 4, No. 2, 1958, pp 25-8.
- (10) Gartland, J. W.; "Transactions of the Electrochem. Soc."; Vol. 38, 1945, p 121.
- (11) Hodgeman, C. D.; Holmes, H. M.; Handbook of Chemistry and Physics; Chemical Rubber Publishing Co., Cleveland, 1956.
- (12) Hougen, O. A.; Watson, K. M.; Ragatz, R. A.; Chemical Process Principles-Part II, 2nd Ed.; 1959.
- (13) Humphrey, Todd; Coughlin; King; "U. S. Bureau of Mines Reported Investigations 4888"; U. S. Bureau of Mines; July, 1952.
- (14) Industrial Carbon and Graphite Products; National Carbon Co. booklet, copyright-1951, 1957, 1961; Union Carbide Corp.

- (15) Jagodzinski, H.; Arnold, H.; "Anomalous SiC Structures"; Conference on Silicon Carbide; April 2-3, 1959, Pergamon Press, New York, 1960.
- (16) Keller, F. E.; "Thermodynamic Study of the Foundation of Silicon Carbide from Montana Silica and Fluid Coke"; Montana State College Chemical Engineering Department Report, 1963.
- (17) Klug, H. P.; Alexander, L. E.; X-ray Diffraction Procedures; John Wiley and Sons, Inc., New York, 1954.
- (18) Knoop, F.; Peters, C. G.; Emerson, W. B.; "A Sensitive Pyramidal Diamond Tool for Indentation Measurements"; J. Research Nat'l. Bureau of Standards, Vol. 23, 1939, pp 39-61.
- (19) Koehler, W. A.; Electro-Chemistry; Vol. II; John Wiley and Sons, 1944, pp 443-8.
- (20) Lawson, D. C.; "Bureau of Mines Inspection No. 8458"; Montana Bureau of Mines and Geology; April 4, 1957.
- (21) McMullen, J. C.; "A Review of Patents on Silicon Carbide Furnacing"; J. Electrochem. Soc.; Vol. 104, 1957.
- (22) Merz, K. M.; "Crystal, Whisker and Microcrystalline Forms of Silicon Carbide"; Conference on Silicon Carbide, April 2-3, 1959; Pergamon Press, New York, 1960.
- (23) Moissan, H.; "Examination of Carbon Silicides from Meteorites of Canon Diablo"; Compt. rend., Vol. 140, 1905, pp 405-6.
- (24) National Cyclopedia of American Biography; Vol. 13, pp 197-8; James T. White and Co., New York, 1906.
- (25) Parche', M. C.; Facts About Silicon Carbide; Carborundum Company Book Series, 1953.
- (26) Regis, A. J.; Sand, L. B.; "Natural Cubic (β) SiC"; Bull. of the Geol. Society of America; Vol. 69, 1958, p 1633.
- (27) Ruff, O.; "The Formation and Dissociation of Silicon Carbide"; Trans. of the Electrochem. Soc; Vol. 68, 1935, pp 87-120.
- (28) Shreve, R. N.; Chemical Process Industries; 2nd. Ed.; McGraw-Hill Book Co., 1959.

- (29) Smith, J. M.; Van Ness, H. C.; Introduction to Chemical Engineering Thermodynamics, 2nd Ed.; McGraw-Hill Book Co.; 1956, pp 331-3.
- (30) Tables of Selected Values of Chemical Thermodynamic Properties, Series I, II; U. S. National Bureau of Standards Circular 500; 1952.
- (31) Tone, F. J.; "High Temperature Products of Silicon"; Ind. and Eng. Chem., Vol. 23, 1931, pp 1312-16.
- (32) Tuller, W. N.; Sulphur Data Book; Compiled by Freeport Sulphur Co.; McGraw-Hill Book Co.; 1954.
- (33) "Typical Inspections of Fluid Petroleum Coke"; Humble Oil and Refining Co. Report, Billings, Montana, Dec. 1962.
- (34) Wylie, C. R., Jr.; Advanced Engineering Mathematics; McGraw-Hill Book Co.; 1951, pp 527-8.

3 1762 10011357 8

[illegible]