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UNITED STATES ATOMIC ENERGY COMMISSION

FINAL REPORT. PART II. TECHNICAL

By
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May 20, 1949

United Carbon Products Company, Inc.
Bay City, Michigan

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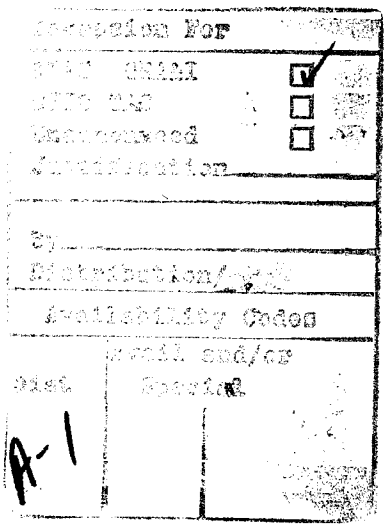
Work performed under Contract No. AT-30-1-Gen-127.

United Carbon Products Company, Inc.
Bay City, Michigan



FINAL REPORT

PART II: TECHNICAL

ABSTRACT

A plant for processing graphite to high purity by the United Carbon Products Company Inc. method was established at Bay City, Michigan. The facilities were capable of producing 900 lbs per day of high purity graphite.

Graphite having a total ash content of 600 ppm and a boron content of < 0.6 ppm was purified so that the total ash was < 10 ppm and the boron was < 0.10 ppm.

The processing was carried out in electric granular carbon resistance furnaces. The purification was achieved by reacting most of the elements out by the use of carbon tetrachloride with nitrogen introduced into the heated zone up to 2000° C; the removal of boron is accomplished by the use of a fluorinated hydrocarbon such as difluoro-dichloro-methane (i.e. "F-12") at temperatures above 2000°C. The "F-12" is used only at the high temperature level to avoid reformation of carbon tetrafluoride in the graphite being processed.

INTRODUCTION

In December 1946, the United Carbon Products Company Inc. submitted to the agents of the U. S. Atomic Energy Commission a sample of high purity graphite. This initial block of massive graphite was a cube four inches on a side that had been purified by the method used by the United Carbon Products Company Inc. to prepare pure spectrographic electrodes. The ash content was < 20 ppm and the boron was down to <.10 ppm. Later four graphite bars furnished by the U. S. Atomic Energy Commission totalling 36 lbs. were processed and the analysis showed that the purity was of the same magnitude. Further trials showed that graphite having a cross-section of 4" x 4" could be processed, having an ash content of <10 ppm and boron as low as .01 - .03 ppm. In individual samples ash was reported as low as 1 ppm. Also, the density of the material showed a decrease of <.10%.

A contract was accepted by the United Carbon Products Company Inc. on May 8, 1947 with the U. S. Atomic Energy Commission to establish a plant for purifying graphite and produce 50,000 lbs of high purity graphite having an ash content of < 50 ppm and boron of <.10 ppm.

High purity graphite was produced at the rate of 900 lbs. per day, complete with a control analysis from the laboratory established within the plant. The analytical procedures were those recommended by the National Bureau of Standards.

Preliminary work established the proper method of packing the material in the electric resistance furnaces for obtaining the high temperatures desired (2400°C). Further work determined the proper amounts of processing materials necessary for good results.

This report will give a summary account of the processing procedure and production facilities of the plant mentioned above.

PLANT ESTABLISHMENT

The United Carbon Products Company Inc. leased industrial property in Bay City, Michigan, consisting of a building having 9,000 square feet of floor space, and surrouding land suitable for expansion.

SERVICE FACILITIES

Services to the building were inadequate for the operations, so that enlargement of the following services were necessary: water, sewer, electric power, gas, and ventilation.

NEW CONSTRUCTION

Additions within the original structure were made to include a laboratory, office, guards' reception room, locker-shower room, and power control room.

SECURITY CONSTRUCTION

The maintenance of security for the operation of restricted areas made it necessary that the building be surrounded by a steel fence, the windows painted and covered with heavy screens, and flood-lights be mounted in suitable positions.

EQUIPMENT

Four electric carbon granular resistance furnaces were installed to carry out the processing. A power distribution system was included to supply 800 KW of power to each furnace. The power equipment is described in an earlier report.

Gas ducts and a scrubbing tower were erected to carry the obnoxious gases away from the units during operation.

PROCESSING PROCEDURE

The process of the United Carbon Products Company Inc. to prepare high purity graphite is shown in the flow sheet, Figure 4. The material to be purified is packed in all-carbon granular resistance furnace and each alternate bar has a gas tube placed under it so that the processing materials may be introduced into the high temperature zone, wherein the bars are situated. Figure 5 shows an elevation and section of the gas tube positioning relative to a single bar. However, each load of 30 bars has 15 such tubes. A closed end carbon tube is placed against a bar in the bed to read temperatures by use of an optical pyrometer. Dry nitrogen is used to flush out the pyrometer tube when reading is taken.

The procedure is outlined graphically on Figure 2 where the time temperature curve shows the temperature levels and superimposed on the curve is the limits wherein the processing chemicals are used. When heating is started the carbon tetrachloride is passed into the zone where the graphite is being heated. The carbon tetrachloride is carried in by saturation of dry nitrogen in a saturation trap which is heated by the use of waste hot water coming from the cooling of the electrodes. The CCl_4 is passed in for 3-$\frac{1}{2}$ hours at which time it is discontinued and $C_2Cl_2F_2$ (Freon "F-12") is passed in for 6.5 hours. Sometimes, the "F-12" is added beyond 6.5 hours to make sure that at least 60 lbs. has been used. It will be noticed from Figure 2 that the $C_2Cl_2F_2$ is added at a temperature above 1900° C; this is done to insure that the gas is well above the range where the F_2 could reform with the graphite to make CF_4. Also, it is desirable that CCl_4 be used until 1860°C has passed so that the magnesium and calcium present will go off as chlorides instead of fluorides, because the fluorides of these elements boil at 1865°C (approx.).

The typical run shown in Figure 2 consumed the materials and power as shown in Table I. Also included are several other runs.

TABLE I

RUN NO.	Wt. lbs	KWH	CCl_4 lbs	"F-12" lbs	N_2 ft^3	Max. Temp. °C.
C-8	874	5010	63	61	125	2460
B-24	866	4700	70	61	120	2339
D-9	876	4695	58	61	105	2375
A-29	872	4920	70	55	125	2470

When 10 hours total elapsed time has transpired, the power is discontinued. "F-12" may be added beyond this time to make up the required 60 lbs, but this may take less than an hour, during which time the furnace will have cooled to 2200°C. Beyond this point the furnace is cooling down.

The salts and volatile halide gases pass off in the hooded collector system built over the furnace and are absorbed in the water spray scrubbing tower provided. Some of the less volatile salts are deposited on or in the coke insulating bed, but apparently there is not any recontamination due to diffusion of this material during the cooling period.

The furnace cycle is as follows: Heating, 10 hours; Cooling 48 hours; Loading, 8 hours; making a 3-day cycle for each furnace, which gives a production rate of 900 lbs per day.

When the material has cooled sufficiently, it is removed from the furnace and taken to the sampling room, and sampled according to the procedure outlined and appended to this report. (See Appendix "A"). The boron analysis follows the scheme of Rodden and Richmond[4] for analysis of small quantities of boron in the project materials. The ash is obtained by weighing the amount of residue from igniting 100 gms of graphite in the platinum crucible at 750°C.

The typical results of purifying AGHT graphite in this manner are shown in Table II. Also shown in this table are scattered results of other types of graphite processed. They were reported as "good functionally" as an indication of the results, but no further report was received by this organization.

TABLE-II

Type MH	Initial Ash ppm	Final Ash ppm	Initial Boron ppm	Final Boron ppm	Remarks
AGHT	600	< 10	0.60	.02	
AGOT					Functionally good
CS121			?	.06	Functionally good at HEW

By way of further explanation, the process as employed by the United Carbon Products Company Inc. makes use of the reaction of the various elements present in graphite, either as compounds or in solution, with the halogens, namely chlorine and fluorine, as obtained by the dissociation of halogenated hydrocarbons at elevated temperatures. The following examples are illustrations of the reactions occurring:

1. $CCl_4 \longrightarrow C + 2Cl_2$

$MgO + Cl_2 \longrightarrow MgCl_2 + CO \uparrow$

2. $CaC_2 + Cl_2 \longrightarrow CaCl_2 + C$

3. $Al_4C_3 + 6Cl_2 \longrightarrow 4AlCl_3 + 3C$

$Al_2O_3 + 3C \quad 3Cl_2 \longrightarrow 2AlCl_3 + 3CO \uparrow$

4. $5C + V_2O_5 + 5Cl_2 \longrightarrow 2VCl_5 + 5CO \uparrow$

etc.

The metallic chloride so formed are volatized and condense in a cooler region, usually on top of the coke bed or in the cold air sweeping across the top of the charge.

However, in the case of boron, it is not possible to remove this element by the use of chlorine alone. By using a hydrocarbon gas containing fluorine such as C_2F_2 Cl_2 at temperatures above 2000°C it is possible to remove the boron to an acceptable level. The boron is present in the mass of the graphite in solution and calls for a very highly reactive agent such as fluorine to remove it. The boron trifluoride formed passes off very readily inasmuch as it boils at -101°C. However, it is to be remembered that the use of fluorine must be done only under the controlled conditions previously outlined, to avoid erosion and disintegration of the graphite due to the formation of CF_4 at lower temperatures[1].

PRODUCTION RESULTS

The data and results given in* Tables III, IV, V, and VI are the results of several trial runs in the units, followed by active production of acceptable high purity graphite. As will be noted, there are more runs in the A and B units because these furnaces were designed and built previous to the choice of a final design. The temperatures shown indicate a lower level than 2400°C in some cases, but these are low when correlated to carbon index rods used to tell temperatures by relative graphitization. Readings taken by an optical pyrometer are from 100° to 200° lower than the actual temperatures of the graphite bars as shown by the index rods.

Some of the material processed was for the Hanford Engineer Works, Richland, Washington, and was done in runs numbered "A-11A" and "B-6". The starting material was CS-121 and the final results were indicated as "functionally good". A variation in processing procedure was employed for run "A-11A", wherein anhydrous ammonia gas was substituted for nitrogen.

*Consolidated into Appendix "B" - Summary

CONCLUSIONS

1. Graphite having a cross-section of 4-5/8" x 4-5/8" can be purified to less than 0.10 ppm boron and less than 10 ppm total ash.

2. Furnace loads of 900 lbs. consisting of 30 blocks of graphite 4-1/8" x 4-3/8" x 26-$\frac{1}{2}$" can be purified to acceptable limits.

3. Graphite can be heated in all carbon bed electric resistance furnace by packing the spaces between the bars with graphitized granular resistor material and then packing the load with ground calcined petroleum coke to serve as the thermal insulation. By packing in this manner the current will follow the central core of graphitized material.

4. Larger loads can be processed, if more power is available.

5. Ammonia (anhydrous) is a suitable substitute for nitrogen as a carrier gas.

6. The density of the purified graphite is reduced by less than 0.10% by weight.

APPENDIX "A"

1. The procedure used on Run "A-1" only was carried out according to the following directions:

Each bar will be sampled by cutting a $3\frac{1}{2}$" piece to be taken from the left end of the odd numbered bars and from the right end of the even numbered bars. A $\frac{1}{4}$" slice will be cut from the end of the sample.

The sample bars will be drilled 16 times along the major axis with a $\frac{1}{2}$" drill and the drillings will constitute the sample for the bar. These drillings will be in excess of 250 grams per bar.

The sample drillings from bars 1 & 10; 2 & 9; 3 & 8; 4 & 7; 5 & 6 will be combined and thoroughly mixed, giving five composite samples for the furnace charge.

Three additional samples of 25 grams will be taken from the top surface of three of the end pieces. They will be obtained by drilling not more than $\frac{1}{4}$" into the bar. These samples are to be run for boron only. Note: As surface impurities are considered to be excessive these samples are to provide a check on the boron content of the bar surface.

Each sample, consisting of the composite of two bars, is in excess of 500 grams. The sample will be split in half, one half being sealed in a glass jar for reference purposes and the other half being used for the analysis. As all analyses are to be run in duplicate the sample will be split into two lab samples of approximately 125 grams each. 25 grams are to be used in running the boron analysis and the remaining portion of 100 grams is to be combined with similar portions of equal weight from the other four samples to give a 500 gram lab sample for total ash analysis. Since total ash is expected to be less than 20 ppm, it will be necessary to have a sample of at least 500 grams.

The complete analyses for the first few runs will be as follows:

For boron:
- 5 analyses in duplicate on the five bar-composites
- 3 analyses in duplicate on the surface drillings from three bars.

For total ash:
- 1 analysis in duplicate on the composite of the five samples

2. Several test runs were conducted in "A" and "B" furnaces while the heating and processing characteristics were being determined. The sampling procedure was altered somewhat so that it was as follows:

A sample piece approximately $1\frac{1}{2}$" to 2" is cut from alternate ends of all the bars except 5, 10, 15 and 20 so that the remaining portion of the bar shall be $24\frac{1}{2}" \pm 1/8"$. Each of the sample pieces shall be drilled 16 times, using $\frac{1}{2}$" drill and the drillings taken from each bar shall be combined and thoroughly mixed to form a single composite sample for the furnace run. This composite shall be split into two parts, one for reference (which shall be adequately bottled, labeled and stored), and one for analysis. Each of these two parts will be approximately 1700 grams. The analysis, as all analyses, shall be run in duplicate and the average value taken as the analytical value.

Bar nos. 5, 10, 15 and 20 are not sampled as above, but instead a 2" sample is cut from both ends of each bar and each sample piece is drilled 16 times using a $\frac{1}{2}$" drill. The total weight of the composite of these drillings will be approximately 1100 gms. This composite will be split into two parts, one for sample and one for reference. The remaining central portion of these four bars shall be sampled by 16 drillings through the bar parallel to the transverse axes, 8 parallel to each axis. These drillings should be spaced along the longtitudinal axis to obtain a representative sample. These drillings from the central parts of the 4 bars shall be combined into a single composite sample, this composite split into two parts, one for reference and one for analysis.

The three analyses outlined above, namely,

a. The routine end sample for the furnace charge (omitting bars 5, 10, 15 and 20).
b. The double end sample of bars 5, 10, 15 and 20.
c. The samples of the middle sections of bars 5, 10, 15, & 20.

will constitute the test samples taken on the test runs from A-8 up to such time as the furnaces are considered producing acceptable material.

3. After the units were accepted as producing, the samples were prepared in this manner and served for the bulk of the production of pure graphite.

A sample piece approximately $1\frac{1}{2}$" for 26" bars, and approximately 2" for $26\frac{1}{2}$" bars is to be cut from alternate ends of all bars of a furnace charge, except for bars 5, 10, 15 and 20. Thus, the remaining portion in the bar shall be approximately $24\frac{1}{2}$" $\pm$ 1/8". Each of the sample pieces shall be drilled 16 times using a clean $\frac{1}{2}$" drill, and the drillings taken from each bar shall be combined and thoroughly mixed to form a single composite sample for the furnace run. This composite shall be split into two parts, one for reference (which shall be adequately bottled, labelled and stored), and one for analysis. Each of these two parts will be approximately 1700 grams. The analysis, as all analyses, shall be run in duplicate and the average value taken as the analytical value.

Bar Nos. 5, 10, 15 and 20 are not sampled as above, but instead a 2" sample piece is cut from both ends of each bar and each sample piece is drilled 16 times using a $\frac{1}{2}$" drill. The total weight of the composite of these drillings will be approximately 1100 grams. This composite will be split into two parts, one for sample and one for reference. A 4" section shall be cut from the center of the approximately 22" length bar which remains at this point. The 4" section of these four bars shall be sampled by 16 drillings through the bar parallel to the transverse axis, eight parallel to each axis. These drillings from the central part of the four bars shall be combined into a single composite sample, this composite split into two parts, one for reference and one for analysis.

The three analyses outlined above, namely

a. The routine end sample for the furnace charge (omitting bars 5, 10, 15 and 20, and

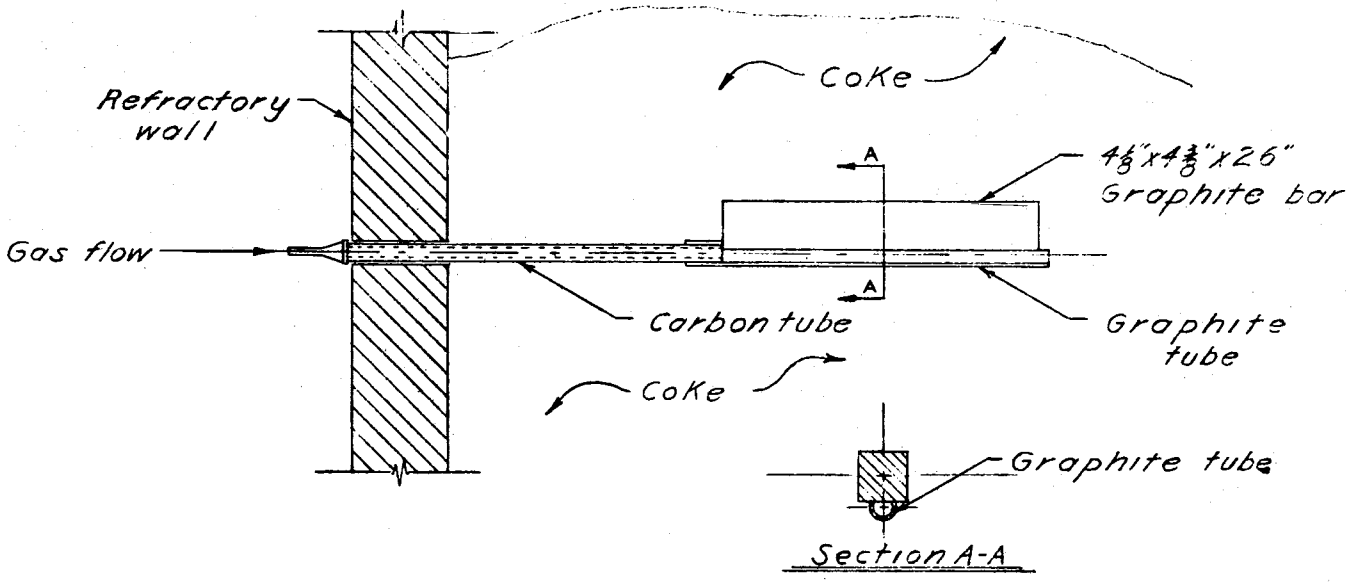
b. The double end sample of bars 5, 10, 15 and 20, and

c. The samples of the 4" middle section of bars 5, 10, 15 and 20,

will constitute the test samples taken.

4. The sampling procedure described above continued on until nearly 50,000 lbs were completed. At this time (May 7, 1948), the procedure was altered so that the less samples were taken.

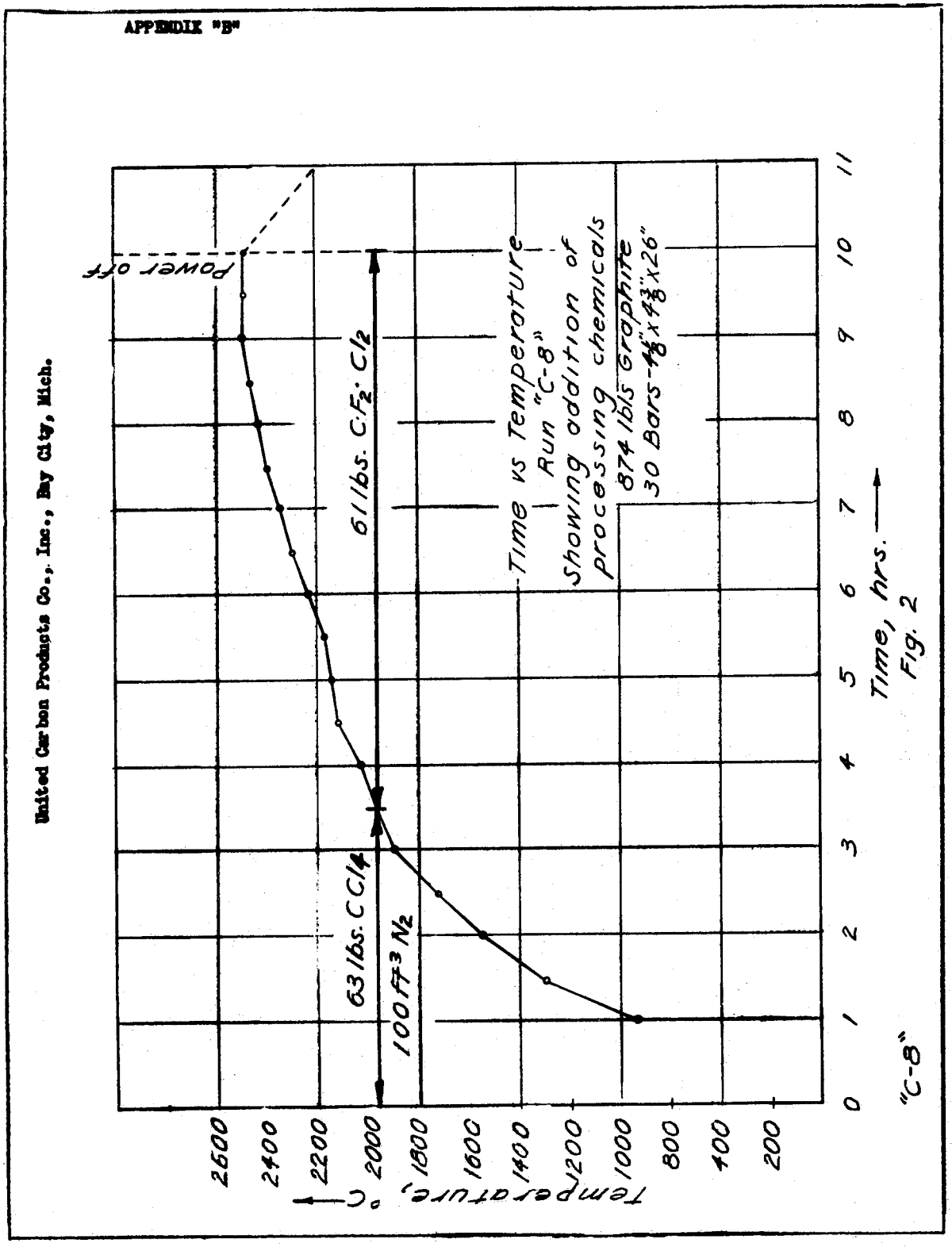
> A sample piece approximately $1\frac{1}{2}$" for 26 bars, and approximately 2" for $26\frac{1}{2}$" bars, is to be cut from alternate ends of all bars of the furnace charge. Thus, the remaining portion in the bar shall be approximately $24\frac{1}{2}$" $\pm$ 1/8". Each of the sample pieces shall be drilled sixteen (16) times using a clean $\frac{1}{2}$" drill, and the drillings taken from each bar shall be combined and thoroughly mixed to form a single composite sample for the furnace run. This composite shall be split into two parts, one for reference (which shall be adequately bottled, labelled and stored), and one for analysis. Each of these two parts will be approximately 1700 grams. The analyses, as all analyses, shall be run in duplicate and the average value taken as the analytical value.



GAS TUBE POSITION

Fig. 1

APPENDIX "B"



United Carbon Products Co., Inc., Bay City, Mich.

APPENDIX "B"

United Carbon Products Co., Inc., Bay City, Mich.

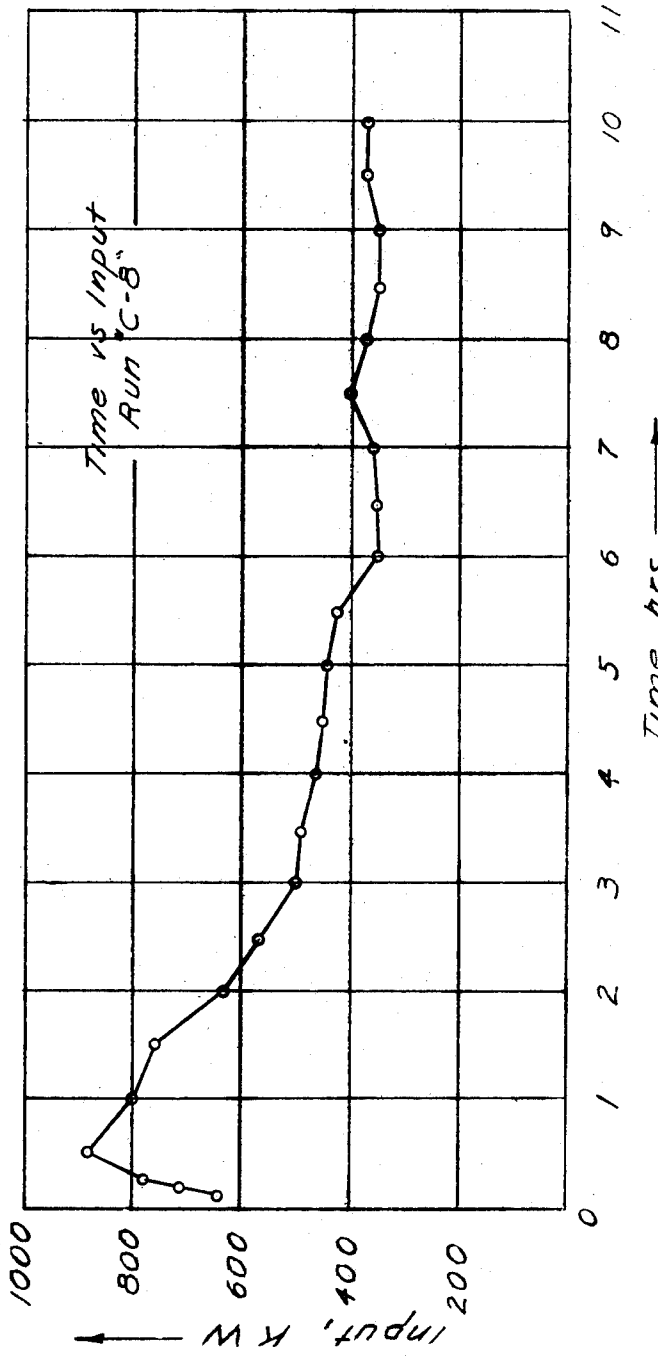
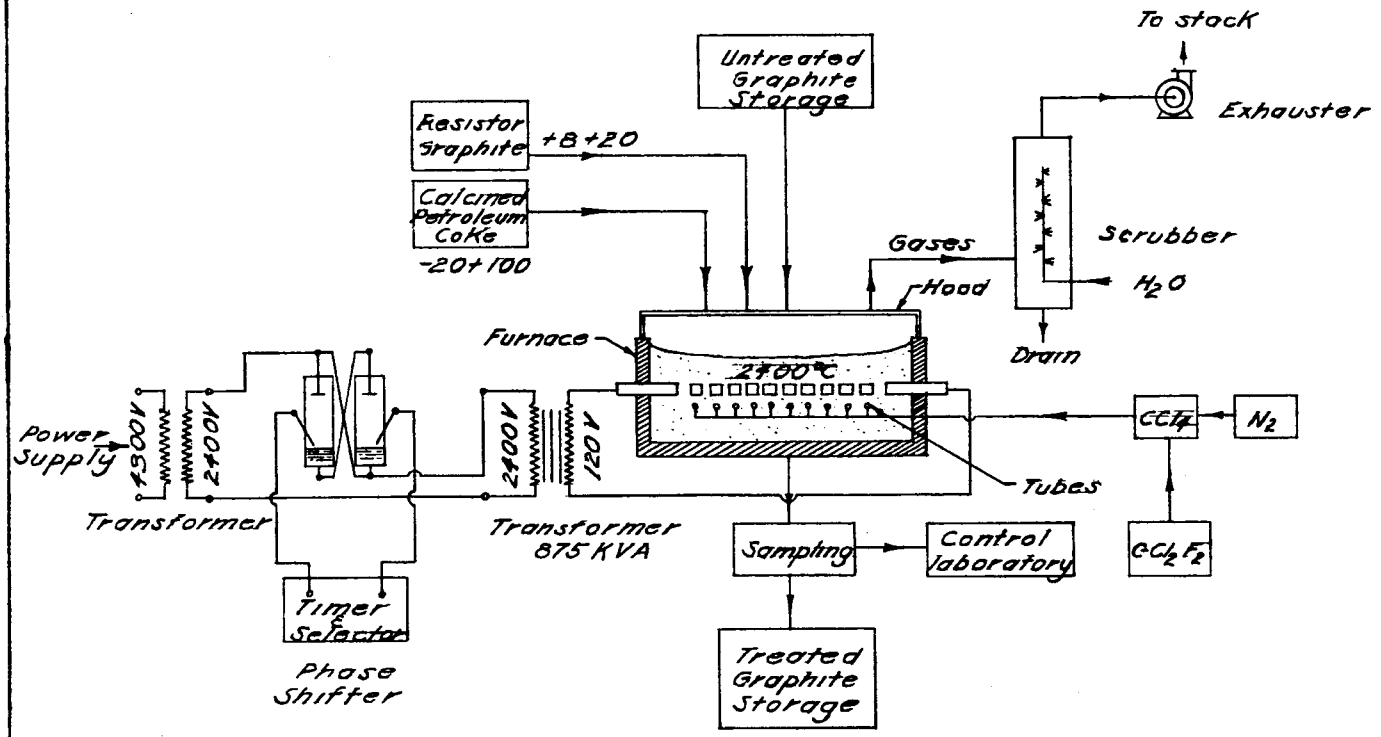


Fig 3

United Carbon Products Co., Inc., Bay City, Mich.

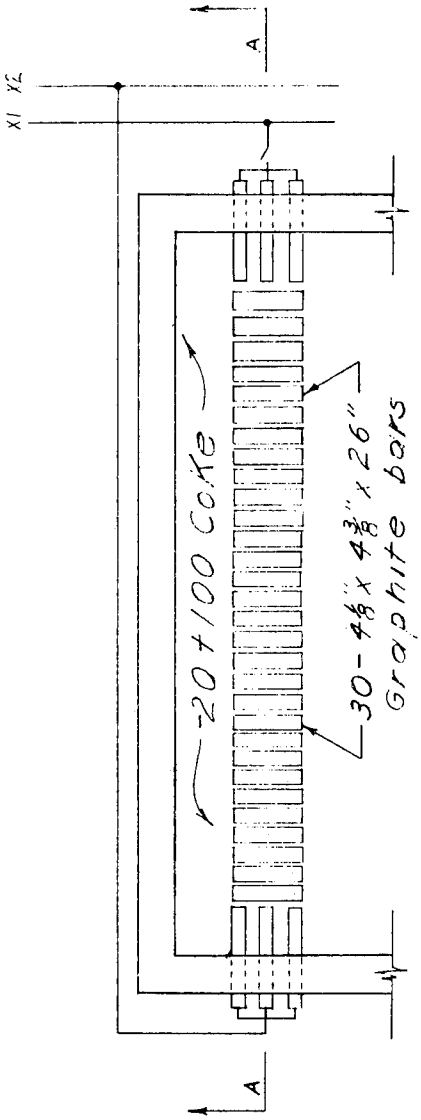


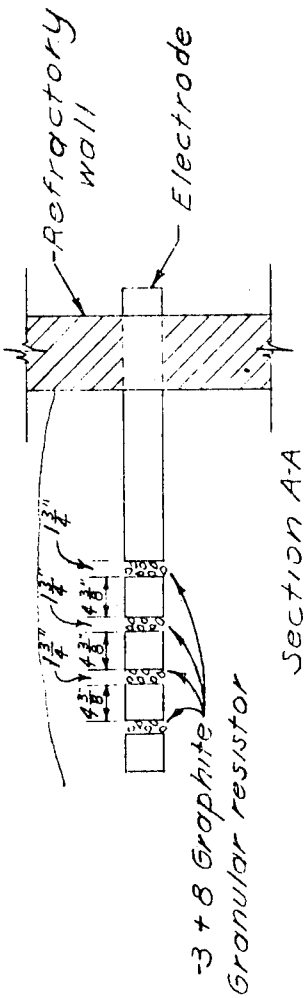
FLOW SHEET FOR GRAPHITE PURIFICATION

Fig. 4

APPENDIX "B"

United Carbon Products Co., Inc., Bay City, Mich.





Section A-A

Section Thru Bars
Fig. 5

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APPENDIX "B"

SUMMARY OF OPERATIONAL DATA ACCORDING TO INDIVIDUAL "RUNS"

	Maximum Variation	Average* Range
Maxium Temperature Observed	2120° C to 2510°C	2250 - 2400°C
"F-12"	30 lbs to 89 lbs	60 - 65 lbs
CCl_4	20 lbs to 98 lbs	40 - 50 lbs
N_2	10 cu ft to 450 cu ft.	100 - 300 cu ft
Boron Analysis	.00 ppm to .10 (spec)	.03 - .06 ppm
Total Ash	1 ppm to 17 ppm	1. to 8. ppm

As the runs were made for production purposes no attempt to control the variables was made. No correlation between the variables and the purity obtained can be drawn from the operational data.

*Majority of the runs fall within these ranges

APPENDIX "C"

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4. Rodden, C. J. Richmond, M. S., National Bureau of Standards unpublished report, "Determination of Small Amounts of Boron in Project Materials".
5. Sermon, G. T., "Heating Tests in Granular Resistance Furnaces for Preparing High Purity Graphite", United Carbon Products Company Report No. 6, (1947)

APPENDIX "D"

PREVIOUS REPORTS

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