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Characteristics of pyrometric cone equivalent test furnaces

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CHARACTERISTICS OF PYROMETRIC CONE EQUIVALENT TEST FURNACES

BY

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Characteristics of Pyrometric Cone Equivalent Test Furnaces

I. Introduction

Though the method of determining the Pyrometric Cone Equivalent of various silicate materials used in the refractories industry has been standardized by the American Society for Testing Materials (A. S. T. M. Designation: C24-35) as to the rate of heating, method of preparation of sample, mounting of test cones, and the interpretation of results, there still remains some variation in the results obtained by different operators using different types of P. C. E. furnaces.

The three types of furnaces most generally used are; the Fulton-Coursen Granular Resistance Furnace, the Denver Fireclay Furnace developed by the American Refractories Institute using gas, and the General Refractories' Oxy-acetylene Furnace. The characteristics of these furnaces may influence the results obtained in testing. It is the purpose of this paper to study such effect.

II. Review of Literature

According to Fairchild and Peters[1] the factors that control the deformation of cones which may be variable with the technique of the user are: (1) mounting and position; (2) oxidation of the organic binder; (3) release of water and carbon dioxide; (4) rate of heating; (5) furnace atmosphere. The first two factors have been standardized by the American Society for Testing Materials in Designation: C24-35 by standard procedure for mounting and preparing the cones. Rate of heating is controlled by a standard schedule which has been adopted by the same authority (see Method).

It is desirable to control the rate of heating because in addition to the effect of the cone absorbing heat from the test furnace, there is also a heat of reaction produced in the cone due to the pyrochemical reactions which result between the fluxing compounds added in the cone to control the melting and deformation point.[2]

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1 "Characteristics of Pyrometric Cones", Fairchild & Peters. Jour. Am. Cer. Soc., Vol. 9, No. 11, p. 706.

2 "Melting Characteristics of Pyrometric Cones", W. J. McCaughey. Properties and Uses of Pyrometric Cones, p. 34.

The melting and deformation call for absorption of heat. It is necessary, therefore, that this heat be supplied at the same rate upon each subsequent test if the results are to be comparable. This requires a standard and uniform rate of temperature rise.

The atmosphere of the furnace used has not been standardized by the A. S. T. M., but the Designation merely states that a neutral or oxidizing atmosphere should be the condition of the test and that excess reducing conditions should be avoided.[3] Fairchild and Peters state that the contamination of cones by gases free from sulphur is not serious because there is a large excess of air in the furnace, and that even slightly reducing atmospheres do not affect the deformation of the cones.[4] A continuous and strong reducing atmosphere, however, will allow the deposition of carbon on the surface of the cone forming a refractory skin.[5] This should affect the deformation of cones even if the condition is

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3 "Standard Method of Test for P. C. E. of Refractory Materials", _Manual of A. S. T. M. Standards on Refractory Materials_, Jan. 1941, p. 19.

4 "Characteristics of Pyrometric Cones", op. cit., p. 724.

5 "Correct Cone Usage", _Properties and Uses of Pyrometric Cones_, p. 23.

only slight when precision results are desired.

Of course, other factors which affect the selection of a P. C. E. furnace for the routine plant or laboratory testing are the cost, convenience, and portability of the apparatus. The range of temperature of deformation which the furnace must handle will also be a factor to consider, particularly in the case where the furnace is to be used in plant testing work.

R. S. Bradley, Director of Research at A. P. Green Fire Brick Co., Mexico, Missouri, has compared the three types of furnaces on the basis of plant adaptability and cost.[6] According to him the Denver Fireclay furnace of the type developed by the American Refractories Institute is the best adapted to plant conditions because: (1) ease of control; (2) uniformity of results; (3) low operating costs praticularly when natural gas is available. The furnace will hold sixteen standard and test cones and is equippedwith an arrangement so it can be fired with either natural or manufactured gas. When fired with bottle gas it can be made portable. It is equipped with a blower and pre-mixer for mixing the gas, oxygen, and air. Temperatures up to cone 40 can be attained by the use of oxygen; without

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6 "The Principal Physical Tests for Fireclay Refractories", R. S. Bradley. <u>Brick and Clay Record</u>, April, 1940, p. 67.

oxygen, cone 32 can be reached.

Mr. Bradley also points out that though the General Refractories' Oxy-acetylene type of furnace will reach cone 39 and higher and is portable, the cost of operation is higher and more experience is required to operate it.

The only drawback to the Fulton-Coursen type furnace is the high initial cost of electrical controlling equipment required, though the furnace is lower in cost than the other two. Operation of the furnace above cone 34 without excessive muffle maintainence is difficult with the alundum type muffle used.

He gives comparative costs as follows:[7]

Gas-fired Denver Fireclay, A. R. I. type: $175.00.

Oxy-acetylene, General Refractories type: including furnace, torches, and gages, $250.00.

Fulton-Coursen Granular Resistance type: $750.00 ($50.00 for the furnace and $700 for the electric control equipment.)

Data collected on the cost of operation of the Oxy-acetylene furnace by L. J. Trostel of the General Refractories Co. Laboratories was as follows:

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[7] "The Principal Physical Tests for Fireclay Refractories", op. cit., p. 68.

[8] Letter of December 30, 1940 to Doc. P. G. Herold, Missouri School of Mines and Metallurgy.
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Total runs:	32
Determinations :	136
Oxygen used :	3720 cu.ft.
cost :	$44.88
Acetylene used :	2691 cu.ft.
cost	$68.62
total cost :	$113.50
cost per run :	3.54
cost per determination:	.83

The protection tube used in the furnace is made 12" long and cut in four 3" lengths. about 15 runs were made per each 3" section and the cost averaged $0.10 per run.

It is evident from these figures that the cost of operating this type furnace is not excessive when the samples to be determined are of the same P. C. E. range within one or two cones, or when the P. C. E. is determined merely to meet specifications where the value must be greater than a given cone.

III. Materials Used

The clays used for the comparison of the P. C. E. values in the three types of furnaces were of the range: cone 29-34, which covers the refractory range of clays. Clays from cone 31-34 were obtained from A. P. Green Fire Brick Co., Mexico, Missouri, and were designated as follows:

Ladle	cone 31-32
220	" 32½-33
330	" 33-34

A light-colored Missouri plastic fireclay having a P. C. E. of cone 29-30 was also used in the comparison.

IV. Methods

In the preparation of the test cones the A. S. T. M. Designation: C24-35 was followed. The dry clays were screened through No. 65 Tyler standard screen (equivalent to A. S. T. M. No. 70 screen), pre-calcined to 1000°C, and mixed with gum arabic and water to the proper degree of plasticity. Cones of the standard size were formed: tetrhedrons 5/16" on the sides at the base and 1" in height. They were dried in air at room temperature.

The plaques for the Fulton-Courseen and Oxy-acetylene furnaces were made by placing four clay and five standard cones of P. C. E. slightly higher and slightly lower than the reputed value in a circle, imbedded to about 3mm and set at an angle of 82° to the vertical in such a manner that the cones would bend tangentially outward.

Plaques for the Denver Fireclay furnace were made 2½" in diameter, the cones imbedded the same amount and set at the same angle, but set in such a manner that they would bend inward toward the center.

The plaques were fired on the standard P. C. E. schedule according to A. S. T. M. Specification, Designation; C24-35;

To reach cone 20 — 45 minutes

Time interval to:

cone 25	20 minutes
26	6
27	4
28	4
29	10
30	4
31	12
32	8
32½	9
33	9
34	6

End points were noted when the clay cones bent down and the tips touched the top of the cone plaque.

Rate of heating was controlled with a platinum, platinum-rhodium thermocouple calibtrated with a Leeds and Northrup Potentiometer up to cone 20. When this temperature was reached (the couple's limit) it was removed and covered with fine-grained greg to protect the tube from heat shock breakage. Above cone 20 the rate of heating was observed with a dissappearing filament type optical pyrometer. In the Oxy-acetylene furnace auxiliary control was facilitated by placing cone 20 in a small wad of diaspor next to the cone plaque.

Analysis of the atmosphere in each furnace was made at various temperatures with a portable Orsat apparatus after the samples had been taken in sample bottles. (see Fig. 6.) The samples are collected in the bottle A by inserting the silica tube B into the the furnace, opening the pinch cocks D, starting the vacuum pump D, and then opening the valve E. The rate of flow of gas from the furnace was observed by the rate of flow of the bubbles in the water trap F. The water trap also tends to cool the gases as they pass through the water and reduce all determinations to the same conditions.

Absorption of the gases is negligable, since the water in the trap is slightly adidified with a few drops of sulphuric acid. After the gas from the furnace has been allowed to flow through the system for two or three minutes, the valves are all closed, the pinchcocks on the sample bottles closed, and the sample set up with the Orsat apparatus.

The pressure of the gas in the sample bottle is not sufficient to cause the gas to diffuse into the graduated tube in the Orsat apparatus, so the gas is displaced into it by allowing slightly adidified water from a constant pressure head G to run into the bottle after it has been connected to the inlet of the apparatus.

Once the sample is in the tube, the stopcock on the inlet is closed. The gas sample, now in the apparatus, is forced into the bulbs containing the absorbing solutions by raising the bottle H. It is exhausted back into the graduated tube by lowering the bottle again. Upon each subsequent absorption the difference in volume is read. If 100cc is the volume of the original sample, the volume loss in each case will be the percent of the gas absorbed. The absorption must be repeated until a constant reading is obtained three times in succession.

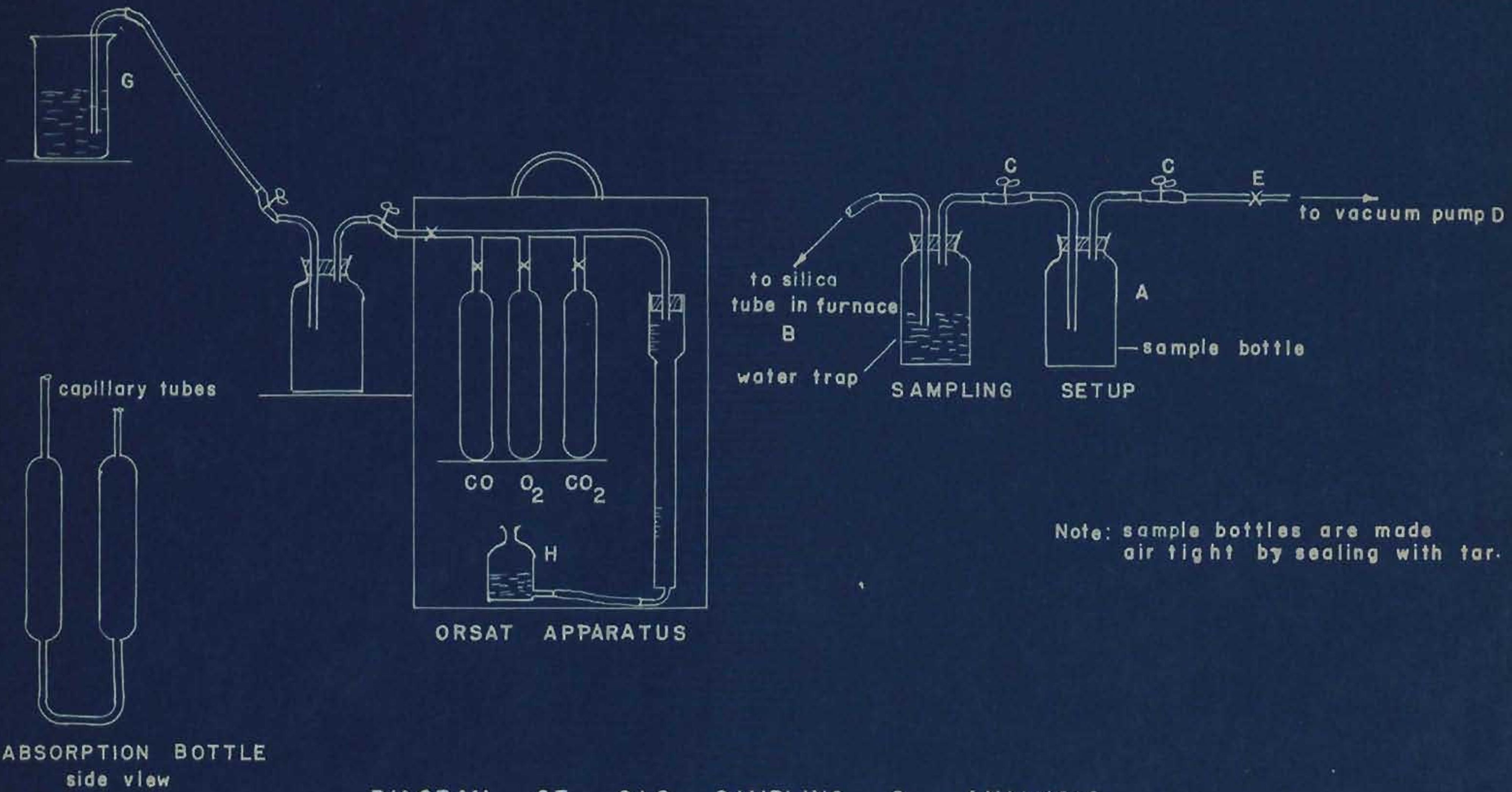


DIAGRAM OF GAS SAMPLING & ANALYSIS

APPARATUS SETUP

The solutions in the bulbs are composed of the following: for CO_2 absorption: 40% solution of KOH in water; for O_2 absorption: potassium pyrogallate solution made by weighing 5 grams of pyrogallol and dissolving in 100cc of KOH solution which has been made by dissolving 500g KOH in a liter of water; for CO absorption: cuprous chloride solution made by filling a bottle containing about 3/8" layer of CuO in the bottom with concentrated hydrochloric acid. A bundle of copper wire is kept in the solution to keep it reduced. The clear solution on top is used for the analysis.

The absorption is carried out by absorbing carbon dioxide first, then oxygen, and finally carbon monoxide.

In the case of the <u>investigation of the draft required</u> to furnish necessary air for the combustion of the gas in the Denver Fireclay furnace, the setting of the manifold and the rehostat for each temperature was marked. After the furnace had cooled, these settings were made and the Ellison Standard Draft Gage attached to the opening in the top of the furnace and the draft produced by the fan read as inches of oil in the gage.

The <u>effect of varying the grain sizes</u> on the operation of the Fulton-Courson Resistance furnace was studied by operating the furnace on the standard P. C. E. schedule and noting the voltage and current supplied to the circuit by the motor generator set as the temperature rose. Before start of the run, the granules were packed closely together to give the minimum current, (i. e., increase resistance and decrease current). Control of the current through the carbon granule resistance was facilitated by an external resistance provided on the switch board. Three grain sizes of carbon were used:

Thru 8 on 10 mesh carbon granules
" 10 " 12 " " "
" 12 " 14 " " "

V. Data and Results

Clay	Fulton-Coursen furnace	Oxy-acetylene furnace	Denver Fireclay furnace
Ladle	cone 31		cone 31
330	" 34	*cone 33	" 34
220	" 33		" 33
Mo. plastic fireclay	" 30	*cone 27	" 29

* Standard cones had frozen, close observation showed a thin refractory skin on the cones, light gray in color.

The data for the atmosphere of the furnaces at various temperatures is plotted on the curves in Figures 1, 2, and 3.

Draft required to operate the Denver Fireclay furnace is plotted in Fig. 4.

Fig. 5 shows the results of varying the grain size in the Fulton-Coursen furnace and observing the volt-amperes required to follow the standard schedule.

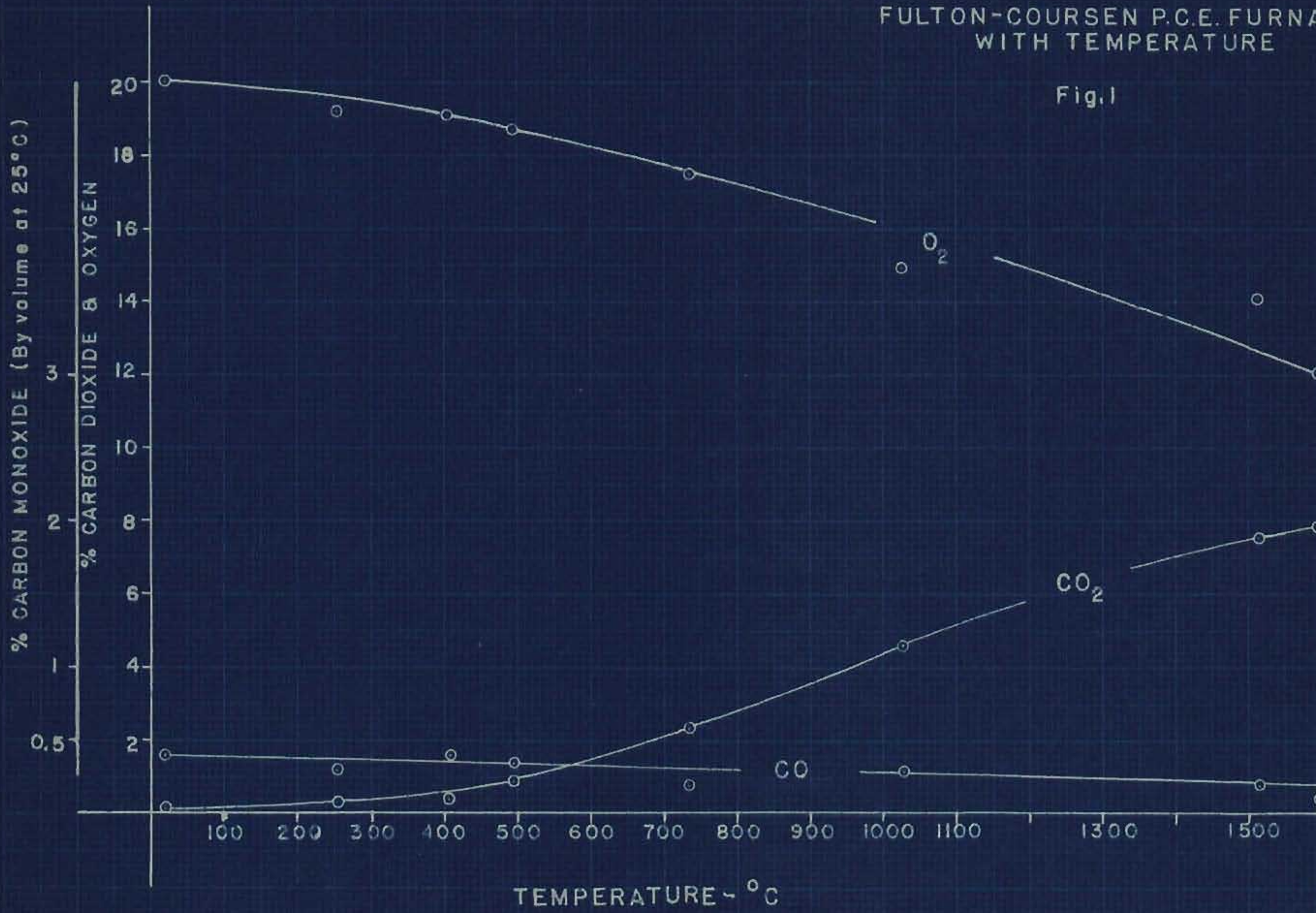
$\frac{\Delta EI}{\Delta T}$ represents the change in volt-amperes per unit change in temperature and is found by plotting the average curve through the points and finding the slope of the tangent to this curve where the rate of change becomes constant.

Results are as follows:

C granule size	$\Delta E/\Delta T$
10	0.75
12	0.84
14	1.07

From the International Critical Tables, Vol. II p. 86 the electrical resistivity of carbon is as follows:

Temp, °C	Resistivity
25	4.6×10^{-3} ohms/cm^3
1000	3.7 " "
1200	3.7 " "
1400	3.7 " "
2000	3.6 " "

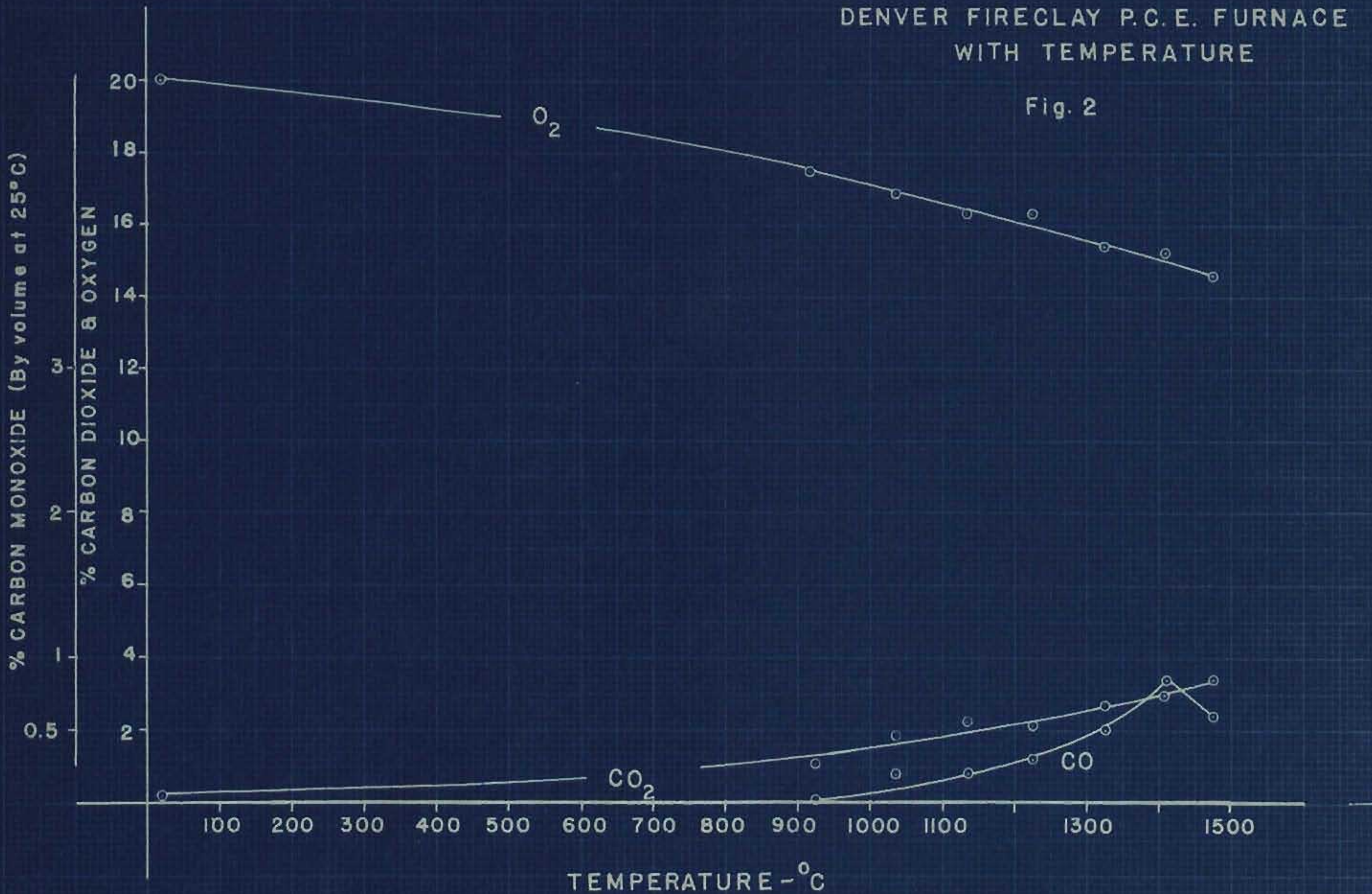


VARIATION OF ATMOSPHERE OF
FULTON-COURSEN P.C.E. FURNACE
WITH TEMPERATURE

Fig. 1

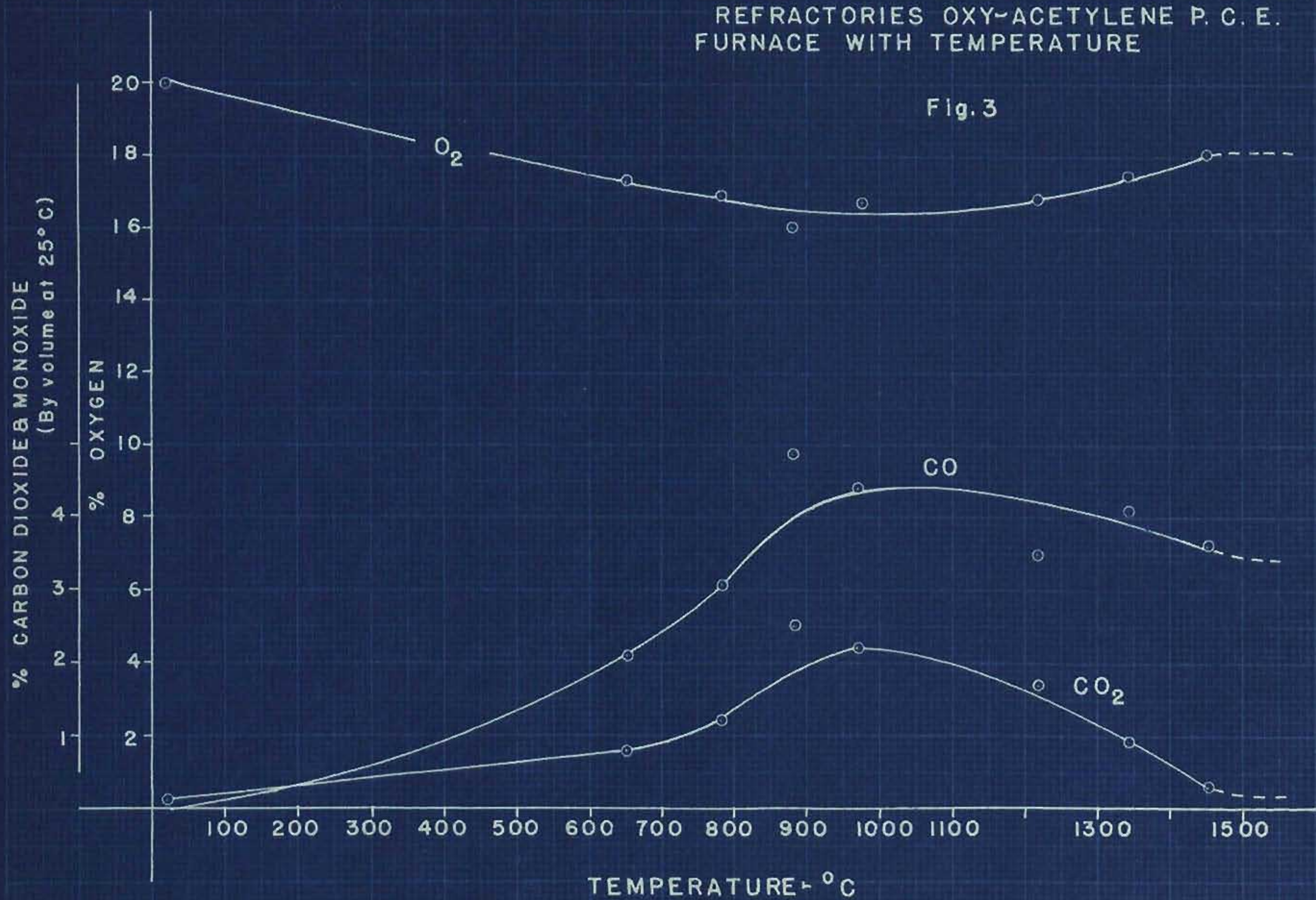
VARIATION OF ATMOSPHERE OF
DENVER FIRECLAY P.C.E. FURNACE
WITH TEMPERATURE

Fig. 2



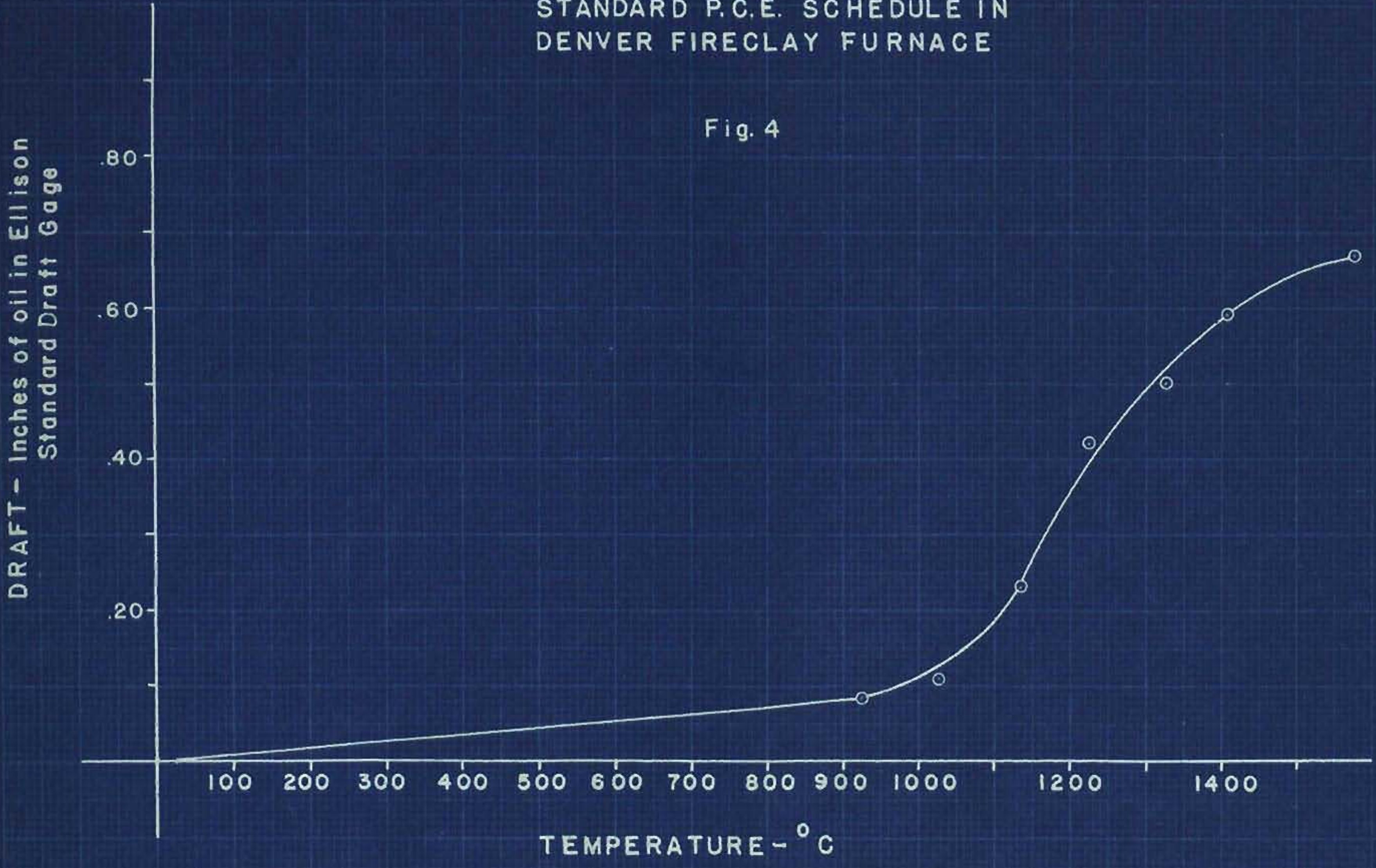
VARIATION OF ATMOSPHERE OF GENERAL REFRACTORIES OXY-ACETYLENE P. C. E. FURNACE WITH TEMPERATURE

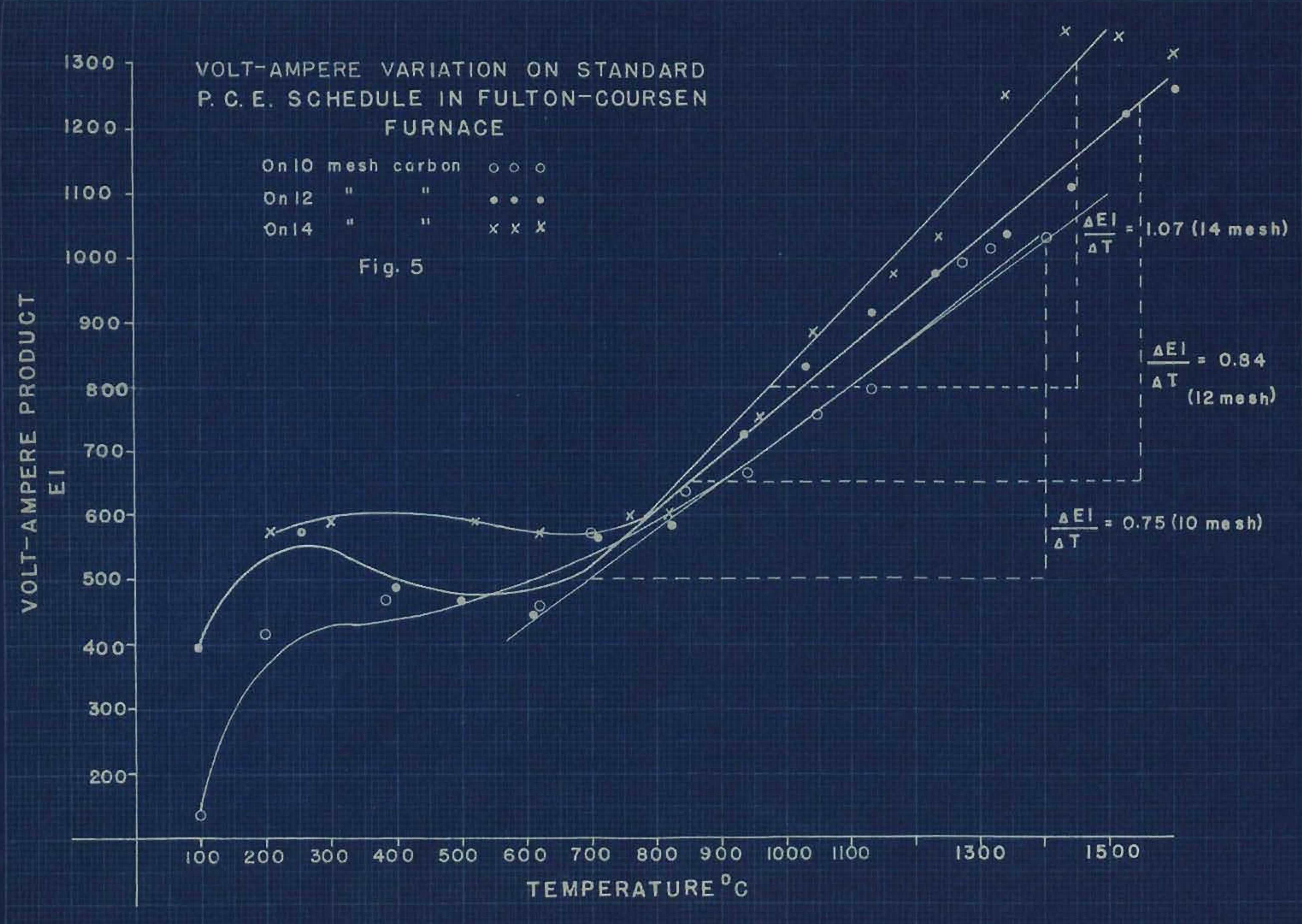
Fig. 3



DRAFT REQUIRED TO FOLLOW
STANDARD P.C.E. SCHEDULE IN
DENVER FIRECLAY FURNACE

Fig. 4




VOLT-AMPERE VARIATION ON STANDARD
P. C. E. SCHEDULE IN FULTON-COURSEN
FURNACE
On 10 mesh carbon ○ ○ ○
On 12 " " • • •
On 14 " " x x x
Fig. 5
VOLT-AMPERE PRODUCT
EI
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
200
300
400
500
600
700
800
900
1000
1100
1300
1500
TEMPERATURE °C
ΔEI/ΔT = 1.07 (14 mesh)
ΔEI/ΔT = 0.84 (12 mesh)
ΔEI/ΔT = 0.75 (10 mesh)

VI. Discussion of Results

Fulton-Coursen Carbon Granular Resistance Furnace: It will be noted from the curves in Fig. 1 that the atmosphere of this furnace is reducing. The percent of carbon monoxide, however, tends to decrease slightly until at 1600°C it is gegligable. Oxygen decreases with the corresponding rise in carbon dioxide, resulting from the oeidation of the carbon resistor.

Though the current supplied by the motor-generator set is alternating current, the following may be said to be true;

I =or rather is proportional to

$$\frac{E}{R_a + R_c + R_L}$$

where E is the voltage supplied, R_a is the resistance of the alumdum muffle, R_c is the resistance of the carbon granules and the carbon electrodes combined, R_1 is the resistance of the line, and I is the current through the furnace to which the temperature is proportional. This may be said to be true since the capacitive and inductive reastance in the circuit are comparatively small and remain constant. The resistance of the line is also constant. The resistance of the alundum muffle is not constant, but decreases mapidly with temperature. It is, however, still a non-conductor at 1600°C where its resistivity is about 190 ohms/cm^3.[9]

Carbon is a conductor of the current at any temperature, but offers enough resistance to the flow of current to cause heat to be dissapated, the amount of which will be proportional to the current flowing through it. Its resistivity decreases with temperature, however, (See data for table) and for the same voltage E, the current I will rise due to the decrease in resistance R_c. At 1000°C the resistivity becomes constant and a rise in current must be accomplished by an increase in voltage.

Thus in operating this type of furnace, an external resistance is provided to compensate for the decrease in resistance up to 1000°C and the rate of increase of the temperature is controlled by the use of this resistance.

Fig. 5 shows the variation of the volt-amperes (proportional to the power supplied) required to follow

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9. "Properties of Alundum", Norton Refractories, Oct. 1935, (catalog) p. 4.

the rate of heating on the standard P. C. E. schedule. The effect of the negative coefficient of resistivity of carbon is shown on the curve from 200-900°C where the volt-amperes required is almost constant or even decreases slightly. This is due to the fact that the voltage may be cut down to give enough current for the desired heating rate as the resistance of the carbon granules decreases. When the resistance of the carbon becomes constant (above 1000°C), the rate of increase of the volt-amperes becomes constant with the standard temperature rise. It is here that the effect of variation in grain size is noted. When the granules are smaller, they pack closer together, more carbon is present, and consequently more resistance is offered to the flow of the current. This requires that the rate of increase in the power supplied be greater.

Comparison of the value of $\Delta EI/\Delta T$, however, for the various grain sizes shown that its value does not vary greatly! For practical purposes any of the three grain sizes could be used with little variation in efficiency.

General Refractories' Oxy-acetylene furnace: It was noted that to hold the temperature down to the required rate, an excess of acetylene was essential because of excess heat when the acetylene was completely burned with oxygen. This gave rise to excessive reducing conditions in the atmosphere of the furnace (see Fig. 3).

Reducing conditions are easy to produce because of the nature of the compound, acetylene. Being an unsaturated hydrocarbon, it readily decomposes at 700-800°C according to the equation:[10]

$$C_2H_2 = 2C + H_2 + 55.3 \text{ kg. cal.}$$

It can be seen from this equation, that if insufficient oxygen is supplied in the torch to burn the carbon as fast as it is formed, it will be deposited on the cones in the furnace. Heat will still be furnished by the reaction as above and the hydrogen formed will burn to give more than enough heat to follow the standard schedule, even when the oxygen is not sufficient to completely furn the acetylene.

That is exactly what happened in the case of the P. C. E.'s determined in this furnace. Examination of the plaques revealed that the standard cones had frozen due to a thin skin of refractory material on the surface consisting of carbon impregnated in the partially fused cone material. This gave rise to low results in comparsion to results obtained in the other furnaces.

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[10] Howard J. Lucas, Organic Chemistry, p. 79.

At higher temperatures in the furnace (above 1200°C) the rate of heating required will permit more oxygen to be used and thus provide a more complete oxidation of the acetylene. The curve shows the increase in the oxygen from the tank and the decrease of the carbon dioxide and monoxide. The combustion is still not complete since the carbon dioxide is decreasing rapidly and carbon monoxide is still present in excess. Heat is produced probably by the oxidation of the hydrogen formed by the incomplete combustion of the acetylene. (See preceeding equation.)

To save on muffle cost it is suggested that a cut could be made longitudinally across the muffle about 1/8" wide. This would allow the muffle to contract and expand upon heating and cooling and lessen the tendency for it to crack.

<u>Denver Fireclay Furnace</u>, <u>A</u>. <u>R</u>. <u>I</u>. <u>type</u>: Fig. 2 shows that the atmosphere of this furnace is somewhat similar to that of the Fulton-Coursen furnace--slightly reducing. This will depend upon the nature of the gas used. Carbon monoxide does increase rapidly from about 1000-1400°C, but the amount at its maximum is still only less than 1%.

The cones have a slight tendency to be blown down by the swirling action of the gases in the furnace due to the sharp increase in draft from 1000-1500°C required to furnish the oxygen for combustion of the gas (see Fig. 4). The temperature is raised by increasing the flow of gas and thus increasing the flow of air to burn it. If oxygen were used, as R. S. Bradley suggests (see Review of Literature, p. 4) the amount of draft required would possibly be less and the swirling action of the gasses in the furnace decreased. The use of oxygen would also tend to cause the atmosphere to become less reducing and even oxidizing, since carbon monoxide present would be ignited at about 600°C.[11]

The gas used in this furnace was a type produced by passing steam over gasoline and causing carbonization to take place. The gas was also passed over a condenser to remove water vapor present. It consists chiefly of pentane (C_5H_{12}) and small amounts of butane and hexane. The heating value was set at 500-800 Btu/pound.

All of the cones are effected in the same manner in this type of furnace, so the results of the P. C. E.

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[11] The temperature of ignition of CO is 637-658°C in oxygen according to: Handbook of Chemistry, Lange, p. 579.

determinations are still reliable. The effect is minimized by placing them farther apart in the plaque and in such a manner that they deform inward.[12] Use of some sort of muffle as in the Oxy-acetylene furnace would further minimize this.

VII. Conclusions

(1) The atmosphere of the Fulton-Coursen Granular Resistance P. C. E. furnace is slightly reducing, but has little effect on determination of the P. C. E. of clays in the range of cone 29-35 and greater.
(2) A decrease in the grain size of the carbon resistor in this type of furnace will cause an increase in the volt-amperes (proportional to power supplied) per degree rise in temperature required to follow the standard P. C. E. schedule as set down by the A. S. T. M. 10 or 12 mesh carbon may be used with practically the same results, however.
(3) The atmosphere of the Denver Fireclay furnace of the type developed by the A. R. I. is slightly reducing above 1000°C depending upon the type of gas used in firing it. This does not affect the results of P. C. E. determination.

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[12] Suggested by A. S. T. M.: "Standard Method of Test for Pyrometric Cone Equivalent of Refractory Materials", _Manual of A. S. T. M. Standards on Refractory Materials_, p. 19.

(4) Action of swirling gases in this type of furnace may be excessive, but does not affect the value of P. C. E. determinations.

(5) The General Refractories' Oxy-acetylene furnace tends to have a very strongly reducing atmosphere if the standard P. C. E. schedule is adhered to and acetylene is not completely burned.

(6) The reducing atmosphere of this type furnace may cause the cones to "freeze" due to the formation of a refractory skin on the surface and cause P. C. E. results to be erroneous.

(7) Considering all the factors involved, including cost, satisfactory performance, uniformity of results, and plant adaptability, the Denver Fireclay furnace is recommended to be used with the following modifications: (1) low cost bottle gas containing saturated hydrocarbons (butane, propane, etc.) with oxygen as an auxilary gas for precise results at high temperatures; and (2) modification of the furnace to contain a protecting muffle of high alumina refractory material.

Bibliography

"Electrical Resistivity of Carbon", International Critical Tables, Vol. II, p. 86.

"Ignition Temperatures of Various Substances and Limits of Inflammability of Gases", Lange's Handbook of Chemistry, Third Edition; Sandusky, Ohio; Handbook Publishers, Inc., 1939, p. 579.

"Standard Method of Test for Pyrometric Cone Equivalent of Refractory Materials", Manual of A. S. T. M. Standards on Refractory Materials; Philadelphia, Pennsylvania, Jan. 1941, pp. 18-21.

Bradley, R. S.
"The Principal Physical Tests for Fireclay Refractories", Brick and Clay Record, Vol. 96, No. 4 pp. 66-68, April, 1940.

Fairchild, C. O. and Peters, M. F.
"Characteristics of Pyrometric Cones", Jour. Am. Cer. Soc., Vol. 9, No. 11, pp. 802-743, Nov. 1926.

McCaughey, W. J.

"The Melting Characteristics of Pyrometric Cones", _The Properties and Uses of Pyrometric Cones_; Edward Orton J. Ceramic Foundation; Columbus, Ohio, pp. 22-23 and 32-34.

Parr, S. W.

"The Analysis of Flue Gases", _The Analysis of Fuel, Gas, Water, and Lubricants_, Fourth Edition; New York; McGraw-Hill Book Company, Inc., 1932, pp. 301-304.

Lucas, Howard J.

"Unsaturated Open-Chain Hydrocarbons", _Organic Chemistry_, New York: American Book Company, p. 79.

Letter of December 30, 1940 from L. J. Trostel, Vice-Chairman Committee C-8 on Refractories of A. S. T. M. to Doc. Paul G. Herold, Associate Professor of Ceramics Missouri School of Mines and Metallurgy, Rolla, Missouri.

"Properties of Alundum", _Norton Refractories_, Worchester, Massachusetts: Norton Co., Oct. 1935, p. 4. (Catalog)