TITANIFEROUS
BLAST-FURNACE SLAGS

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A STUDY OF TITANIFEROUS BLAST-FURNACE SLAGS

Thesis Submitted

by

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Part - One

Introduction

History shows that the development of civilization has gone hand in hand with metallurgical industry. The nations that have attained the foremost places in the civilized world have been workers in bronze, brass, or iron. To-day the world is dominated by the countries that have made the greatest advance in the art and industry of iron, and its[1] ally coal. This contention is substantiated by the figures for the production of iron in the year 1925. The United States, Great Britian, Germany, and France, head the list; and they are the leading nations of the day.

This national greatness is closely associated with economic independence. To attain the above standing, the country must have large natural resources, and its people must have the ability to develope them fully.

Canada's position in this regard is rather peculiar. There is little doubt but that she has large resources, including iron ore and coal. Allowing for[2] the sparse population, her production of pig iron, 570,000 tons for 1925, is very small compared with the leading countries. The per capita production of pig iron for these countries illustrates this fact. Moreover 99% of the smelted ore is imported. Also, for the same period, 58% of the coal consumed is imported.

The coal resources are of good quality, compared with the imported material; but their geographical position is unfavorable for full development. Solution of this problem is mostly an economic one.

The iron ore deposits in Canada are found reasonably near the industrial centers. However they are of a quality inferior to the imported ore. This problem requires scientific as well as economic solution. It is the work of the Canadian people to solve these problems. The work of this research is being conducted as an aid in trying to solve the scientific problem of the iron ores.

Numberous iron ore deposits occur in Ontario and Quebec. Due largely to their titanium content they cannot compete with the rich ores of the United States. Nevertheless it is becoming increasingly important to determine whether these ores can be economically smelted.

Ores containing iron and titanium may be classed as follows:-

(a) Those with less than 3% $Ti\ O_2$ listed with ordinary iron ores.

(b) Those above 3% and less than 25% $Ti\ O_2$ called titaniferous magnetites.

(c) Those with more than 25% $Ti\ O_2$ are called ilmenites, and are really titanium ores. It is the titaniferous magnetites that are of most interest as possible commercial ores. As a rule the iron content of the ilmenites is too low for them to be smelted economically.

A hydrometallurgical process is now being experminted with by the Canadian Department of Mines.

It has as its aim the production of TiO_2 from the ilmenite with electrolytic iron as a by-product.

The problem of dealing with the titaniferous ores for smelting purposes may be attacked in two ways. First, by eliminating the TiO_2 from the ores and so making them suitable for smelting as ordinary iron ores. Second, by altering the smelting practice so that these ores can be smelted in competition with non-titaniferous ores.

The first method involves a physical problem,and numerous experiments have been conducted on magnetic separation of the TiO_2 from the iron oxide. This depends on the fact that iron oxide (Fe_3O_4) is highly magnetic, while the ilmenite($Fe\ TiO_3$) containing the TiO_2 is feebly magnetic. If the ores are aggregates of ilmenite and magnetite then this separation is possible. If the TiO_2 is part of the megnetite molecule, then magnetic separation is not feasible.[3]

Various degrees of success have been obtained in magnetic separation experiments conducted on titaniferous ores found in Norway and the United States. Work performed by Prof. Dulieux[4] on Canadian deposits at St. Charles, Lake St. John District, Que., were of an unsatisfactory character. These results show that the constitution of titaniferous magnetites varies according to location, and that the association of iron and titanium in these ores is not as simple as has been believed.

Microscopic examination readily shows that titaniferous magnetites are composed of magnetite and ilmenite grains, also some hematite (Fe_2O_3) crystals. They occur in minute crystallographic intergrowths, in many cases the magnetite grains enclosing a minute ilmenite grain. Also some chemical investigations seem to indicate that part of the titanium is connected with the magnetite molecule. In the light of these observations it is apparent that magnetic separation is not practicable. A complete physical separation of all the iron and TiO_2 will never be possible where ilmenite is present.

For similar reasons, flotation, the latest development in concentration work would be impracticable.

Controversy is rife over the use of titaniferous ores in the blast furnace. Iron-masters refuse to use them because they believe the TiO_2 causes pasty slags, forms accretions of nitrocyanides of titanium, and the ore is more difficult to reduce, causing a high fuel consumption. On the other hand they admit that a better pig iron is produced, due to the cleansing properties of the titanium, and the low sulphur and phosphorus content of the ore. Despite the objections, titaniferous ores have been smelted satisfactorily; but blast-furnace managers remain firm in their stand to boycott titaniferous ores. Ordinary iron ores usually refer to hematites. There are also the magnetites which contain a greater iron content. They are difficult to reduce, and therefore blast-furnace managers refuse to use them. The titaniferous ores generally contain magnetites. It is thus seen that, besides the titanium content,they have the prejudice of the magnetites to overcome.

Iron ores are commonly smelted in a blast-furnace, the oxygen of the iron oxide going off in the gases, the gangue material beingfluxed away in a slag, and the iron remaining. Metallurgists consider the slag forming reaction as the most important factor in blast furnace operation. In smelting titaniferous iron ores, the TiO_2 enters the Slag. Thus the Slags are the logical places to study the effect of TiO_2 in iron smelting.

History of Titaniferous Iron Smelting

For over a century, titaniferous ores containing 7% TiO_2 have been successfully smelted in Norway and Sweden. This practice was continued until the present century. The large modern furnaces with their lower fuel consumption on non-titaniferous ores forced them to discontinue operation.

From 1840 to 1856, a furnace was operated at Lake Sanford, N. Y.[6] No difficulties were encountered in smelting an ore containing 20% TiO_2. Work ceased due to the inaccessible location of the deposits. The slag contained 25% TiO_2, 32% CaO & MgO, 27% SiO, 12% Al_2O_3, and was quite fluid.[7]

In 1868, the Norwegian Titanic Iron Company smelted a 39% TiO_2 ore at Norton, England. The iron content of this Norwegian ilmenite was 36%, and this gave a high ratio of fuel consumed to pig iron produced (3:1). Consequently operations were found unprofitable. In this case the slag analysis showed 36% TiO_2, 25% CaO and MgO, 28% SiO_2, 9% Al_2O_3 No unusual trouble occurred during the operations.

About the same time, iron was made at St. Urbain, Que. The ore was an ilmenite containing 40% TiO_2 and 45% Fe. They operated for a few months under economic conditions similar to those found in using Norwegian ilmenites.

A. J. Rossi[8,9] has published numerous articles on this subject, both reviewing the work of others and giving his own experiments and conclusions. Silicon and titanium fall in the same group in the Periodic Table; and they form similar compounds. Reasoning on this basis he assumed that lime should be added to a blast furnace charge to flux the TiO_2. His experiments did not fully prove this rule. He studied various slags as regards the silicate minerals that might be formed. Replacing the silicon with equivalent quantities of titania, he obtained a more fusible compound. His method was to melt the slag mixtures at ordinary blast furnace temperatures and observe their fluidity as they were poured. Fusible slags of 40% TiO_2 content were obtained.

The first large scale test in a modern commercial furnace was performed by the MacIntyre Iron Co. They leased a furnace belonging to the Northern Iron Co. Port Henry, N. Y. An account[10] of the experiment was written by F. C. Backman, who had charge of the investigation. They smelted some of the Lake Sanford deposits, which were magnetically concentrated from 20% to 12% TiO_2. The iron content of the concentrate was 55 %. The furnace, which had a capacity of 200 tons per day, had been working on magnetic ores. The regular charge was altered so that the burden contained 1/8, 1/4, or 5/16 titaniferous ore. The furnace was run in the same way, and no unusual happening occurred that could be traced directly to the TiO_2 in the charge. The fuel consumption remained unchanged, an excellent pig iron was produced , and the slag containing 5% to 20% TiO_2 was very fluid. With low amounts of TiO_2 in the charge, a foundry iron was made, but with higher amounts only malleable iron was obtained. This inability to make foundry iron from ores with high TiO_2 content has been one of the factors preventing their usage. The reason is that a high temperature is required to reduce the SiO_2. The TiO_2 is partially reduced at the same time, and is supposed to form highly infusible compounds in the furnace. Thus titaniferous ores are usually run at a low temperature which prevents the reduction of silica. The results of the Port Henry experiments proved that titaniferous ores can be smelted in competition with magnetites.

Electric smelting was used by J.W.Evans[11] and Dr. A. Stansfield to obtain good carbon tool steel direct from an ore containing 57% Fe and 7.5 % TiO_2. The work was not conducted on a scale large enough to prove of more than experimental interest.

At about the same time, Gustave Gin and Dr. E.Haanel separately carried out experiments on the electrical reduction of titaniferous ores. They were particularlly interested in the electrical and economic side of the problem.[12] Dr. Haanel made a run on an ore containing 18% TiO_2 and 44% Fe. He obtained a good foundry iron and a very fluid slag. The slag contained 17% TiO_2 32% CaO and MgO , 19% SiO_2 , and 12% Al_2O_3 , also 9% F. With the high temperatures available in such furnaces, no trouble would be experienced with infusible slags or accretions.

Recent Work on Titaniferous Blast Furnace Slags

In reviewing the data up to this time, Dr. Stansfield noticed that the Slags did not conform to Rossi's idea that the TiO_2 should be fluxed with CaO . With the aid of W. A. Wissler[13], he undertook further investigations of the fusibility of titaniferous slags. An ore of 6% TiO_2 content was smelted electrically the charges being figured on the assumption that a fusible slag would be formed according to Rossi's idea. A very pasty slag was obtained, which did not contain all the lime in the charge This threw further daubt on Rossi's belief. They next determined the softening temperatures of various slag mixtures of CaO, SiO_2, Al_2O_3 , and TiO_2. A second smelting operation was then carried out, the charge for which was calculated so as to give a slag corresponding to the mixture with the lowest softening temperature.

	Calculated Slag	Slag Obtained
TiO_2	25%	20.0 %
SiO_2	35%	29.4 %
CaO and MgO	30%	20.2 %
Al_2O_3	10%	8.1 %
FeO		22.3 %

The results of these experiments indicate that TiO_2 was fluxed by silica instead of by lime.

In 1921 W.M. Goodwin[14,15] worked on Canadian titaniferous ores at Queen's University. He succeeded in getting the vanadiun into the pig iron, with very little titanium. The viscosity of the slags was measured by a machine patterned after one used by the United States Bureau of Mines. Some of the results obtained were comparable with the viscosities of the Canadian blast furnace slags at Sydney and Hamilton; but very few reliable measurments were recorded as the slags effervesced, preventing the operation of the apparatus. The slags then became less fluid and a secondary reaction took place between them and the carbon of the graphite container.

His most notable achievement was in smelting slags averaging in composition as follows:- SiO_2 34%, TiO_2 25%, Al_2O_3 10%, CaO and MgO 20%. The ordinary blast furnace slag is composed of 35% SiO_2, 50% CaO and MgO, and 12% Al_2O_3. Though his slags were fusible with a low CaO content, it must also be noticed that the sulphur in the iron was high; being as much as 0.2 % in some cases. To overcome this trouble a more limey slag would be required, thus somewhat offsetting the self fluxing advantages.

The main facts to be noted from his research are:- (a) the TiO_2, instead of requiring material to flux it, actually fluxes the remaining gangue in the ore, (b) The TiO_2 acts as a base instead of an acid, (c) Some unknown reactions are taking place between the slag and carbon.

M. Billy[16] published an extensive report of work performed on the oxides of titanium. Reducing TiO_2 by hydrogen, chemists had obtained lower oxides supposed to be Ti_7O_{12} and Ti_3O_5. The existence of these oxides was doubtful; but Ti_2O_3 was known. Billy carefully repeated this work with hydrogen, at temperatures ranging from 900°C to 1700°C. In each case he obtained a blue colored product, of the composition Ti_3O_5. He fused this Ti_3O_5 with MgO expecting to get a titanate of magnesium. Treating the fusion with acetic acid, the MgO dissolved. This proved that the new material did not have acid properties. In order to get the known lower oxides of titanium, he fused TiO_2 with metallic titanium. The results of his experiments with the reduction of TiO_2 to lower oxides may be summarised as follows:-

Reducing Agent	Temperatures	Oxide	Color
H	900 - 1700	Ti_3O_5	blue
Ti	700 - 800	Ti_3O_5	blue
Ti	900 - 1000	Ti_2O_3	violet
Ti	1100 - 1200	Ti_3O_4	black
Ti	1400 - 1500	TiO	brown

In the light of the above knowledge, Dr. Stansfield and C. M. Anson[17] conducted a research on the reducing power of carbon monoxide on TiO_2. At temperatures of 750°C to 900°C a gray powder resulted; but above 1000°C a blue powder was obtained. It corresponded with Billy's Ti_3O_5. Quantitative tests were carried out by reducing the TiO_2 with carbon monoxide and calculating the composition of the resulting oxide from the loss in weight. The composition was found to be Ti_3O_5 in each case. Using Ti_3O_5 instead of TiO_2 in the slag mixture they determined some of the softening temperatures, as found by Wissler. Both Wissler's and Anson's cone results will be more fully discussed later in this paper.

Present Research

It had been supposed that titanium existed in a slag as TiO_2. This oxide, analagous with SiO_2, is known to be an acid. The reason for this statement is based on the formation of such minerals as ilmenite ($FeO.TiO_2$), titanite[26] (CaO, TiO_2), and sphene ($CaO.SiO_2$). Also in wet chemistry it generally acts as an acid, though in a few instances it behaves as a weak base.

Recently it has been shown that the action of the titanium compound in the slag is basic. At the same time it has been proven that in the presence of such reducing agents as hydrogen and carbon monoxide, a blue oxide, Ti_3O_5, is formed. The conditions in a blast furnace are highly reducing, especially in the bosh where the formation of the slag takes place. Thus it is reasonable to suppose that the basic action of titanium in a slag id due to the formation of this oxide Ti_3O_5.

Titanium has a strong affinity for nitrogen and carbon. Goodwin noticed in his research that a reaction between the slag and the carbon of the crucible was taking place. The possibility of forming compounds of titanium, carbon, and nitrogen in the blast-furnace has been recognized for some time; but there is little definite information on the subject.

The knowledge of the conditions for the existence of Ti_3O_5 is vague, especially in a blast-furnace where the effect of nitrogen and carbon is pronounced. Therefore, it was deemed expedient to devote some experimental work to these matters. The relation of TiO_2 to Ti_3O_5 as regards the fluidity of slags is also very important.

The experimental work of this research may be divided into four sections:-

(1) The oxidizing effect of carbon dioxide on Ti_3O_5.

(2) A revision of the softening point determinations of slag mixtures containing Ti_3O_5.

(3) The determination of a few softening points of slag mixtures containing TiO_2

(4) The action of nitrogen on titaniferous slags.

Part Two

Experimental Work

Preparation of Ti_3O_5

Anson proved in his work that above 1000°C TiO_2 was reduced by CO to Ti_3O_5[18]. Powell, working on "The Economic Production of Titanium Oxide from Ilmenite," claimed that he produced an oxide of the composition Ti_3O_5. He also used CO as the reducing agent at temperatures of from 900°C to 1100°C. Assuming that Ti_3O_5 is a definite chemical compound, this reaction may be represented by the following equation.

$$3TiO_2 + CO \rightleftarrows Ti_3O_5 + CO_2$$

In order to have all the TiO_2 reduced, a stream of pure CO may be passed over the oxide. This will carry away the CO_2 formed and prevent the action being reversed.

Carbon monoxide may be prepared in numerous ways, three of which are:-

(1) Passing carbon dioxide over hot charcoal

$$CO_2 + C \rightleftarrows 2\,CO$$

(2) Reducing lime with carbon to form calcium carbide.

$$CaO + 3C \rightleftarrows CaC_2 + CO$$

(3) Reducing silica with carbon to form carborundum.

$$SiO_2 + 3\,C \rightleftarrows SiC + 2\,CO$$

Methods (2) and (3) require the high temperature of an electric furnace, and a gas tight apparatus under these conditions would involve some difficulties. A small electric furnace was specially constructed in the Metallurgy Laboratory at McGill University for the production of carbon monoxide by method (2). The operation of this furnace was successful. However method (1) can be carried out at lower temperatures and under more favorable conditions.

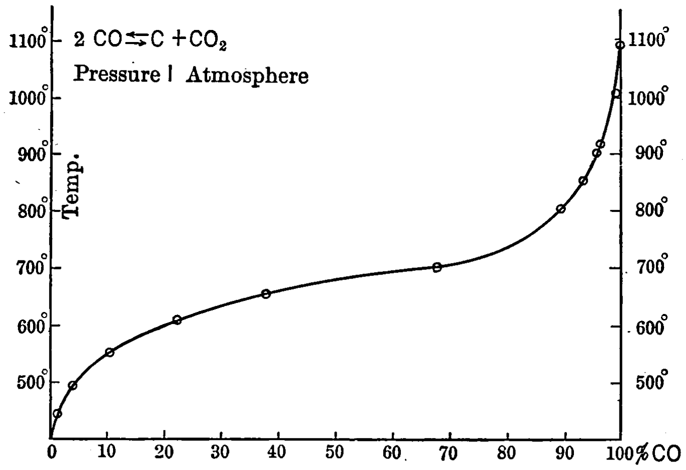


FIG. 96.

Figure -1-

Figure 1 shows the equilibrium conditions obtained by Boudouard between carbon, carbon monoxide, and carbon dioxide at atmospheric pressure. By heating the carbon to 1000^{o} C it will be seen that all the carbon dioxide will be converted to carbon monoxide, if sufficient time is allowed for equilibrium to be reached. To offset the possibility of equilibrium not being reached, or the temperature being too low, a solution of sodium hydroxide may be used to absorb the unchanged carbon dioxide.

Apparatus for Production of Ti_3O_5 Graphite plugs were carefully ground and fitted into the ends of a graphite tube, 1½" bore and 18" long. 1/8" iron tubes were fitted into the ends of the plugs. The graphite tube was placed in the broken carbon between the electrodes of an electric furnace. The carbon acted as a resistance to the flow of electricity, and in so doing was highly heated. In this manner the graphite tube was heated to temperatures up to 1200°C .

The openings, where the tube protruded from the brickwork of the furnace, were carefully luted with fire clay. This prevented air from seeping in through the carbon and oxidizing the graphite of the tube. In the first run before this precaution was taken some air leaked in and oxidized the tube so that a hole formed. However the gas pressure within the tube was strong enough to prevent air from entering and harming the oxide.

The electric furnace was composed of bricks placed so that the outside dimensions were 3'0" X 2' 3" X 1'4" and the inside 2'3" X 1'0" X 1'0". The inner space was filled with carbon. Water cooled electrodes, 1½" diameter, fit into graphite blocks, the latter acting as inside electrodes. Power was supplied by a 30 K.W. motor generator producing alternating current. By means of a transformer, 27, 55, or 110 volts were obtainable.

A washing train was supplied to clean the gas before it enters the graphite tube. It consisted of (a) sodium hydroxide solution to absorb carbon dioxide, (b) pyrogallic acid solution to absorb oxygen, (c) a safety bottle containing no liquid, and (d) strong sulphuric acid to absorb moisture. The strength of the solution is the same as those used in an Orsat gas analysing apparatus. The corks in the bottles containing the solution were sealed with wax to prevent the escape of the gas. An Orsat apparatus was used to analyse the gas after it left the wash train, to see if all the carbon dioxide and oxygen had been absorbed.

For details of the carbon monoxide apparatus see section A of the appendix.

Figure 2 illustrates the apparatus set up for Ti_3O_5 production.

<u>Material</u> Considerable difficulty is experienced in getting a pure TiO_2. Material marked C.P. may often be found to contain as low as 85% TiO_2.

TiO_2 is prepared from titanium ores by obtaining it in solution as a sulphate, and then hydrolysing the titanium as $Ti(OH)_4$. This is a flocculent precipitate which may contain various salts occluded in it. On dehydrating the $Ti(OH)_4$ at 960°C, TiO_2 results which may still contain some of these impurities. Several precipitations are necessary before a pure product can be obtained. Four lots of oxide, prepared by previous workers at this University, were carefully heated to 1000°C to expel all volatile products, and then analysed for purity. That some of the material contained sulphates was evidenced by the SO_3 fumes given off on heating. This would leave the metallic oxide behind as an impurity. The results of the analysis gave 92.3%, 99.4% 72.0% and 98.2% purity. The 99.4% material was considered pure enough for this work.

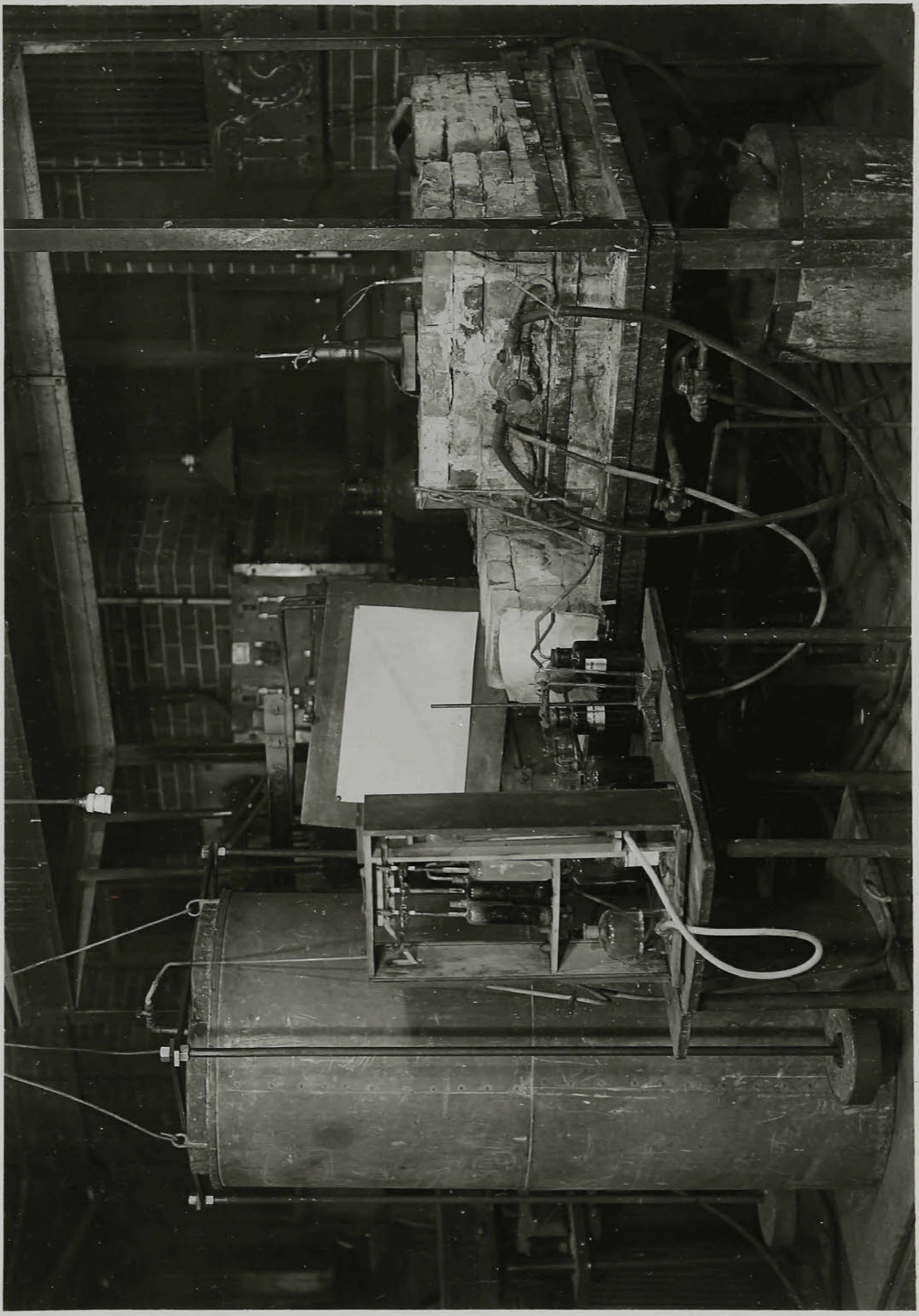


Figure 2.

<u>Production</u> Three runs were made for the production of Ti_3O_5. The analysis of the gas in the holder for the first run was 4% CO_2, 0% O_2, 66% CO. After passing the washing train analysis showed no carbon dioxide present. The gas used for the second and third runs contained 1% CO_2 and 86% CO before washing. The unanalysed portions of the gas were hydrocarbons. In the electric furnace they would decompose and deposit some carbon which would add slightly to the weight of the reduced oxide.

A silica tube, placed upright on the graphite tube and supported by the carbon, contained the hot junction of a platinum platinum-rhodium thermocouple. In this way the temperature of the furnace was observed. The temperature was regulated by changing the field current of the generator. For 1200°C about 18 K.W. was required. The voltage applied at the start was 55, but it dropped to 40 at the end. At the latter voltage the current was about 440 amperes.

In each run the power was first turned on for one hour or until the temperature reached 800°C. The gas was then passed through the graphite tube for three hours, the temperature averaging 1100°C for the last two hours. Carbon monoxide flowed at the rate of 0.7 cu. ft. per hour, which was sufficient to cause a small carbon monoxide flame at the outlet tube. At the end of the run the flow of gas was increased slightly, the graphite tube removed from the furnace, and allowed to cool quickly. In ten minutes it cooled below redness, after which the connections were broken and the charge removed.

Each charge rested on a piece of paper, which was placed in the middle of the tube. The charge was white on entering, and a slightly sintered, blue mass on removal. Some carbon particles were probably removed with the oxide so that the following weights in Table A cannot be taken as accurate quantitative determinations. However they roughly confirm Anson's more positive results.

Table A

Charge No.	Weight of TiO_2	Weight of residue	If Ti_3O_5 should be
1	15.2000 grs.	14.32 grs.	14.21 grs.
2	25.00 g	23.41	23.34
3	23.28 g	21.77	21.73

This blue oxide was crushed to - 100 mesh and kept for future experiments.

Experiments on Oxidation of Ti_3O_5

Cone Test in the Gas Heated Muffle Furnace. The next step in this work was to make cones of various mixtures of lime, silica, alumina, and Ti_3O_5 . For details of ;preparing the cones see the Appendix, section B. The Ti_3O_5 was obtained in a strongly reducing atmosphere and would be easily oxidized by air. Thus in order to obtain the softening points of the cones, they must be heated in the absence of air.

With this idea in view, a muffle furnace was used for the first tests. It consisted of a 15" X 13" X 13" brick furnace, encased in sheet iron, with a 7" X 3½" X 2¾" crystolon (SiC) muffle supported within it. A Meker gas burner was placed in the bottom so that the flames passed around the sides of the muffle and out through the top of the furnace. The back of the muffle was carefully closed and sealed with alundum cement. An opening was left for a pyrometer tube closed at one end. The front end was also carefully luted so that apparently no gas could leak in. A 5" X 5" piece of brick served as a door. A 1" diameter peephole was chipped in the door, and a plug made to fit the hole. The door was cemented in place with fire clay. Charcoal was placed in the muffle to combine with any oxygen that might leak in. The softening temperatures of the cones were obtained by an optical pyrometer, which was checked by a platinum platinum -rhodium thermocouple.

Four runs were made with the cones of the following composition.

Table B

Cone Numbers	SiO_2	CaO	Al_2O_3	Ti_3O_5
1	50%	40%	10%	0%
2	40	40	10	10
3	30	40	10	20
4	20	40	10	30
5	10	40	10	40
6	60	30	10	0
7	70	30	10	10

A standard Orton cone was placed on each pat to check the temperature readings. The results are tabulated in Table C.

Table C

Cone Number	Temperature Optical Pyrometer	 Pt.Pyrometer	Color of fused con
1	1310 °C	1315 °C	White
2	1230	1240	"
3	1290	1250	"
4	1335	1340	"
5	crumbled		
6	1310	1280	Gray
7	1260	1240	"
Orton 6	1240 - 1273	1253- 1275	White

In each run one or more of the cones crumbled or fell over. The platinum pyrometer was working badly and not all the readings were checked. The Orton cone should fall at 1250 °C. The coke in the muffle was completely burnt, showing the presence of oxygen. Also a large amount of gas issued from the hole in the muffle door. After each run, attempts were made to make the muffle gas tight. The attempts were unsuccessful as the cement cracked on heating. The cones containing Ti_3O_5 were dark in color on entering the muffle; and yellowish white on removal.

The conclusions drawn from these results are:-

(1) Under ordinary conditions the muffle furnace is not gas tight.

(2) Under such conditions the Ti_3O_5 is oxidized to TiO_2, and the softening points obtained will not be those of the Ti_3O_5 mixtures.

Conditions in Electric Muffle Furnace. An alundum pot holding a small amount of powdered Ti_3O_5 and TiO_2 was placed in a muffle which was surrounded by carbon resistor blocks. These in turn were enclosed in a brick furnace. Heat was obtained by passing a current through the resistor blocks. The pat and some charcoal were kept in this furnace for 1 hour, when a temperature of 1200°C was reached. The furnace was allowed to cool and the specimens were removed. Oxidation occurred in this muffle as was shown by the following observations:- (1) On removing the plug in the door, a small flame of carbon monoxide was observed, (2) the blue Ti_3O_5 was changed to a yellowish powder, while the TiO_2 remained white, and (3) the charcoal was completely burnt.

Second Experiment in the Gas Muffle Furnace. The previous experiment was repeated in the gas muffle under slightly different conditions. A 1" iron tube, with a mica eye piece at one end, was fitted into the peep hole. A piece of 1/8" pipe was threaded into the large tube so that city gas was forced into the muffle, with the idea of keeping out the burning gas mixture. The pressure of the city gas was 6" of water gange, while that of the burning gases in the furnace was 1/8" of water. The city gas was passed through sulphuric acid in order to absorb the moisture it contained. The blue Ti_3O_5 was again changed to a yellowish powder, while the TiO_2 was unaffected. The gas was kept flowing while the furnace and oxide cooled to below 400°C.

An analysis of the city gas showed the presemce of 1.8% oxygen, which would account for the oxidizing conditions. Therefore the experiment was repeated using pure carbon monoxide in place of city gas. The carbon monoxide was delivered from the gas holder under a pressure of 9.5" of water. After leaving the washing train its pressure was 3" of water. The conditions were again found to be oxidizing.

The general conclusion from these results is that a muffle furnace, used under the conditions herein, is not sufficiently gas tight to prevent the oxidation of Ti_3O_5. Oxidation of Ti_3O_5 to TiO_2 may take place in two ways under the conditions outlined above:-

(1) By the direct addition of oxygen

$$2\ Ti_3O_5 + O_2 \rightleftarrows 6\ TiO_2 \text{ ——————— } (1)$$

(2) By the reverse of the action by which the Ti_3O_5 is formed.

$$Ti_3O_5 + CO_2 \rightleftarrows 3\ TiO_2 + CO \text{ ——————— } (2)$$

Titanium has a great affinity for oxygen and it forms one of the stablest compounds known, namely TiO_2. Consequently there is little doubt but that the merest trace of oxygen present would rapidly oxidize the Ti_3O_5 according to equation (1)

The effect of carbon dioxide on Ti_3O_5, according to equation (2), is not so apparent. The following set of experiments were undertaken in trying to get some light on this reaction.

For this purpose, there was obtained a silica tube 1" diameter, 24" long, and closed at one end. It was fitted with a rubber stopper through which two pieces of glass tubing passed. One piece of tubing went in a distance of 12", while the other was flush with the stopper. The short piece was in the shape of a T. A water manometer was attached to one arm and a tapered outlet tube to the other. The long piece was connected to the same washing train as was used in the preparation of Ti_3O_5. Pieces of glass tubing in the shape of a

Y were placed in the gas system before the washing train, after it, and at the outlet tube. This allowed gas samples to be obtained at these points.

That portion of the silica tube 10" from the closed end was placed within the gas heated muffle furnace used in the cone tests. The remainder of the tube was supported outside by a clamp, connected to a ring stand. The temperature of the furnace was obtained by a platinum platinum-rhodium thermocouple placed in the back of the muffle. Figure (3) illustrates the apparatus in position.

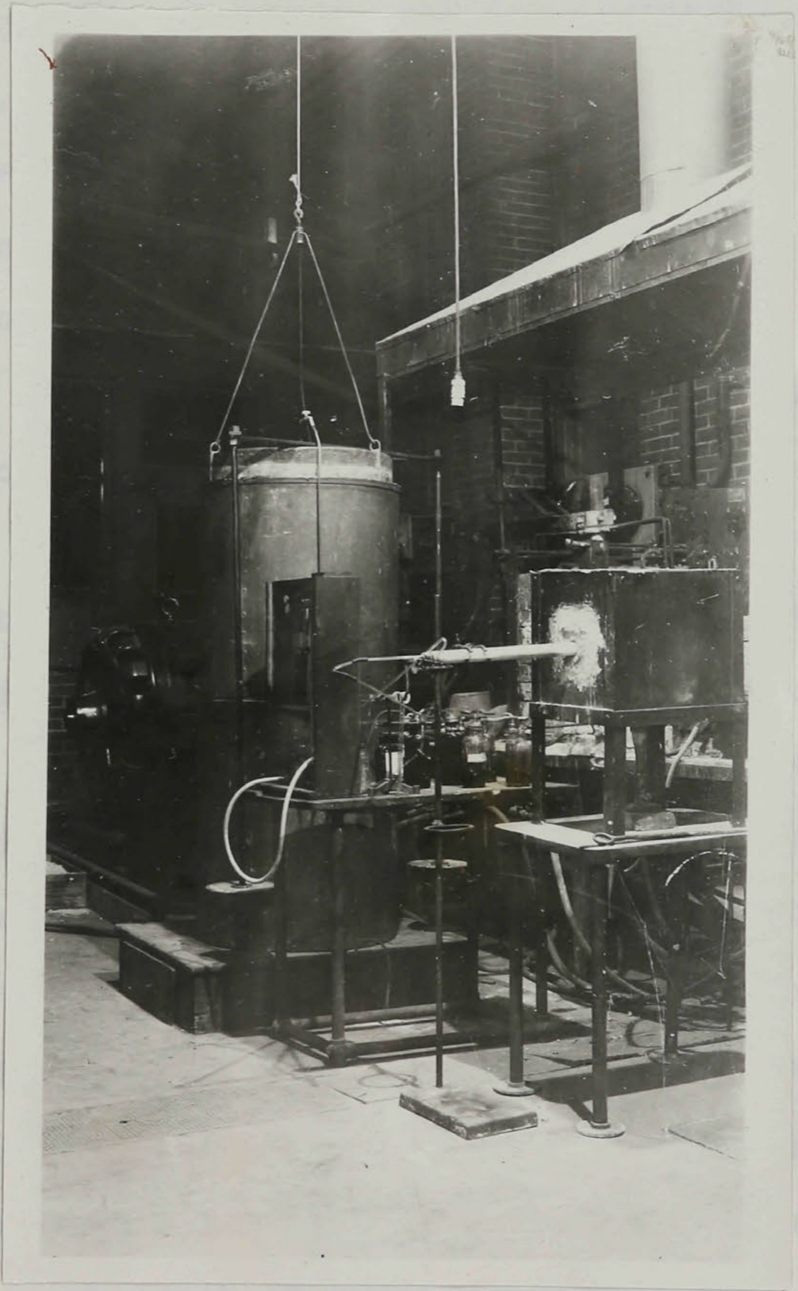


Figure -3-

For performing the experiments, a small carbon boat, containing small amounts of TiO_2 and Ti_3O_5 powder, was placed within the silica tube 1" to 2" from the closed end. The tube was then closed, sealed with wax, placed in the furnace, and connected to the gas system. Gas from the holder was allowed to pass through the washing train, into the silica tube, and finally burnt in the air. The air in the silica tube was gradually removed by the diffusion of the gas in its passage through the system. The exit gas was analysed in an Orsat apparatus, in order to determine when all the oxygen was expelled. The time required was two to three hours.

The muffle was then heated for one hour. A temperature of 1000^oC was reached in fifteen minutes and $1200^o C$ in one hour. The tube was cooled either rapidly in air or slowly in the muffle, according to the requirements of the experiment. Except in one run, the gas flowed continually throughout the heating and cooling. The color of the cooled powder was examined to see if the TiO_2 was reduced, or the Ti_3O_5 oxidized.

After the runs with pure carbon monoxide were finished, all the oxygen in the gas holder had been washed out. Carbon dioxide was then forced in to make a gas of a definite carbon monoxide - carbon dioxide composition. Experiments with these mixtures were made in the same manner. In this work the oxygen and carbon dioxide wash bottles were removed.

The pressure of the gas in the silica tube varied from 2" of water to 8" of water, according to the number of wash bottles and depth of solution within them. For the pure carbon monoxide runs, the gas in the holder usually contained

2% to 3% CO_2 which was absorbed by the washing train, The flow of gas was regulated by a pinch cock at the exit tube. In washing out the air, for the first twenty minutes the flow of gas was rapid. For the remaining time it was small, giving it time to diffuse. The results of these runs are found in Table D.

Table D.

Oxidation by CO_2

Maximum Temperature 1200° C . Time for washing out air 2 to 3 hours. Mean Temperature 1050° C. Time of heating 1 hour. Volume of gas used per run averaged 2.0 cu. ft.

Color of TiO_2 before heating -white

Color of Ti_3O_5 before heating-blue

	Gas Analyses		Method of	Color after Heating	
Run Number	CO	CO_2	Cooling	TiO_2	Ti_3O_5
1	100.0%	0.0%	Rapidly	Light blue	Blue
2	100.0%	0.0%	Slowly	" "	"
3	100.0%	0.0%	"	" "	"
4	97.5	2.5	"	" "	"
5	94.6	5.4	"	" "	Gray
6	94.0	6.0	Rapidly	" "	Blue
7	90.2	9.8	"	" "	"
8	91.2	8.8	"	" "	Gray blue
9	75.6	24.4	"	" "	Gray
10	79.8	20.2	"	" "	"
11	52.2	47.8	"	" "	"
12	26.0	74.0	"	Blue	Light Gray
13	14.0	86.0	"	Gray white	" "

Table D. Continued

14	0.0	100.0	Rapidly	White	Light brown
15	(98 - C_xH_y)	2.0	Slowly	Black	Dark blue

Rapid cooling means cooling the silica tube in air, which requires ten minutes. Slow cooling means cooling in the furnace, which requires two hours. Oxidation or reduction is determined by the color changes of the TiO_2 and Ti_3O_5. For reduction the TiO_2 changes from white to blue, the Ti_3O_5 remaining blue. For oxidation the TiO_2 remains white and the Ti_3O_5 changes from blue to white. The material from run 8 onward was saved for future experiments.

Two holders of gas were necessary for run 1. The first contained 0.9% oxygen which was only reduced to 0.3% in passing through the washing train. By carefully washing out the holder several times, a gas containing 0.1% oxygen was obtained.

Runs 1,2, and 3 show that, with either slow or rapid cooling, the silica tube was practically gas tight. As expected, conditions in these runs were reducing. In run 3, after the air was expelled, the flow was stopped by closing the outlet stop cock. Some carbon dioxide would form in the tube but not enough to affect the general result. The gas leakage in the system amounted to one bubble per minute.

In runs 4 to 11 inclusive, the carbon dioxide in the gas was increased from 2.5% to 47.8%. The white TiO_2 was changed to a blue material in each case, which distinctly indicates reduction. The blue Ti_3O_5 remained unchanged or assumed a dark grayish color. This gray was not light enough to believe that the Ti_3O_5 was being appreciably oxidized by the carbon dioxide. In all runs after 7, a platinum boat instead of a carbon one was used to hold the oxide. This change was made to eliminate any possibility of the carbon affecting the results.

In run 12, the Ti_3O_5 assumed a light gray color while the TiO_2 became decidely blue. This TiO_2 was used from a bottle marked "TiO_2 C.P" It was tested by heating to 900°C in air. Instead of remainig white, it took on a dirty brown color which indicated the presence of impurities. These impurities may have produced a more intense blue color. Run's 13 and 14 were performed with the original TiO_2.

Run 13 showed evidence of reduction of the TiO_2 while oxidation was changing the Ti_3O_5 .From the color changes the reduction seemed stronger than the oxidation. In run 14, with 100% carbon dioxide, there was distinct oxidation. A noticeable feature was that the Ti_3O_5 became a light brown color instead of white.

Run 15 was performed with city gas. This gas contained 3.4% carbon dioxide and 1.8% oxygen To remove the latter the gas was passed through a silica tube filled with pieces of brick. A Hoskins Electric muffle heated the tube to 1000°C. At this temperature the oxygen combined with the inflammable portions of the gas to form carbon dioxide or water. At the temperature of the gas muffle (1200°C), the hydro-carbons decomposed, leaving a deposit of soot. This soot probably caused the TiO_2 to become black on reduction, and the blue Ti_3O_5 dark blue. The use of city gas was rejected for these reasons.

Two unsuccessful experiments were performed by completely closing the silica tube after expelling the air. When heated to 1200°C for 2½ hours, the various reactions should take place and an equilibrium should be reached. Three grams of TiO_2 and a small amount of Ti_3O_5 were placed in the tube. The large amount of TiO_2, was provided so that there would be enough oxide for the gas to work on. The gas, before heating, contained 20% carbon dioxide and 80% carbon monoxide.

In the first run there was not sufficient pressure behind the gas to get an accurate sample for analysis. The sample contained 19% carbon dioxide and 13% oxygen. In the second experiment more precautious were taken in getting a gas sample. That obtained analysed 49% carbon dioxide and 3% oxygen. Neither of these samples are correct as the gas in the tube should not contain oxygen. In both cases the Ti_3O_5 became gray and the TiO_2 a light blue color.

The conclusions to be drawn from this set of experiments are very unsatisfactory. Since Ti_3O_5 is readily oxidized in air, it was thought that a relatively small amount of carbon dioxide would cause a similar result at high temperatures. The observations indicate that as long as there is an appreciable amount of carbon monoxide present, reduction takes place. Also with 100% carbon dioxide, the Ti_3O_5 was oxidized to a light brown instead of a white material.

Quantitative Tests on Oxidation of Ti_3O_5 in CO - CO_2 Atmosphere

Billy[16] tried to reduce TiO_2 with zinc. He obtained a blue product which resembled Ti_3O_5. Analysis however showed that no reduction had taken place. His explanation was that the reduction had only been superficial.

Experiments were now tried to see if the colors of the material in the previous experiments were superficial. For this purpose the two platinum boats were carefully cleaned, heated to redness, and weighed. Small amounts of some of the material, treated in the silica tube tests, were carefully weighed, dried to constant weight at 125°C, then heated to constant weight in a roasting muffle at a temperature of 900°C. Half an hour was found sufficient to get a constant weight. Changes in the color the material were carefully observed. Some of the Ti_3O_5, direct from its preparation, was similarly treated. Changes in the weight of the samples indicate its state of oxidation.

The results of this work are tabulated in Table E. In explanation of this table it must be stated that, for example in run 1, the oxide used is that resulting from the action taking place on TiO_2 in run 10, Table D. In Table E the oxide is designated in all cases, by its composition before treatment in the silica tube tests of Table D.

Run's 1 and 2, Table E, were conducted with the TiO_2 and Ti_3O_5 previously heated to 1200°C in a 20.2% carbon dioxide 79.8% carbon monoxide atmosphere. When heated in air, No.1 material changed in color from blue to white with no weight change. The No.2 material changed from a gray to brownish white color, losing 0.7% in weight. This loss in weight is unaccountable except as an experimental error. Assuming that it was such, then the deductions from the color changes in run 10, Table D are inaccurate. Conditions, that were thought to be reducing at that time, were really oxidizing according to this experiment. This means that the blue and gray colors of the oxide were superficial.

Runs 3 and 4, and 5 and 6 gave pratically the same results as runs 1 and 2. The material in 3 and 4 was previously treated in a gas containing 14.4% carbon dioxide and 75.6% carbon monoxide, while that of 5 and 6 in a 74.0% carbon dioxide 26.0% carbon monoxide atmosphere. The material

Table E.

Oxidizing the Materials Previously Treated in CO-CO_2 Atmosphere

Time for drying - 1/2 hour. Temperature of drying - 125°C Temperature of heating - 900°C

Run	Previous Treatment of Material	Wt. of Oxide	Wt. of oxide after drying	Wt. of oxide after heating	Time of heating	Change in Weight Grams	%	Change in color
1	#10 Table D, TiO_2	0.0117 grs.	0.0116 grs.	0.0116 grs.	1 hour	0.0000	- 0.0	blue to white
2	10 " D, Ti_3O_5	0.0435	0.0433	0.0424	1 "	0.0007	- 0.7	gray to yellow
3	9 " D, TiO_2	0.0227	0.0226	0.0224	½ "	0.0002	- 0.9	blue to white
4	9 " D, Ti_3O_5	0.0652	0.0651	0.0649	½ "	0.0002	- 0.3	gray to yellow
5	12 " D, TiO_2	0.0401	0.0398	0.0394	½ "	0.0005	- 1.3	blue to white
6	12 " D, Ti_3O_5	0.0475	0.0474	0.0473	½ "	0.0001	- 0.2	gray to brown
7	Untreated Ti_3O_5	0.1923	0.1921	0.1993	¾ "	0.0072	+ 3.75	blue to yellowish brown
8	" Ti_3O_5	0.1129	0.1128	0.1171	¾ "	0.0043	+ 3.81	blue to yellowish brown

Table F.

Quantitative Tests in CO-CO_2 Atmosphere

Time for drying - 1/2 hour Temperature of drying -125°C Temperature of heating-1200°C. Time of heating-2 hours

Run	Material	Gas Analysis CO	Gas Analysis CO_2	Wt. of Oxide	Wt. of oxide after drying	Wt. of oxide after heating	Change in Weight Grams	%	Change in color
1	Untreated TiO_2	100%	0%	0.0907 grs.	0.0906 grs.	0.0853 grs.	0.0053	- 5.85	white to clue
1	" Ti_3O_5	100%	0%	0.1896	0.1895	0.1914	0.0019	+ 1.00	remained blue
2	" TiO_2	89%	11%	0.0934	0.0933	0.0886	0.0047	- 5.04	white to blue
2	" Ti_3O_5	89%	11%	0.2120	0.2118	0.2191	0.0073	+ 3.45	blue to steel gray

lost weight in each case, where no weight change, or an increase, was expected. The amount of oxide available for this work was so small that a difference of 0.1 milligram in weighing made an appreciable per centage change in weight. Thus these small weight losses may be largely due to experimental errors in these rough experiments.

Runs 7 and 8 were conducted on the untreated Ti_3O_5. The increase in weight agreed very closely. From the weight figures on its production, see Table A, this oxide was practically pure Ti_3O_5. Calculations show that on oxidizing Ti_3O_5 to TiO_2, the weight increase should be 7.14%. Thus the light brown material obtained in each case does not correspond to TiO_2, but to some intermediate compound or mixture.

Quantitative Tests in Silica Tube. Two quantitative runs were made in the silica tube under the same conditions as the experiments tabulated in Table D. The material was handled in the same boats and weighed in the same manner as the oxidizing experiments of Table E. The results of these runs are in Table F.

In run, 1, the gas atmosphere was pure carbon monoxide. The boats and their contents were heated for two hours at 1200 ^{o}C, weighed, then heated for two hours more, and reweighed. This first two hours was found to be sufficient. The TiO_2, as expected, lost weight (5.85%), but not as much as it should (6.67%) if reduced to Ti_3O_5. The Ti_3O_5, instead of keeping the same weight, increased it to the extent of 1.0%.

The conclusion from this run is that the diffusion of the gas is not enough to wash out the carbon dioxide formed. It collects and causes the reaction to be partly reversed.

Run 2 was performed in an atmosphere of 11% carbon dioxide and 89% carbon monoxide. The TiO_2 lost weight and the Ti_3O_5 gained, showing that both reduction and oxidation has taken place.

Discussion. The results of the preliminary cone and powder tests showed that Ti_3O_5 cannot exist at high temperatures in the presence of burning gas. In the tests made, there was always an excess of carbon monoxide issuing from the muffle. Thus any oxygen within the muffle would combine with the carbon monoxide, forming carbon dioxide. The composition of the gases in the muffle was not known; but it was expected that there would be a large proportion of carbon dioxide present. If such is the case, the oxidation would be conducted by this gas.

Experiments conducted with the expectation of oxidation taking place by carbon dioxide were unproductive of definite results. In all cases, except with a 100% and 86% carbon dioxide gas, the color of the oxide indicated that reduction had taken place. That this indication of reduction was wrong, was shown by attempting to oxidize the material back to TiO_2 . The white oxide (TiO_2), which had become blue, did not increase in weight while changing to white again. This showed that the superficial coloring did not indicate the correct conditions. The Ti_3O_5 material did not increase in weight, showing that it had also been oxidized in the previous tests. No tests were made of the material treated in gas atmospheres containing 8.8% carbon dioxide, or less, as the product of those experiments had not been preserved. The two quantitative experiments in the silica tube covered this range, and they showed that partial oxidation and partial reduction occurred in gases analysing from 0% to 11% carbon dioxide.

From the above experiments the conclusion is reached that, with a gas containing as much as 14% carbon dioxide Ti_3O_5 will be oxidized. With less than 14% carbon dioxide in the gas, both oxidation and reduction take place, that is both TiO_2 and Ti_3O_5 will be present in amounts according to the equilibrium resulting.

$$Ti_3O_5 + CO_2 \rightleftarrows 3TiO_2 + CO$$

0-14%

$$Ti_3O_5 + CO_2 \rightarrow 3\ TiO_2 + CO$$

14-100%

Run 1, Table F, showed that the apparatus was not suitable for this work. It should have been arranged so that the gas flowed in a stream over the oxide. A much greater length of time would be required for the diffusion method to bring about the desired results.

One remarkable thing in these tests was that Ti_3O_5, on being heated in air, did not change into TiO_2. Instead it became a yellowish oxide which had taken on only half as much oxygen as was expected. No reason can be brought forward to explain this action other than the possible formation of a solid solution of TiO_2 in Ti_3O_5. Billy used this oxidizing method successfully in his analytical work.

The constitution of the oxides of titanium is open for much discussion and experimental investigation. The existence of such oxides as Ti_2O_5 and Ti_7O_{12} has been claimed, but it is believed that they are really mixtures or solid solutions of TiO_2 and some lower oxide, presumably

Ti_2O_3 . The ratio of TiO_2 to Ti_2O_3 in these oxides would depend on the conditions under which they were formed. The Ti_3O_5 may be a mixture of Ti_2O_3 and TiO_2 just as ferric and ferrous oxides of iron combine to form magnetite. This explanation is highly probable since TiO_2 is mostly acid in character and Ti_2O_3 is basic.

When the work on the oxidation of Ti_3O_5 by carbon dioxide in a silica tube was undertaken, it was expected that a few tests would indicate the desired results. As definite results were not obtainable the work was extended beyond its original scope. For this reason it had to be discarded in an unfinished state and the main work of the research taken up.

Softening Points of Slag Mixtures Containing Ti_3O_5

Theoretical Considerations. Information on the fusibility of slags may be obtained in three ways. (1) By temperature-viscosity curves, (2) by the softening points of synthetic slag mixtures, and (3) by the miscrosopic examination of chilled samples. In pratical work the fluidity of a slag is of the greatest importance. A slag may be fusible yet not fluid. With viscosity measurements, a direct relationship is established between temperature and fluidity. The United States Bureau of Mines[19] have devised a complicated mechanism for determining the viscosity of slags.

By the determination of the softening points, valuable information can be obtained on the temperative-fusibility relationship of slags. No definite relation is known between fluidity and softening points. In the softening point method, gaseous conditions can be obtained that would be impracticable in the viscosity apparatus. Microscopic examination can be used to show the constitution of the slag. Experimental results can be explained by this method.

Rankin and Wright[20] made an exhaustive study on the ternary system of lime-alumina-silica. These three oxides are the principal slag forming materials. They showed that in the range of blast furnace slags, there were principally three minerals present, anorthite, gehlenite and calcium bisilicate. When a slag cooled, one of these minerals solidified until a binary eutectic was reached, which in turn solidified until the termary eutectic was reached.

The eutectic structure of slags is of the utmost importance in explaining the softening temperatures obtained by means of cone tests. These cones contain the slag forming materials in very intimate contact, so that when heated to a ternary eutectic point part of the cone will liquify. The temperature at which the cone falls will depend on the proportion of this eutectic present.

In the ordinary blast-furnace slags, the constituents present, other than lime, alumina, and silica, are in so small proportions that they have little effect. However in titaniferous slags, TiO_2 is present in such amounts that we are dealing with a four component system. Its action on solidification is the same as the three component system; except that due to the fourth addition the final eutectic may be lower. In this case three eutectics may form. Consequently the softening point temperatures of titaniferous cone mixtures may be lower than non-titaniferous mixtures.

Besides this mininum softening point by eutectic formation, Lewis and Ries[21] have enumerated two other cases in which it will exist. They are:- (1) When the least refractory phase has a sharp melting point and no solvent action on the other phases, and (2) when this phase has a high viscosity coefficient. In this work, the least refractory phase is too high above the eutectic points to cause any softening due to these reasons. They also conducted experiments to show the variable effect of the rate of heating on the softening points of cones.

The authors of several articles[21,22,23] on Seger cones agree that these softening points cannot be taken as standard temperature measurements, unless obtained under specific conditions. The following list illustrates the difficulties in obtaining proper softening point temperatures:-

(1) Rate of heating

(2) Inclination of the cone on the bat

(3) Reflection on a cone of light from a hotter part of the furnace, thus affecting the optical pyrometer.

(4) Shrinking of the cones, thus making it difficult to observe the true softening points.

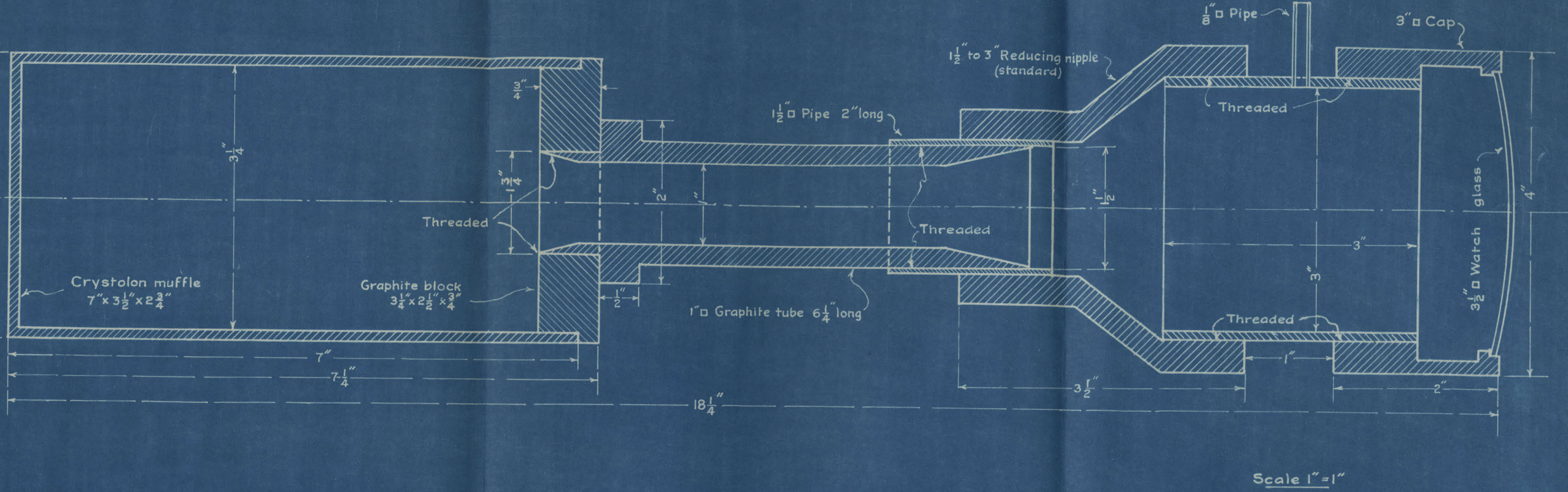
(5) Nature of the furnace atmosphere.

The cones used in this research are subject to the above conditions. Thus despite all precautions, the results obtained will probably vary as much as 25°C from the theorectical results. In commercial work, differences of 50°C have been obtained, usually on the high side. To simplify the investigation, the alumina in all mixtures is kept constant at 10%. This is about the proportion existing in all blast furnace slags.

Apparatus. Early experimental work demonstrated that Ti_3O_5 cones cannot be heated in ordinary muffle furnaces without undergoing oxidation. A special apparatus was designed whereby these cones could be heated in a highly reducing atmosphere.

It consisted of a crystolon muffle fitted with a graphite door. A graphite tube, 1" bore and 6" long, was threaded into the center of the door. A piece of iron pipe, 2" long, fitted over the end of the graphite tube, a piece of asbestos acting as packing. The outer end of the pipe threaded into a 1½" X 3" reducing nipple. A piece of 3" pipe, 3" long with an iron cap over its outer end, threaded into the muffle. The iron in the face of the cap was cut out so as to admit a 3" watch glass, which was placed in it as a window. The glass was cemented in with sodium silicate. The overall length of this apparatus was 18". A short piece of 1/8" pipe was threaded into the 3" diameter pipe. For further details see the accompanying blue print.

Reducing gas was forced into this apparatus through the 1/8" pipe. It diffused into the air present, and the gas and air escaped through the inperfectly fitted door of the muffle, or the small hole in the back of the muffle where the pyrometer tube came through. The muffle was placed between the electrodes of an electric furnace, and packed in broken carbon. Carbon was also placed around the graphite tube. In this way no air could get in; yet the air could be forced out of the muffle by the reducing gas. Any air that did tend to enter by diffusion through the hot


1/8" □ Pipe
3" □ Cap
1 1/2" to 3" Reducing nipple (standard)
1 1/2" □ Pipe 2" long
Threaded
Threaded
Threaded
Threaded
3/4"
3 1/4"
1 3/4"
2"
1"
1 1/2"
3"
3"
4"
3 1/2" □ Watch glass
Crystolon muffle 7"x 3 1/2"x 2 3/4"
Graphite block 3 1/4"x 2 1/2"x 3/4"
1/2"
1" □ Graphite tube 6 1/4" long
7"
7 1/4"
18 1/4"
3 1/2"
1"
2"
Scale 1"=1"

carbon would combine with the carbon to form carbon monoxide, very little carbon dioxide, and nitrogen.

In designing the apparatus, the hole in the muffle door was kept as small as possible in order to lower the heat transferred to the front. With this small hole, it was necessary to enlarge the diameter of the outer sections in order to see the back of the muffle. The graphite tube was flared at both ends in order to help the vision. The heat conduction through the graphite tube and connections was considerable, so in the later experiments a 2" block of silocel was placed inside the muffle door. A flared rectangular slit was cut in it to allow a clear view of the cones.

The apparatus was handled in two parts, (1) the muffle and (2) the door, tubes, and fittings. To set it up, the muffle, with the cones inside, was placed in the furnace. The door, with the other parts connected to it, was cemented in with graphite paste. This did not give a very tight joint. The furnace was then filled with carbon. Connections were made from the gas holder and complete washing train to the 1/8" inlet tube. A small piece of pipe, closed by rubber tubing and a pinch cock, was threaded into the cap. This enabled the gas flow to be short circuited, if necessary.

A hole was cut in the back of the muffle. A silica tube for holding the platinum platinum-rhodium thermocouple fitted into this hole. The other end of the tube was outside the brick-work. For heat protection, a porcelain sleeve was fitted over the tube between the muffle and brickwork. An optical pyrometer obtained direct temperature readings on the cones. The electric furnace was the same that was used for the production of Ti_3O_5.

Operation. After the apparatus was fitted together as described above, the gas was turned on for one hour. This allowed sufficient time for the expulsion of the air from the muffle. The flow of gas was regulated to 0.5 cu.ft. per hour. Its pressure at the end of the washing train was observed by a water manometer. At the end of the hour, with the gas still flowing, the power was turned on. 700° C was reached in one hour.

Above this temperature the rise, unless controlled, was very rapid. The rate of heating was kept at 6° C per minute.

From 1000° C up, temperature readings were taken every 15 minutes by the optical pyrometer. A check reading was obtained by the platinum platinum-rhodium themocouple. The reading of the optical pyrometer were taken at first on the individual cones and the protruding end of the silica tube. Later on it was observed that the work could be simplified by dividing the cones into groups of equal temperature readings. Some cones fall without a temperature observation by the optical pyrometer. By plotting time -temperature curves and knowing the time of falling, the correct point can be found.

When all the cones had fallen, the power and gas were turned off, and the muffle allowed to cool below redness. At first the carbon was removed from around the muffle during cooling. This caused the muffle to crack, so slow cooling was allowed to take place, generally over-night. Also during the first runs, the gas was left flowing throughout cooling in order to observe the condition of the fallen cones under true reducing conditions.

The silocel baffle, also a crystolon plate

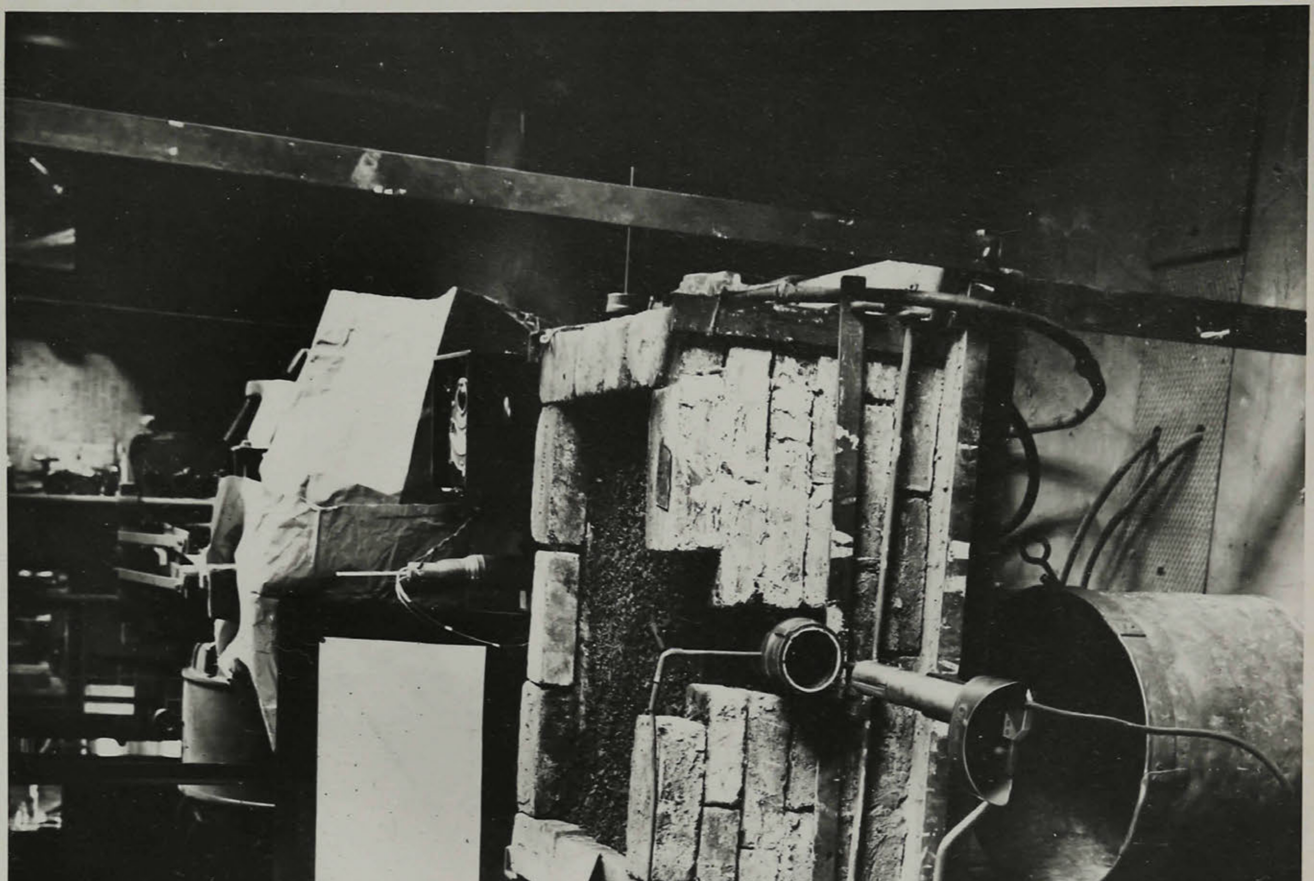


Figure 4.

under the muffle in the furnace, were some of the improvements added in the later tests. They tended to produce a more even temperature inside the muffle. The thermocouple was not used in the first runs. Figure 4 shows the apparatus set up for operation.

Data. In order to obtain the required softening points, including accurate checks, it was necessary to make twenty-five runs in the electric furnace.The record of each run was kept in the same manner.The results of all runs (Table I) will be placed in this report with a typical run given in detail. Table G gives the record for the run of March 15th/26.

Table H shows the composition of the cones, and Table J a summary of the results obtained. Graph Sheet No. 1 gives the time-temperature curves for the run of March 15th/26.

Table G.

Record of a Softening Point Run.

March 15/25 20 22 23 24

Carbon Monoxide-Nitrogen Atmosphere 21 25

Muffle Temperature			Cone Temperatures (Opt).			
Time	Pt.	Opt.	20-24	22-23	21-25	Remarks
2.45	1300° C	1127° C	1130° C	1130° C	1121° C	#21 fell very quickly.
3.00	1210	1202	1202	1202	1197	
3.20	1310	1302	1293	1293	1293	#22 partly crumbled, but not enough to harm result.
3.30	1350	1340	1332	1332	1332	
3.45	1410	1402	1394	1394	1394	
4.00	1450	1446	----	----	----	Power off for 2 minutes at. 4.00
4.10	1480	1468				

No.21 fell at 3.01 at 1202° C.Black color with coppery surface

" 20 " " 3.10 " 1250 " " " " "

" 24 " " 3.35 " 1363 " " " " "

" 23 " " 3.55 " 1435 " " " " "

Table G. Continued.

#22 Fell at 3.50 at — Black color with coppery surface.
25 " " 4.05 " — " " " " "

No. 20 cone is black on surface and light colored within.

Interpretation. The figures in the upper part of the table are plotted in Graph Sheet No.1. Since the cones have the same temperature readings, one curve does for the three sets. The dotted line means an interruption in the rate of heating, and that the results beyond that point cannot be plotted accurately. The temperatures obtained at the time of falling are corrected readings of the optical pyrometer. The blank spaces after cones 22 and 25 indicate that readings were not obtained at the time of falling.

Table H.

Composition of the Cones

Al_2O_3 constant at 10% in all cases

	Composition				Composition		
Cone No.	SiO_2	CaO	Ti_3O_5	Cone No.	SiO_2	CaO	Ti_3O_5
1	50%	40%	0%	19	60	10	20
2	40	40	10	20	40	50	0
3	30	40	20	21	30	50	10
4	20	40	30	22	20	50	20
5	10	40	40	23	10	50	30
6	60	30	0	24	0	50	40
7	50	30	10	25	0	40	50
8	40	30	20	26	0	30	60
9	30	30	30	27	0	20	70
10	20	30	40	28	30	60	0
11	10	30	50	29	20	60	10
12	70	20	0	30	10	60	20

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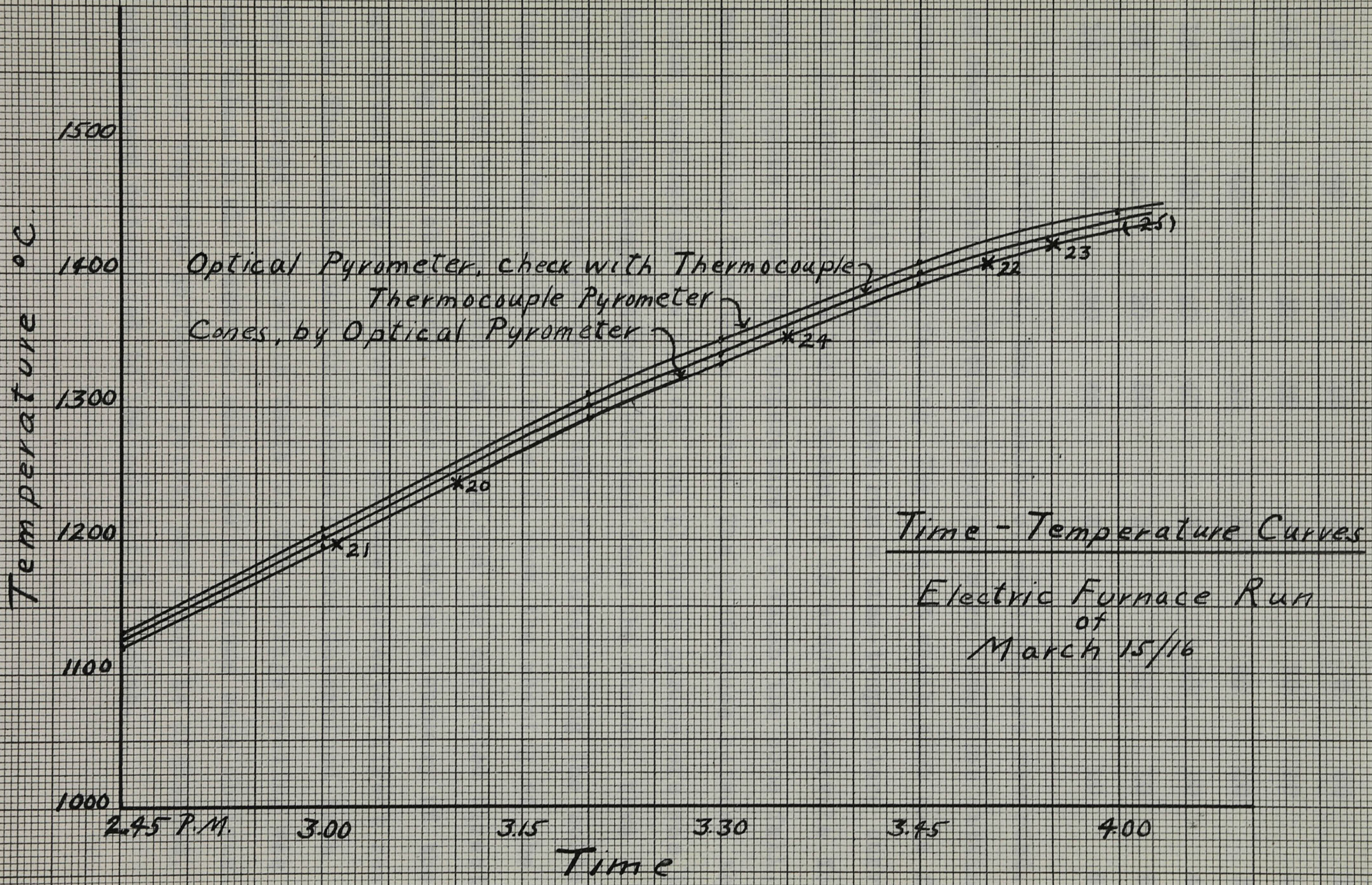


Graph Sheet No. 1.

Table H. Continued.

Cone No.	SiO_2	CaO	Ti_3O_5	Cone No.	SiO_2	CaO	Ti_3O_5
13	60	20	10	31	10	60	30
14	50	20	20	32	70	10	10
15	40	20	30	33	50	10	30
16	30	20	40	34	40	10	40
17	20	20	50	35	30	10	50
18	10	20	60	36	20	10	60

In Table I, the results of each run are recorded. As shown in Table J, optical readings were sometimes obtained just as the cone was falling. The time at which each cone fell was noted in all cases. In each run a time-temperature curve was plotted, readings being taken at 15 minute intervals for this purpose. Thus the temperature, at which the cone fell, was determined from these curves. The difference between the check readings of the optical and platinum pyrometers was then added to the temperatures obtained from the curves, thus giving the corrected reading used for determining the softening points. The results in Table I. show the meaning of the corrected readings from the curves and the corrected direct reading (when obtained). Table J. contains a summary of the corrected curve determinations and the corrected direct readings. The figures used in diagram.1. were determined from the readings contained in Table J. The average reading was not taken in all cases as some determinations were obviously not near the true softening point, and could be discarded. The points were determined to the nearest 5° point.

Table I

Results of Runs

Run No.	Date	Cone No's and Temperatures °C.	Remarks
1	Jan. 22/26	3-1200,7-1180	100% CO atmosphere for runs 1-8
2	" 25/26	3-1190,6-1205,7-1180	
3	" 28/26	No results,cones crumbled	
4	Feb. 1/26	2-1215,4-1270	
5	" 4/26	2-1217,4-1270	
6	" 6/26	1-1290,2-1205,8-1200,9-1185	
7	" 8/26	1-1255,8-1180,9-1185,12-1330	Using Pt.Pyrom. from here on
8	" 11/26	1-1255,8-1195,10-1185	
9	" 17/26	13-1347,14-1195,15-1205,16-1200	CO-N_2 atmosphere for remaining runs
10	" 18/26	10-1190,11-1300,12-1326,13-1200	
11	" 22/26	13-1239,14-1215,15-1200,16-1205	
12	" 25/26	11-1332,13-1260,16-1227,17-1236,18-1275,19-1410	
13	" 25/26	No results,cones crumbled	No Orton cones in remaining runs.
14	Mar. 1/26	5-1285,6-1255,4-1245,17-1235, 18-1385,19-1500	
15	" 11/26	1-1273,5-1325,6-1217,7-1180,8-1180,11-1300	
16	" 12/26	21-1235,20-1270,22 to 25 - - 1400.	Silocel plate
17	" 13/26	21-1210,22-1400,23-1450,24-1440 25-1420,25-1445	
18	" 15/26	20-1245,21-1200,22-1410,23-1430,24-1360	
19	" 16/26	26-1345,27-1370,28-940,29 — 1500,31-990	
20	" 17/26	26-1335,27-1415,28 — 1500,29-1395,30-1500,31-1070	
21	" 22/26	32-1500,33-1450,34-1364,35-1500,36-1500,19-1500	
22	" 23/26	32-1500,33-1469,34-1500,35-1500,36-1500,19-1500	
23	" 25/26	21-1240,24-1500,28-1500,29-1500,30-1500,31-1500	
24	" 27/26	6-1240,13-1245,20-1288,27-1408,18-1330,34-1320	
25	" 29/26	1-1290, 6-1259,12-1370,18-1280,20-1280,28-1271	

Table J.

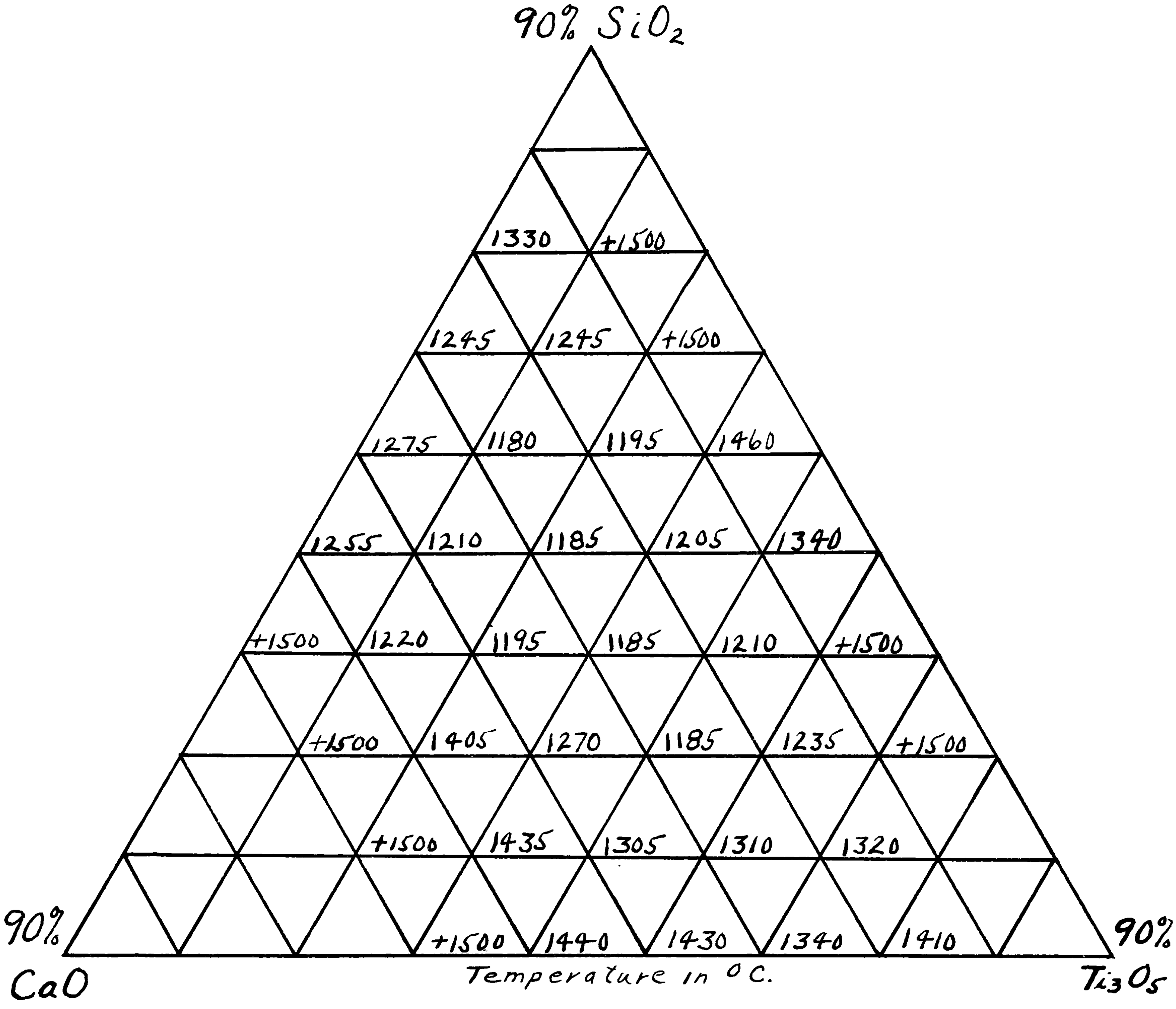
Summary of Softening Point Results of Cones Containing Ti_3O_5

	Softening Temperatures		Figure
Cone No.	Corrected Temp. from Time-Temp. Curves	Corrected Direct Reading Temp.	Used in Diagram
1	1285,1270,1270,1290	1302,1240,1275	1275
2	1210,1215,1190	1210	1210
3	1195,1190	1210	1195
4	1270,1270,1245		1270
5	1285,1325		1305
6	1205,1255,1255,1225, 1260,1240	1249,1256,1210,1240, 1258	1245
7	1180,1180,1180		1180
8	1200,1175,1195,1180,	1183	1185
9	1185,1180	1188	1185
10	1185,1190	1182	1185
11	1295,1340,1300	1302,1324	1310
12	1330,1315,1365	1332,1267,1371	1330
13	1345,12 ,1245,1260,1245)	1347,1232,1263,1249	1245
14	1195,1215	1192	1195
15	1205,1195	1202	1205
16	1195,1215,1235	1197,1197,1219	1210
17	1240,1230	1232,1240	1235
18	1275,1385,1340,1295,	1271,1317	1320
19	+ 1500,+ 1500 + 1410 + 1500		+ 1500
20	1270,1220,1240,1280 1290	1267,1202,1250,1275	1255
21	1235,1200,1240	1202,1240	1220
22	+ 1400,1400,1410		1405
23	+ 1400,1450,1425	1435	1435
24	+ 1400,1440,1360,1502	1363,1510	1440

Table J. Continued.

25	+ 1400,1420,1440		1430
26	1350,1335		1340
27	1370,1415,1405	1347,1410	1410
28	+ 1500,1275,+ 1500	940,1267	+ 1500
29	+ 1500,1395,+ 1500	1394	+ 1500
30	+ 1500, + 1500		+ 1500
31	+ 1500,+ 1500,+ 1500		+ 1500
32	+ 1500, + 1500		+ 1500
33	1450,1470	1468	1460
34	1365, + 1500,1330	1363,1309	1340
35	+ 1500, + 1500		+ 1500
36	+ 1500, + 1500		+ 1500

Notes on Operation. During the first run, a large amount of fume was given off within the muffle. Above 1300° C it was impossible to see the cones. After three or four runs, this fume diminished, so that it was possible to see them at 1400° C to 1450° C. For temperatures above this the muffle was heated for several minutes, and then cooled until the condition of the cones could be seen. The temperature was then raised to a higher point and the procedure repeated until all the cones had fallen. By taking 30° to 40° C jumps, the softening points were determined quite accurately. The temperature, at which the cones became invisible, varied from 1300° C to 1500° C according to the age of the muffle and the conditions of the run. By allowing a rapid flow of gas into the muffle, the fume was sometimes swept out long enough to make the cones visible.



Softening Temperatures of Mixtures
of
Silica, Lime, Ti_3O_5, with 10% Alumina

Diagram 1.

The first six runs were made in a pure carbon monoxide atmosphere. To produce a true blast-furnace atmosphere, the carbon monoxide-nitrogen gas mixture was used. The cones in the first runs were later repeated so that all the cones were tested under the carbon monoxide-nitrogen atmosphere.

A fume deposited on the cooler portion of the apparatus, and on the cones during cooling. It was a white, snow like substance, which was unaffected by ordinary acids at various concentrations and temperatures. It is possible that it is a lower oxide of silicon, namely monox. Also the carborundum crystals, in the construction of the muffle, are held by a bond, usually clay. This bond may give rise to the fume. The watch glass, acting as a window, was occasionally darkened by the fume. It was cleaned by unscrewing it from the apparatus and wiping off the dirt.

The power required for the motor generator varied from 17 K.W. to 27 K.W., according as the temperature rose from 1200°C to 1500°C. It was transformed from 220 volts to 55 volts. The latter voltage dropped to 40 as the resistance of the carbon became less with increase in temperature.

The pyrometers, after being thoroughly overhauled, worked satisfactorily. The optical pyrometer was checked against the thermocouple in an oxidizing atmosphere to see that there were no large differences. The clear silica tubes, holding the platinum wire, lasted three to four runs. They were not supposed to stand temperatures higher than 1300°C. In this work they were used at 1500°C. At this temperature, they crystallized and cracked. The platinum wire carbonized and broke off several times, due to faulty silica tubes.

Discussion. The cones containing Ti_3O_5 were dark in color when placed in the muffle. On removal, they were still black or dark gray. On fracturing them, a glassy, vesicular condition was noticed in the interior. Some of the cones, particularly the high Ti_3O_5 ones, often had a reddish coating. This was observed particularly on some of the low softening point cones, which were liquid at the higher temperatures. Some of the - 1500 ^{o}C. cones had an infusible skin which kept them upright, while the interior appeared to fuse and shrink away. This coloring and shrinking may be due to the formation of nitrides or carbides of titanium. The carbon in the bond may help this reaction. One run was made in which there were no cones containing Ti_3O_5 and no dextrine was used in moistening the cones. These white cones, after testing, were found to be white inside, but they had a dark outer surface. This showed that the dark color of the lime-alumina-silica cones was largely due to the carbon in the bond.

Many cones disintegrated on heating. Occasionally, a reading was obtained from the part left standing. For this reason, some of the tests were repeated several times in order to secure fairly close checks. This difficulty was overcome by a change in the procedure of making the cones (See Appendix, section B). The cones were well arranged so that those falling first did not interfere with those near them.

The correct softening temperature is reached when the top of the cone touches the pat. Most of the low softening point cones did not bend over gradually, but seemed to collapse suddenly, while those with high softening points fell slowly. In the case of those that collapsed, no fluxing action was observed at the base, but the pat may have been hotter than the top of the cone. To obtain more even temperatures, the silocel baffle was placed in the muffle, and a crystolon plate beneath it. A comparison of Graph Sheet No. 1., when the baffle was used, and Graph sheet No. 2., when it was not used, shows the effect of silocel.

Standard Orton cones were used to check the temperature readings in the first ten runs. These cones were white before entering the muffle, and a black, glassy, vesicular mass on removal. In an oxidizing atmosphere they remain white and are not vesicular. The softening points obtained were low, the discrepancy increasing with the cones of higher softening points. Table K shows the results.

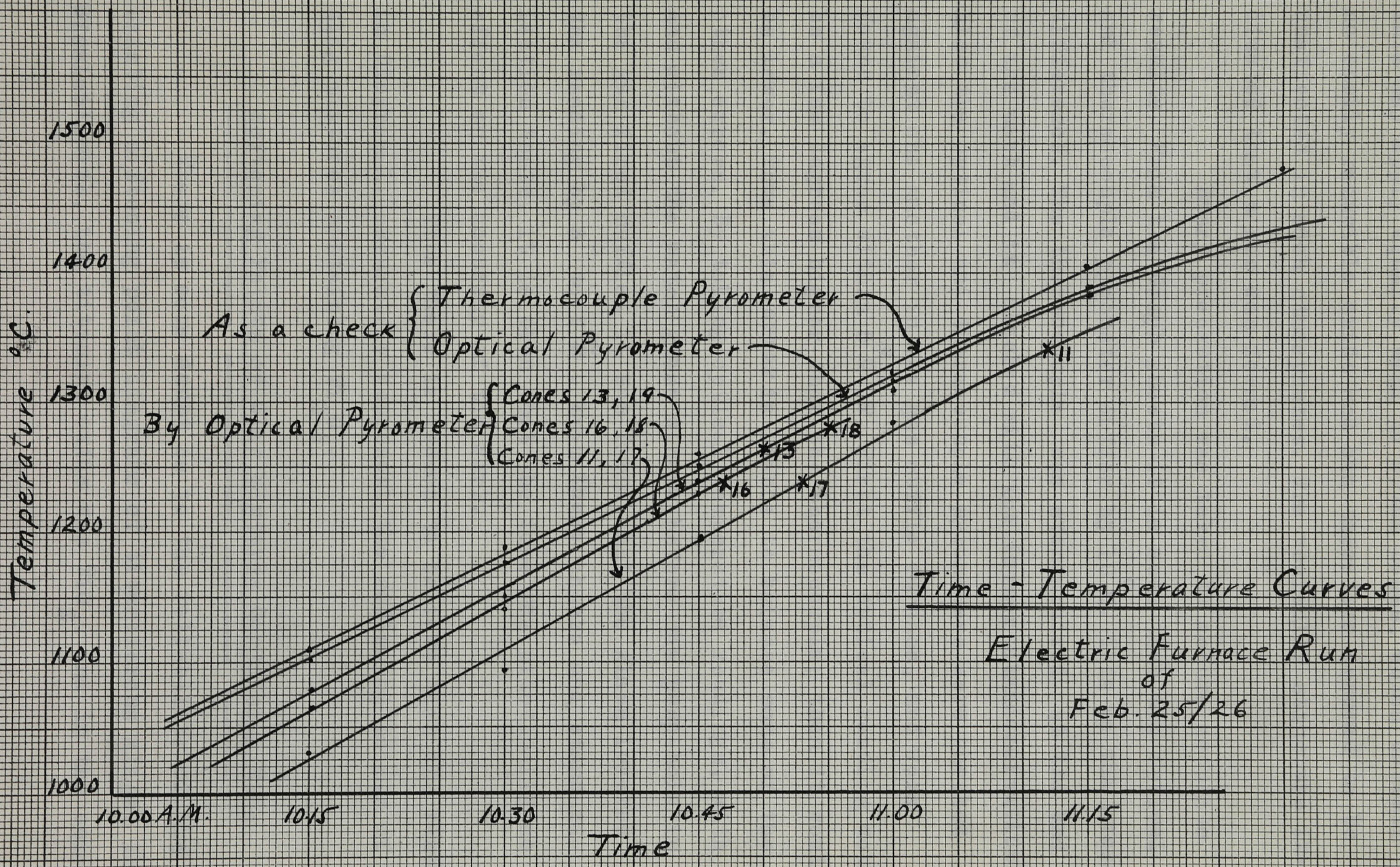
Table K.

Standard Cones in a Reducing Atmosphere

Softening Temperatures

Orton Cones	Maximum	Minimum	Mean	Should be
#4	1220 °C	1175 °C	1200 °C	1210 °C
7	1250	1235	1250	1270
10	1305	1270	1290	1330

These cones contain lime, alumina, and silica, with small amounts of potassium oxide. The carbon monoxide atmosphere may reduce some of these oxides. Carbon, deposited in a manner similar to the carburizing of steel, may be the reducing medium. According to the makers, reducing conditions should not affect the softening points of the cones.[28] It is believed that in the past sufficient thought has not been given to the action of refractories in reducing atmospheres.



Graph Sheet No. 2.

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This may apply equally well to Orton cones, which contain no easily reducible oxide and are therefore assumed to be unaffected in such atmospheres. The vesicular structure indicated that a gas was formed.

Every precaution was taken to secure accurate results. From the Graph sheets it is seen that the optical and thermocouple pyrometer differ by 10°C. This is the average difference. The thermocouple was standardized at the end of the work and it checked with the former standardization. Also the optical and thermocouple pyrometers were checked against one another in the gas muffle furnace, and were found to agree within 5°C .F. First the optical reading would be a few degrees higher than the thermocouple; then it would be lower. Thus this error is liable to balance some of the other errors. By taking optical temperature readings, with and without the watch glass window before the peep-hole in the gas fired muffle, it was found that the glass lowered the reading by 5° to 7°C . From these checks and standardization tests, it is seen that the fume has practically no effect on the accuracy of the work.

Thus there is reason to believe that the results in Diagram 1. accurately represent the softening points of slag mixtures containing Ti_3O_5.

Softening Points of Slag Mixtures Containing TiO_2

There is some doubt as to the reliability of the existing softening point diagrams of titaniferous slags. In Wissler's work, the titanium oxide was TiO_2, and in the conditions of his experiments some of it would be reduced to Ti_3O_5. Anson worked with Ti_3O_5 in his mixtures, but in such conditions that the Ti_3O_5 would be oxidized to TiO_2.

The work performed on the cones containing Ti_3O_5, as described herein, left little chance for the Ti_3O_5 to be oxidized to TiO_2. For comparison, it was desirable to make a few softening point determinations of cones containing TiO_2. This will eliminate the personal error present in comparing the results of independent workers, as well as checking their reliability.

The theoretical considerations discussed in the previous section will apply to the softening point determinations of the cones containing TiO_2,

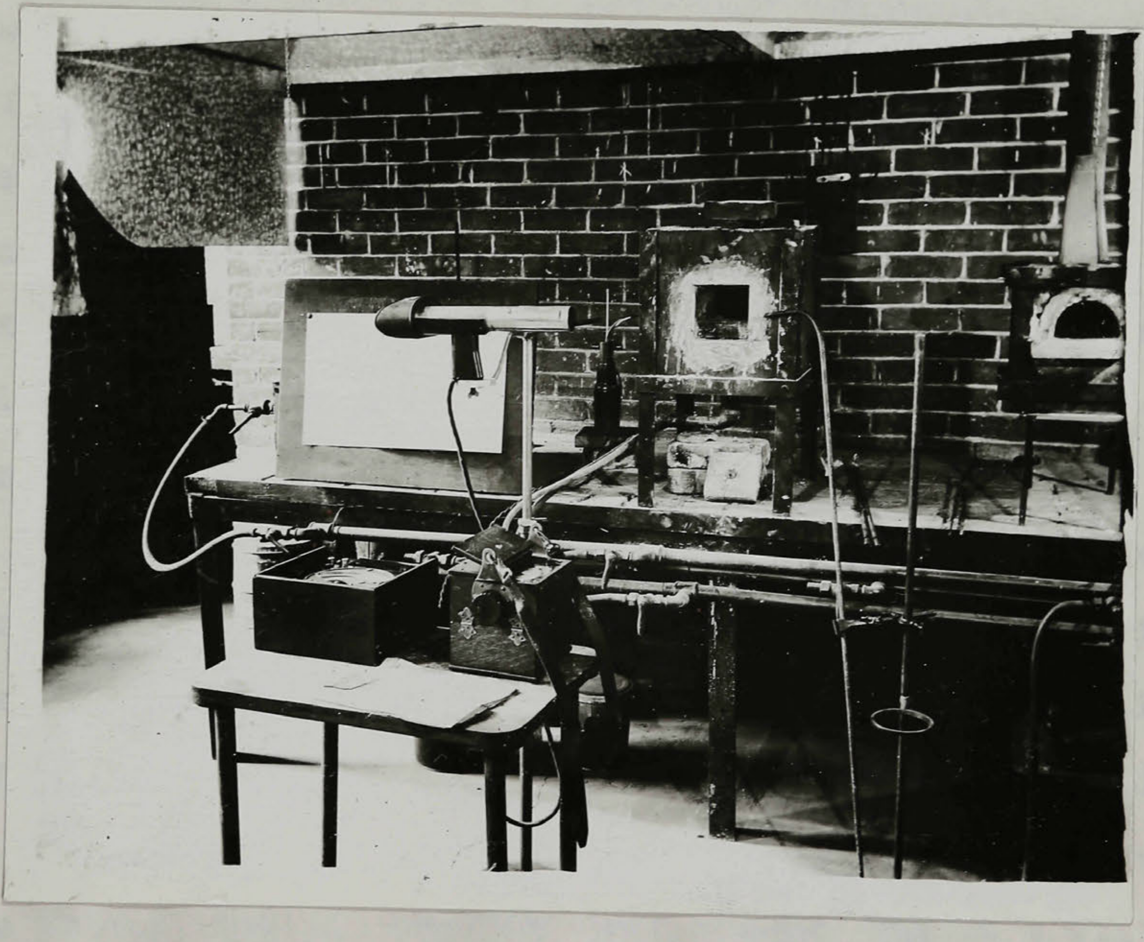
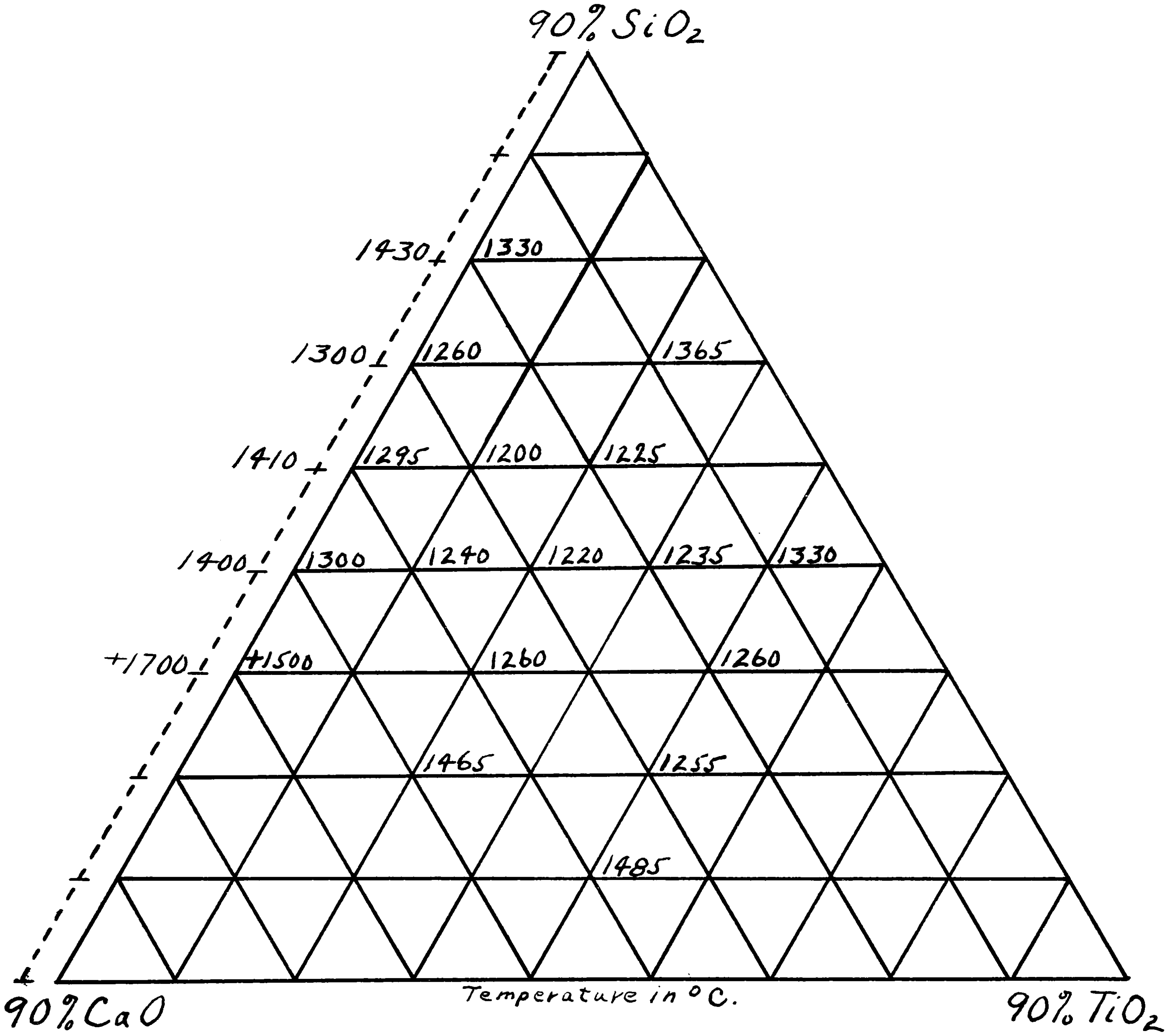


Figure -5-

<u>Apparatus and Operation</u>. The same apparatus was used for these tests as for the preliminary cone tests. Figure 5 illustrates the apparatus in position. The only difference was the absence of charcoal in the muffle in these tests. With this furnace a temperature of 1500° C may be attained in 2½ to 3 hours. To do this, a baffle of bricks was placed on the top of the furnace to prevent the escape of too much heat with the gases. Also the gas mixture was regulated so that there was not an excess of either gas or air to carry away heat.

After the first hour of heating, the temperature reached 1100° C. From this temperature upwards, the rate of heating was 3° C per minute. A blue glass was necessary to view the interior of the muffle at temperatures over 1200° C. Each pat held from six to eight cones. The softening points of the cones were obtained by readings through the optical pyrometer. The platinum platinum-rhodium pyrometer was used from time to time to check the optical pyrometer, which was sighted on the end of the silica tube for this reading. To obtain checks, each cone was run twice.

All the 99.4% pure TiO_2 was used for the production of Ti_3O_5. For these experiments, potassium titanium oxalate was dissolved in water , slightly acidified with sulphuric acid. The titanium was hydrolysed to $Ti(OH)_4$ by the addition of excess ammonia. The flocculent precipitate was washed several times by decantation, and on a filter paper until the wash water did not give a basic test with litmus. The precipitate was dehydrated, and the paper burnt



Softening Temperatures of Mixtures
of
Silica, Lime, TiO_2, with 10% Alumina

Diagram 2.

away, at a temperature of 1000 °C. The oxide thus obtained was analysed and found to be 99.1% pure. This material was ground and used in making the slag mixtures. The composition of the various cones is the same as that listed in Table H, except that Ti_3O_5 is replaced by TiO_2. For example cone 7 in that table has a composition of 10% Al_2O_3, 50% SiO_2, 30% CaO, 10% Ti_3O_5. In this work, cone 7 contains 10% Al_2O_3, 50% SiO_2, 30% CaO, 10% TiO_2. Table L. contains the results.

For the five runs, a comparison of the average readings of the optical and thermocouple pyrometer show the following differences between the two instruments, the optical being respectively, - 2 °C, - 3 °C, + 3 °C, + 3 °C, and, + 7 °C compared with the thermocouple reading.

No difficulties were experienced in these runs. The cones softened and fell at a fairly slow rate so that there was no doubt as to the softening point. Cones 7 and 12 were the only ones to fall very quickly. The high temperature cones 5,22, and 28 shrunk somewhat before falling. Cone 28 did not fall at 1500 °C, and on cooling it crumbled to a fine white powder. This indicated that its softening point was well over 1500 °C. All the cones were yellowish white after falling. At the higher temperatures, cones softening at low temperatures became fluid and were absorbed by the alundum of the pat. There was no indication that the alundum was fluxing the cones. A temperature-concentration diagram is plotted in Diagram 2.

Personal Error. In order to determine the personal error in this work on the softening points, a run was made using six Orton cones. The same apparatus and conditions were employed as in the previous cone tests on slag mixtures containing TiO_2. Table M shows the results.

Table L.

Softening Point Results of Cones Containing TiO_2

Cone	Softening Point	Check	Temperature used in Diagram
1	1293° C	1293° C	1295° C
2	1240	1235	1240
3	1260	1260	1260
5	1490	1480	1485
6	1267	1249	1260
7	1202	1202	1200
8	1230	1211	1220
10	1249	1258	1255
12	1330	1332	1330
14	1220	1230	1225
15	1230	1240	1235
16	1255	1267	1260
19	1370	1363	1365
20	1302	1302	1300
22	1460	1465	1465
28	+ 1500	+ 1500	+ 1500
34	1340	1317	1330

Table M.

. Determining Personal Error by Orton Cones

Orton Cone	Found to be	Should be
#4	1206	1210
7	1280	1270
10	1333	1330
13	1383	1390
16	1464	1450

Averaging the optical and thermocouple pyrometer readings taken as a check, the optical readings were found to read 7°C higher. It is evident from these results that there is no serious personal error affecting the determination of these softening point diagrams.

Pyrometer Standardization. As a further check on the accuracy of the work, the platinum-platinum-rhodium thermocouple was standardized. The wire used in the first experiments had been broken several times, and finally had to be replaced. The cold junction of the new wire was 1°C, while the old one was 15°C. Making allowance for this difference at the cold junction, a perfect check was obtained on the freezing point of copper, a difference of 0.1 millivolt on the melting point of platinum, and 0.2 millivolts on the boiling point of water. A difference of 0.1 millivolt correspomded to a temperature change of 5°C, when working at temperatures over 800°C.

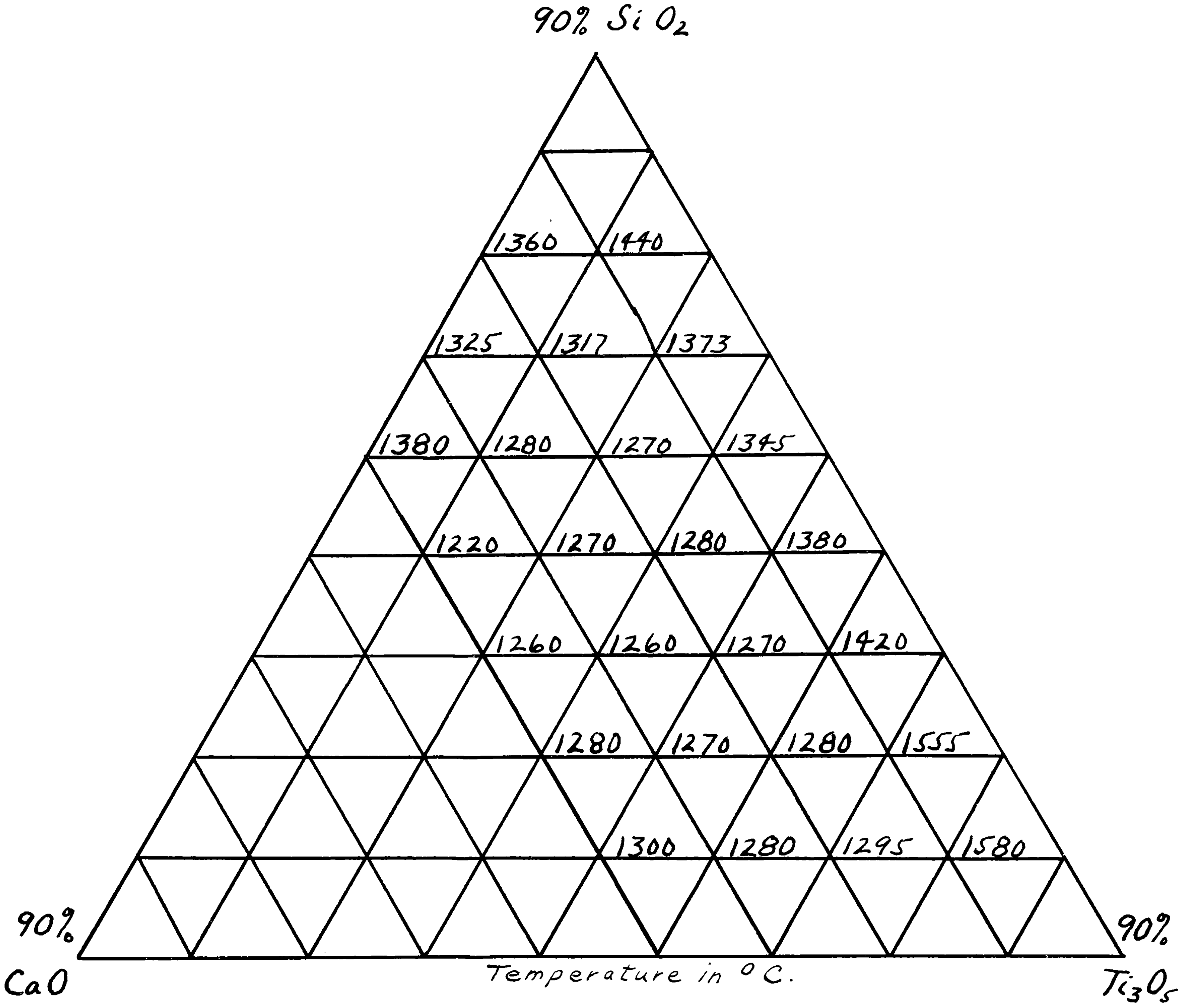
The softening temperatures are in the range between the freezing point of copper and the melting point of platinum. Thus the old chart of temperature-millivolt readings can be used for the new wire without danger of affecting the accuracy of the results.

Discussion. In Diagram 2, a dotted line of equal length is placed parallel to the lime-silica side of the triangular diagram. The five figures[20] placed on it are obtained from Rankin and Wright's treatise on "The Ternary System CaO-Al_2O_3-SiO_2." These points correspond in composition to the five points determined on the adjacent line. The Rankin and Wright values are much higher. In performing their work, they melted the various slag mixtures, cooled them slowly until solidification began to occur and then quickly chilled the mass. The temperature at which the crystals first formed, was called the melting point. A microscopic examination followed. As the temperature of the melt decreases, a primary mineral crystallizes, thus changing the composition of the liquid until a point is reached when two minerals crystallize. As the temperature drops still further and the two minerals separate out, the liquid composition changes until a second point is reached, when three minerals crystallize out. At the end of the solidification of the three minerals, the mass becomes solid. Thus there are really three solid phases taking part in the solidification of such a slag mixture. Rankin and Wright's melting points are obtained when the first solid phase crystallizes. In the cone tests, the softening points depend on the amount of the third solid phase that liquifies. The temperature range between the first and third phases may be considerable. Therefore it is readily seen that Rankin and Wright's determinations cannot be compared with the softening points of cone mixtures.

The composition of points on the 0% Ti_2O_5 line in Diagram 1, and the 0% TiO_2 line in Diagram 2, are identical. In the first case the cones were treated in a reducing atmosphere producing results lower than in the second case, where an oxidizing atmosphere was used. This difference varies from $0^{o}C$ to $45^{o}C$. These results may be used as further evidence that refractories and cones are affected by reducing atmospheres.

Comparing all the points in Diagram 2 with the corresponding ones in Diagram 1, it is observed that the majority of the latter are somewhat lower than the former. In both diagrams the softening point temperatures drop as the composition changes from the sides to the center of the diagram. The lowest point occures at the same place in both diagrams. The mixtures containing no titanium oxide (0% Ti_3O_5, or TiO_2, in both diagrams) soften at a lower temperature in the reducing atmosphere. Allowance for this effect must be made in comparing the other points. The exception in the diagrams occur on the 10% lime line, where the points in diagram 1 are higher. Comparison of Diagram 1 with Diagram 3 shows the same fact. It was in cases of this composition, containing Ti_3O_5, that the infusible skin with the copper color was noticed.

There is a difference of approximately 7% in the weights of equivalent amounts of TiO_2 and Ti_3O_5. Thus corresponding points in Diagrams 1 and 2 will not be exactly comparable. In a mixture containing 50% Ti_3O_5, there will be a difference of 7% of 50% = 3.5% between the Ti_3O_5 and an equal weight of TiO_2. However it must be remembered that the weight of the Ti_3O_5 present in such a mixture, compared with the TiO_2 present, will be as 50% - 3.5% = 47.5% is to 50%. Therefore the actual difference in comparing cones containing 50% of the titanium oxide will be $\frac{3.5\%}{47.5\%} =$ 1.7%. Calculations show that as the amount of titanium oxide increases or decreases from 50%, this difference decreases. Thus the maximum error, in comparing points in these diagrams, is not more than 1.7%. If the points are compared by the titanium content then the greatest difference will occur in mixtures containing the largest amount of titanium oxide. The error in this case will be (90% X 9/14) - (90% X 3/5) = 3.9%, where 9/14 and 3/5 are the ratios of Ti to Ti_3O_5 and Ti to TiO_2 respectively. Diagram 3 is a



Softening Temperatures of Mixtures
of
Silica, Lime, Ti_3O_5, with 10% Alumina
as
Determined by Anson

Diagram 3.

copy of one prepared by Anson from his results. He used Ti_3O_5 in his cone mixtures, but under such conditions that probably it was oxidized to TiO_2 . The majority of his points are much higher than the corresponding ones shown in both the diagrams illustrating this work. Again an exception is noted in the points on the 10% lime line of Diagram 1. Hid determinations on cones containing no titanium oxide are much nearer Rankin and Wright's values than the determinations made in this research.

In Wissler's figure[13], there is no regular decrease in softening points as the composition of the cones proceeds to the center of the diagram. There are high and low points adjacent to one another in both the center and borders of the diagram. These results look more like some that would be obtained by using methods such as Rankin and Wright's. The even trend of the softening points in Diagrams 1,2, and 3 is what would be expected from the constution of solid slags. The temperatures will vary according to the amount of the low melting solid phase where the three minerals separate out together. This may also explain why some cones fall rapidly and others slowly.

The Effect of Nitrogen on the Fusibility of Titaniferous Slags

Compounds of Titanium with Nitrogen and Carbon. Titanium combines with nitrogen with avidity to form two compounds Ti_3N_4 and TiN_2. Also the nitride TiN is known to exist. Generally Ti_3N_4 and TiN_2 are made by complex reactions[24] between ammonia and various titanium compounds. Moissan prepared TiN from

TiO_2 and carbon in the presence of nitrogen. His charge was contained in a graphite crucible kept at a high heat. TiN appeared as bronze yellow crystals.Ti_3N was described as being of a copper-red[25] color.

Only one carbide of titanium is known to exist, namely TiC. It is a black substance[26] formed by the direct combination of titanium and carbon in cast iron[5].Moissan obtained TiC while trying in an electric furnace to reduce TiO_2 to titanium by carbon.

Wohler analysed some coppery colored accretions formed in iron blast-furnaces, and he gave them the formula $Ti\ (CN)_2 . 3\ Ti_3\ N_2$. Later he made this compound artificially from potassium ferrocyanide, TiO_2, $Ti\ Cl_4$, and KCN. He claimed that he obtained the CN radical in both cases.

Possibilities of Nitride and Carbide Formation in a Blast-furnace. Conditions in a vlast-furnace are most suitable for the formation of titanium nitrides and carbides. The temperature of the furnace is more important than the presence of large amounts of carbon and nitrogen. The higher the temperature, the more carbide and nitrodes will be formed. These compounds are relatively infusible so that their increased presence might offset the greater fluidity of the slag at the higher temperature. This may explain the pasty slags obtained by Goodwin[14]. He noticed a reaction talking place between the carbon of the crucible and the slag, as the latter was getting pasty. In this case the supply of nitrogen was limited, compared with that of a blast-furnace, so that the carbide would predominate.

There has been some doubt, as to the existence in blast-furnaces, of the coppery compound whose formula was determined by Wohler. This formula may be rearranged to read 2 Ti C. 8 TiN. The presence of the CN radical, as related by Wohler, will strengthen the contention of the other formula. Kinney and Guernsey[27] took gas samples from the slag notch of a blast-furnace and analysed them for potassium cyanide. They found amounts present varying from 0 to 19 grams per cubic meter. This shows that the CN radical is formed in a blast-furnace. The action[24] of CN on metals is similar to that of oxygen. They both have a strong affinity for the most reactive metals, but very little affinity for the noble metals. Titanium is a very reactive metal, so that its cyanide will tend to be stable at blast-furnace temperatures. From this reasoning there is every probability of Wohler's compound existing in a blast-furnace.

The Effect of Nitrogen on the Softening Points. The temperature of the softening points of the Ti_3O_5 cones varied from 1180° C to + 1500° C. At temperatures above 1400° C, a reddish yellow coating was noticed on some of the cones, and others appeared to have formed an infusible outer skin. This outer skin kept the cone fairly rigid while the interior was fusible. These observations seemed to indicate that above 1400° C, the nitrogen, carbon monoxide and carbon (in the pat) were combining with the titanium in the cones to form nitrides, carbide, or nitrocyanides, The bond used in making the cones would supply some carbon for the reactions. In this case the softening point temperatures above 1400° C. will not be accurate.

Reduction of TiO_2 in a Carbon Monoxide-Nitrogen Atmosphere.

The apparatus for the production of Ti_3O_5 was set up so that quantitative tests could be made on the reduction of TiO_2 in a carbon monoxide-nitrogen atmosphere. Weighed amounts of TiO_2 were contained in a carbon and an alundum boat placed in the graphite tube in the furnace. Gas was passed over the oxide for 2½ hours, while the temperature increased from 800°C to 1400°C or 1500°C in the first hour, and remained stationary thereafter. The tube was cooled as previously (see section on "Production of Ti_3O_5"). Two runs were made, one at 1400°C, the other at 1500°C. The oxide used contained 98.2% TiO_2. The results are shown in Table N.

Table N

Reduction of TiO_2 in a CO-N_2 Atmosphere

Time of heating-3½ hours. Time of gas flow 2½ hours + cooling time

Analysis of gas in holder: CO_2 3.6%, O_2 0.1%, CO 31.0%, N_2 65.3%

All the CO_2 was absorbed in the washing train.

Run	Temperature	Boat	Wt. of Boat	Wt. of boat - Oxide	Wt. of material	Wt. of boat - oxide after heating	Wt. of material as calculated while in boats	Wt. of material after removing it from boats
1	1400°C	Alundum	7.3669 grs.	9.3669 grs.	2.0000 grs.	9.0792 grs.	1.7103 grs.	1.9755 grs.
	"	Carbon	9.2423	10.7423	1.5000	10.0330	1.0607	1.4250
2	1500	Alundum	7.0754	8.0754	1.0000	7.9978	0.9224	0.1995
	"	Carbon	8.8852	9.8852	1.0000			

N.B. In the above table column 8 is found by subtracting column 4 from column 7. Column 9 is a direct weighing of the material .

The weight of the oxide after heating was obtained in two ways:- (1) By removing the material from the boats and weighing it, (2) by subtracting the weight of the empty boat before heating from the weight plus the oxide after heating. The results obtained are lower by method (2), except with the alundum boat in run 2, where some of the oxide fused to the boat. The loss in the alundum boat is probably due to the reduction of some of the compounds used in its construction. The loss in the carbon boat may be caused by the formation of titanium carbide, or the establishing of equilibrium between carbon, carbon dioxide, and carbon monoxide.

In run 1, the incoming gas passed over the carbon boat first. The material in this boat was blue, with a few yellowish crystals at the inner end. The material in the alundum boat was blue throughout with a top layer of dull yellow colored crystals. Some of these particles were very shiny. A few very small black and white globules were noticed on the surface of the slightly fused mass. They are probably due to impurities in the oxide. The incoming gas probably cooled the carbon boat below 1400° C at which temperature it would not react with TiO_2 . The second boat was hot enough for the nitrogen to act on TiO_2 , producing the yellow crystals

In run 2, the temperature was at 1500° C at the end of the run. Both boats contained a blue material with a superficial layer of coppery colored crystals. Some of these crystals were brassy in color. In the carbon boat, the crystals were somewhat darker than in the previous run, probably due to the effect of the blue color beneath. The coppery color is very noticable where the material is in contact with the carbon. In the alundum boat a greater amount of coppery material is formed, and it fused somewhat to the sides of the boat.

The flame, burning from the outlet tube during both runs, had a yellow color like a sodium flame. In the previous work on the production of Ti_3O_5 , a carbon monoxide flame was obtained. This yellow flame was due to some white solid which collected in the outlet tube.

Table O is formed to illustrate the losses in weight that would occur if certain compounds were formed. Of the two losses obtained for the material in each boat, the least loss is taken for this table.

Table O

Weight Losses in Converting TiO_2 to Lower Oxides or Nitrides.

Run	Boat Holding Oxide	Experimental Loss in Wt.	Loss in Wt. if TiO_2 Converted to			
			Ti_3O_5	TiC	TiN	$Ti(CN)_2 \cdot 3Ti_3N_2$
1	Alundum	1.2%	6.7%	25.0%	22.5%	21.7%
	Carbon	5.0%				
2	Alundum	7.8%				
	Carbon	13.7%				

From this table it is seen that in run 1 not all the TiO_2 was reduced to Ti_3O_5. However in run 2 it went far beyond this stage, indicating the partial formation of nitrides, carbides, or nitrocyanides.

Discussion. There was not sufficient time available to make more exhaustive experiments in this direction. The little work accomplished tends to show that under the conditions present in a blast-furnace, the formation of nitrides and carbides will take place at temperatures over 1400° C. It is the formation of these compounds which has caused the difficulty in determining the softening point of cones that soften above 1350° C. Much interesting experimental work remains to be done on the relations between TiO_2, carbon, and nitrogen in blast-furnaces smelting titaniferous iron ores.

The results of these few experiments substantiate the finding of previous investigators who handled titaniferous ores. They declared that freedom from infusible accretions would result if the furnaces were run at a low temperature. If the temperature of the furnace is between 1400° C and 1500° C some of these infusible compounds will form. The amount present will be relatively small and probably will be flushed out with the slag. Above 1500° C, they will form more readily. The increased amount may cause the slag to become pasty, or may result in the building of an infusible accretion on the side of the furnace. The temperature of slags in normally operating furnaces is about 1500° C.

In order to complete this work on softening point determinations, it would be advisable to treat some TiO_2 in a carbon monoxide-nitrogen atmosphere at 1500° C until it reached a constant weight. Softening points should then be determined, using the new material in place of Ti_3O_5 in the cone mixtures.

Conclusions

The conclusions to be drawn from these experiments may be summarized as follows.

1. Carbon monoxide reduces TiO_2 to Ti_3O_5 at temperatures above 1000^{o} C.

2. Ti_3O_5 will not exist at high temperatures in the presence of a gas containing over 14% of carbon dioxide.

3. TiO_2, in the presence of gases containing 100% to 14% carbon monoxide, will have a superficial coloring which incorrectly indicates reduction to Ti_3O_5.

4. An equilibrium exists between TiO_2 and Ti_3O_5 in an atmosphere containing 0% to 14% carbon dioxide.

5. Standard Orton cones are unreliable in strongly reducing atmospheres.

6. Above 1400^{o} C nitrogen, in the presence of carbon, acts on Ti_3O_5 producing infusible compounds which prevent the accurate determination of the softening points of slags containing Ti_3O_5.

7. Above 1400^{o} C, the action of nitrogen and carbon monoxide on TiO_2 produces copper colored or yellow colored crystals, presumably nitrides of titanium.

8. The charts of softening points of titaniferous slags will prove of value in making up charges for smelting. An examination of this chart shows a range of slags that would be easily fusible at blast-furnace temperatures.

9. A study of these softening point charts, in comparison with Rankin and Wright's work on "The Ternary System $CaO-Al_2U_3$ - SiO_2, should give much interesting information on the action

titanium oxide in slags.

10. A great deal of interesting research remains to be done on the relations between TiO_2, carbon monoxide, carbon dioxide, and lower oxides of titanium; also the effect of nitrogen on titaniferous slags.

In concluding, the writer wishes to acknowledge the advice and assistance received from the following:-

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Mr. A. T. Powell, M.Sc.

Part Three

Appendix

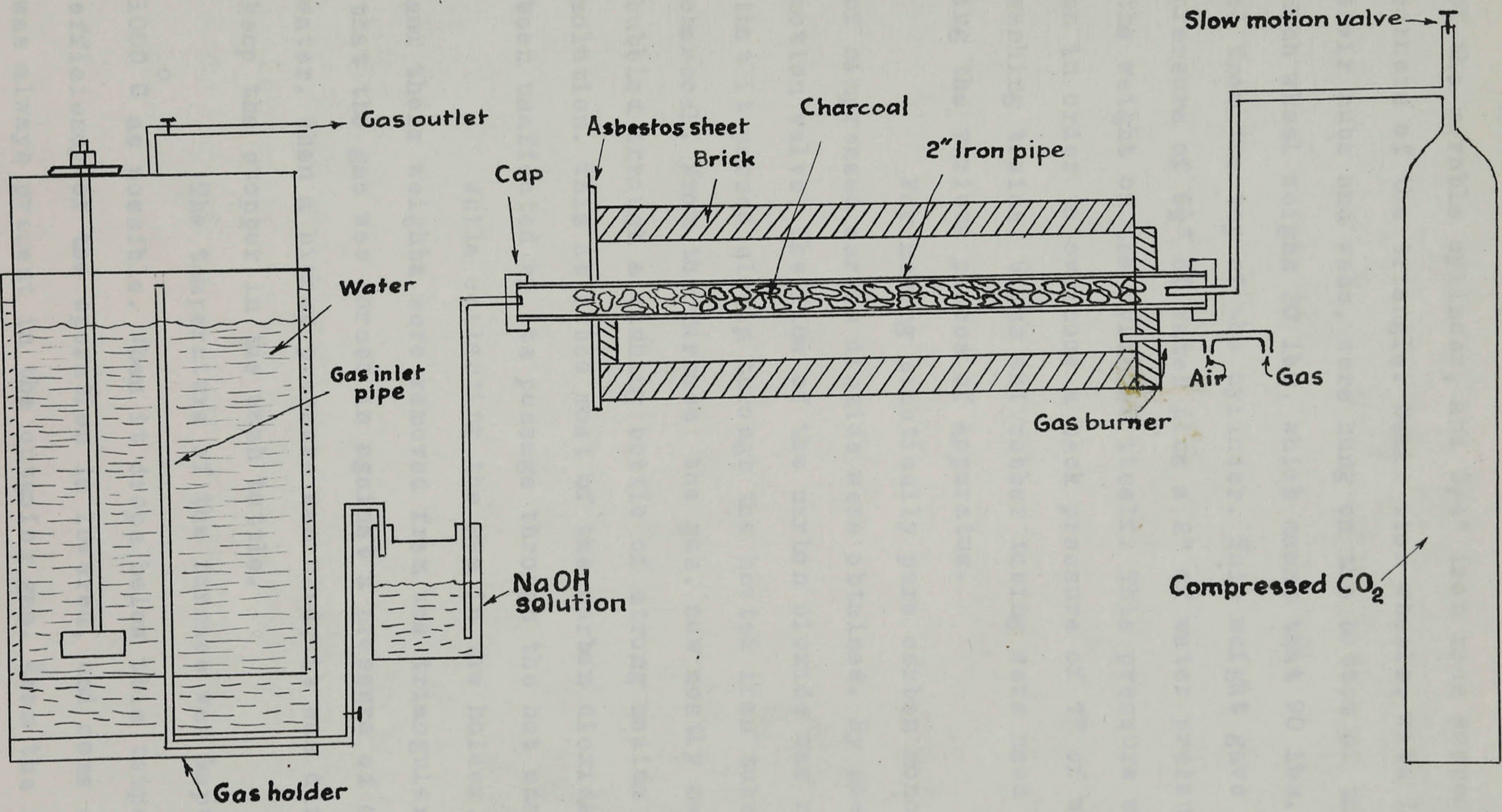
Preface. Carbon monoxide, either pure or containing varying amounts of nitrogen and carbon dioxide, was used continually throughout the tests described in the previous sections of this report. Similarly, the preparation of cones for determining softening points was often necessary. It is more convenient to discuss these processes under the heading of an appendix, than in the main body of the report.

Section A.

Preparation of Gas.

An illustration of the apparatus appears in Figure 6. It consisted of a 2" iron pipe, 3'9" long, capped at both ends. Short pieces of 1/8"iron tube were threaded into the caps to provide for entrance and exit of the gas. The tube was enclosed in a brick furnace 3'6" X 9" X 9", outside dimensions. The inside section is 4" X 4". A gas burner was placed at the end of the furnace at which the carbon dioxide enters. As the flame was shot the length of the furnace, the exit end was the hotter. At this end the pipe projected through a piece of sheet asbestos which fitted against the bricks and seemed to keep the heat within the furnace.

The gas was collected in a gas holder capable of holding 14.15 cu. ft. It consisted of a cylinder, 2' diameter and 4'6" high, enclosed in a slightly larger tank which is filled with water. The gas flowed into the inner cylinder and forced it upward, the water acting as a seal against the escape



SKETCH OF APPARATUS FOR GENERATING GAS

Figure 6

of the gas. A triangular frame work of iron was placed on top of the movable cylinder, and 3/4" iron rods suspended from the corners of the triangle. Small iron wheels, with lead cast in their hubs and webs, were hung on the bottom of these rods. Each wheel weighs 30 lbs, which means that 90 lbs. was suspended from the top of the cylinder. This weight gave the gas a pressure of 6½" of water plus a 2" of water pressure due to the weight of the cylinder itself. This pressure was decided on in order to overcome a back pressure of 7" of water in the washing trains. Glass and rubber tubing were used for connecting the various pieces of apparatus.

For making practically pure carbon monoxide, cylinders of compressed carbon dioxide were obtained. By means of a slow motion valve, the flow of the carbon dioxide was regulated so that it passed slowly through the heated iron tube, filled with charcoal. From the furnace the gas, now mostly carbon monoxide, bubbled through a washing bottle of strong sodium hydroxide solution. This absorbed most of the carbon dioxide that had been unaffected by its passage through the hot charcoal.

While collecting the gas in the holder, the rods and their weights were removed from the triangular frame so that the gas was forced in against a pressure of only 2" of water. When a higher pressure was used, it was difficult to keep the stopper in the wash bottle.

The temperature of the furnace was kept as near 1000 °C as possible. When it drops below this temperature, the efficiency of the operation is lowered, and some carbon dioxide was always present in the outgoing gas. From the reaction.

$$CO_2 + C \rightleftarrows 2\ CO$$

22.4 cu.ft. 12oz..   44.8 cu.ft.

it is seen that 7 cu.ft. of carbon dioxide and 3 oz. of carbon would be required to fill the holder. This weight of charcoal has a volume of 0.025 cu.ft. The iron pipe has a volume of 0.082 cu.ft., but when filled with charcoal there is about 40% air space. Thus the actual charcoal present is about 0.05 cu.ft. Then a tube full of charcoal should be sufficient to fill the holder twice, and as a matter of fact, it lasted for two runs.

Before filling the holder the first time, city gas was run in several times so as to remove as much air as possible. Also the charcoal gives off volatile hydrocarbons at the temperature of the furnace. At first they were collected in the holder; but in later runs they were burnt in the air before beginning to collect the gas. The furnace was heated from 1 to 2 hours for this purpose before passing in the carbon dioxide.

By this process, 10 to 11 cu.ft. of gas was formed in 4 to 5 hours. An Orsat gas analysing apparatus was used to regulate the operation so as to give the best results.

For the oxidation runs in the silica tube, carbon monoxide was made in the manner described above, but without washing by the sodium hydroxide solution. The amount of gas was measured and an analysis made to determine the amount of carbon dioxide already in the gas. The amount of additional carbon dioxide required for a given gas composition was then calculated and added from the carbon dioxide cylinder. After finishing one run, further calculations and additions of carbon dioxide were made in order to have a gas of a higher carbon dioxide composition for the next run.

The carbon monoxide and nitrogen mixture used in the later experiments was prepared in the same apparatus, but instead of using carbon dioxide, compressed air was slowly passed over the heated charcoal. The oxygen united with the carbon to form carbon monoxide, while the nitrogen remained unaffected. The gas passed through a carbon dioxide absorbing solution of sodium hydroxide, and an oxygen absorbing solution of pyrogallic acid. The amount of gas absorbed by these solutions was very small, and they were maintained merely as a safety measure.

The reaction between the oxygen and carbon is

$$2\,C + O_2 \rightleftarrows 2\,CO$$

24 g., 22.4 l. 44.8 l.

Air contains approximately 80% nitrogen by volume. Therefore from every 100 cc of air used, 80 cc of nitrogen and 40 cc. of carbon monoxide will be obtained, that is the resulting gas will analyse about 66% nitrogen and 33% monoxide. The experimental results agree closely with this calculation.

A solution of 35 grams of 98% sodium hydroxide in 150 cc. of water was used for absorbing carbon dioxide. For absorbing oxygen, 15 grams of pyrogallic acid was dissolved in 100 cc. of a sodium hydroxide solution of the above strength. About 2" of solution was kept in each wash bottle.

The only trouble with this method of preparing carbon monoxide was the rapid oxidation of the iron tube. If the amount of air supplied to the burner was lowered, incomplete combustion resulted, with a corresponding drop in temperature. Complete combustion was required to obtain a temperature of from 900° C to 1000° C. Under the best conditions, a pipe lasted from 7 to 8 runs. In two runs a burner was supplied at each end of the furnace, but the life of the iron tube was lessened instead of being increased by this change.

Section B.

Preparation of Cones

For determining the softening points of the slag mixtures, the method adopted was to make test cones of mixtures of the various ingredients. The materials for these cones, except the titanium oxide, were the purest obtainable from the chemists. The analysis of the lime was:-

Sulphate - None   Iron - 0.012%
Chloride - Trace   Magnesium - 0.45%
Silica - 0.011%   Alumina - 0.002%

The analysis of the alumina was:-

Sulphate - None   Calcium - None
Chloride - None   Iron - Trace

The silica was labelled "natural pure".

The aluming and silica were already in a powdered form (- 200 mesh). The lime was ground to pass a sieve of 100 mesh, and was heated in a casserole to $1000^{\circ}C$ to drive off any carbon dioxide. The Ti_3O_5 was ground to - 100 mesh in an agate mortar. All materials were kept in tightly corked bottles so that neither moisture nor carbon dioxide could be absorbed.

At first the materials were weighed out according to the different proportions so that the mixture in each case amounted to two grams. This amount was found to be sufficient for four cones. Since only two cones were required, the mixtures were then weighed in 1 gram lots. Due to the construction of the apparatus for determining the softening points, small cones weighing 1/2 gram were desirable, as they required less space and therefore more could be handled in a run. Of the two cones, the second one was required as a check. In a large number of cases the checks were not accurate, and the mixtures had to be made a second time.

The mixtures were ground dry until well mixed, moistened to a thin paste, and allowed to stand in the air for several days. They were then reground, moistened, and moulded into cones. This procedure of drying in air for several days applied particularly to the high lime mixtures. If they were moulded directly, they cracked, probably due to the absorption of carbon dioxide. This second moistening was not followed in making cones for the first four runs, so that many of them crumbled in the muffle. After that it was found safer to apply this to all the mixtures. The moistening solution contained four grams of dextrine per 100 cc. of water. The dextrine acted as a bond in forming the cones.

The cones were three sided pyramids made in a V - shaped groove cut ina block of wood. This groove was frequently sand papered, coated with paraffin wax, and oiled. The stiff paste was pressed into the mould, smoothed off, and removed by means of a spatula to a piece of glossy paper. The cones were preferably allowed to dry over night, though they may be handled carefully after three hours.

As the Ti_3O_5 cones were being treated in a reducing atmosphere, they were placed on a block of graphite, 2" X 3" X ½". Graphite was used in view of the possibility that an alundum pat might flux the cones. Five triangular holes about 1/2" apart, were made in the block, and the cones cemented in with alundum. Three cones stood in the back and two in the front row so that all five were visible at one time. They were inclined so that those falling first would go in a certain direction and would not touch those around them. After getting the cones in position, the block was heated on a hot plate for 30 minutes. The cones were now ready for the softening tests.

In the first two runs, moist graphite was used to hold the cones in place. On heating,it lost its moisture and became powdery. It was then useless as a cement. On replacing it with alundum, no fluxing action was noticed. Thus alundum cement was used in practically all the runs.

For the TiO_2 cones, which are run in an oxidizing atmosphere, an alundum sheet was used as a support. Alundum was moistened to a thin paste, and poured into a sheet of the desired size. This was dried, and triangular holes cut in it. It was then baked at a red heat in order to make it hard. These sheets, with careful arrangement, held as many as eight cones.

Section C.

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