

13047
49

The efficiency of the reduction of iron ore
by gaseous reducing agents, and the effect of
catalytic agents,

A T H E S I S

presented to the faculty of the Graduate School
of the University of Minnesota, by

G. Leonard Pitchford

in partial fulfillment of the requirements for the
degree of Master of Science in Chemistry

June 2, 1910

From theoretical speculations and previous work¹ it appeared probable that by the use of catalytic agents, the efficiency of the reduction of iron ore by various gaseous reducing agents could be increased.

The first work on the reduction of iron ore of which we have a record was performed by Lowethian Bell, who published his results under the title of "Chemical Phenomena of Iron Smelting".

He demonstrated that the temperature of initial action of carbon monoxide on ferric oxide varied from 141° to 211° C., according to the physical condition of the ferric oxide.

He also showed that by passing carbon monoxide and carbon dioxide over ferric oxide, and raising the temperature sufficiently that it was reduced to FeO or possibly $Fe_{1.6}O_{1.7}$.

The next work to be done on the subject was by Alder Wright, A.P.Luff, and E.H.Rennie. They published four papers in the Journal of the Chemical Society of London in 1878 to 1880.

They worked with the oxides of copper, iron, zinc, lead, and manganese. From their work they drew the following conclusions.

1. Differences in physical state are attended with correlating differences in the temperatures at which the actions of the reducing agents carbon monoxide, hydrogen, and carbon on metallic oxides are first manifested.
2. In the case of the oxides of the metals, iron and copper, which form different oxides corresponding with different series of salts, the temperature of initial action of a given reducing agent on all the oxides of any one metal is sensibly the same unless the difference in physical structure is very marked.
3. The temperature of initial action of carbon monoxide on a given metallic oxide is lower than that of Hydrogen on the same sample of metallic oxide. That the temperature of hydrogen is similarly lower than that of carbon on the same sample. In some cases the differences between the temperature of

initial action of the carbon monoxide and the hydrogen is not very large.

In their later work they showed that when a metallic oxide was acted upon by a reducing agent under constant conditions:

1. In many cases the existence of chemical induction is tracable, ie. the action is at first slight, but after a time it commences, and proceeds at an accelerated rate until other retarding influences cause the rate of reduction to diminish.
2. The period of incubation, when measurable, is shorter the higher the temperature. The rate of reduction attained to after any given time (before the retarding action comes markedly into play) is greater the higher the temperature, as is also the maximum rate attained.
3. On comparing two reducing agents, the oxidation of which gives rise to different amounts of heat per given amount of oxygen consumed, the action on these of a given metallic oxide (under conditions the

the same for each reducing agent) may be expressed by two curved surfaces, such that the surface corresponding to the reducing agent evolving the least heat during oxidation, lies inside the other surface.

(e.g. hydrogen and carbon monoxide.)

4. A partial exception to this is noticeable when iron is employed with hydrogen and carbon monoxide, as reducing agents, owing to the interference with the reducing action proper, of the tendency of carbon monoxide to give a second reaction, indicated by the equation:
$$\text{Fe}_x\text{O}_y + \text{CO} = \text{Fe}_x\text{O}_{y+1} + \text{C}$$

This second reaction tending to reoxidize the iron, and having no analogue when hydrogen is used as the reducing agent.

5. Another partial exception to the rule was noticeable when manganese dioxide is employed, and hydrogen and carbon monoxide are the reducing agents, owing to the unequal retardation in the rate of reduction produced by the formation of a film of the partially reduced substance on the exterior of the particles of metallic

oxide employed, the superior diffusive powers of hydrogen and steam over those of carbon monoxide and carbon dioxide respectively, causing the retardation to be markedly less in amount with the hydrogen than with carbon monoxide, so that after a certain lapse of time the total amount of reduction produced by hydrogen under given conditions rises up to and then surpasses that produced by the carbon monoxide.

The present work was begun with the idea of studying the efficiency of the reduction of iron ore by various gaseous reducing agents, at various temperatures, and to learn if this efficiency could be increased by means of catalytic agents.

In the work of Bell, Wright, Luff, and Rennie only temperatures below 360° C. were used. In the experiments which are described below a temperature of about 730° C. was used.

In the construction of the apparatus the most essential points are:

- 1..The best method of bringing the reducing agents

in contact with the ore.

in contact with the ore.

2. A satisfactory means of measuring the temperature.
3. A method of collecting the water and carbon dioxide formed during the reduction.

Apparatus

After considerable preliminary work with stationary tubes it seemed advisable to construct a special rotating furnace so that the ore could be thoroughly exposed to the reducing agents.

Plates I, II, and III will give a clear idea of the furnace as finally constructed. Plate I shows the rotating joint. On account of the high temperature to be used the babbitt ring and bearing were left out. The joint was ground so that the two faces were in perfect contact, and were held together by means of the spring device. Plate I & III. The tension on this spring could be easily regulated.

Plate III shows an assembled view of the furnace.

The motor is $1/8$ H.P., rotating the furnace by means of the worm gear at about 15 R.P.M.. The gas was passed in through the tube beside the pyrometer wires. Iron cones were placed in the furnace pipe to prevent the ore from rolling away from the heat. The tube holding the pyrometer wires was supported by a spider so that it was stationary in the center of the furnace.

Pyrometer

The pyrometer constructed for measuring the temperature was a recording instrument, with one wire of platinum and the other an alloy of platinum and 10 % rhodium. The hot junction was inserted in the center of the furnace, encased in a small iron pipe, while the cold junction was kept in a beaker of ice water. The instrument was set so that it recorded every thirty seconds.

In calibration the pyrometer the M.P. of copper was taken as a starting point. About three pounds of electrolytic copper were placed in a graphite

crucible in the electric furnace. The wires were inclosed in a magnesia tubing, the bottom of which was near the bottom of the graphite crucible. The temperature was then raised to about 1250° C., and the amount of current reduced so that the cooling took place very gradually. At the freezing point the temperature remained constant for about four minutes, and the resistance was adjusted so that the instrument recorded 1084° C.. The temperature was again raised and allowed to cool as before. The instrument recording 1084° as before.

The melting point of antimony (630° C.) was next determined. The antimony was placed in a fire clay crucible and heated by a blast lamp. The antimony was covered by powdered charcoal to prevent oxidation, and the crucible was enclosed so as to better control the temperature. The general procedure was the same as in the case of the copper. The instrument recorded 650°.C.

The melting point of lead (327° C.) was then

determined. The procedure was the same as in the case of antimony. The instrument recorded 382.5°. The M.P. of the test lead used was checked with a normal thermometer and found to be 327° C.

The next point to be determined was the boiling point of naphthalene. (217° C.) The Naphthalene was placed in a flask and the boiling point taken with a normal thermometer. The magnesia tube which contained the wires was lowered so that the bottom was just above the surface of the liquid. The boiling was continued until the recording was constant, at 285°.

The boiling point of water was also taken in the same way. I then had the following points located, and from which the correction curve plate IV was plotted.

	Temperature	Recorded
Copper M.P.	1084° C	1084°
Antimony "	630	650
Lead "	327	382.5
Naphthalene	217	285.

The ore was the ordinary haematite or iron ore from the Mesaba Range, containing 62.27 % iron. This would give 283.1gms of iron per pound of ore. The ore was crushed so that it passed a 60 mesh sieve, then thoroughly mixed and placed in a wide mouthed glass stoppered bottle.

The gas used for the reduction was the Minneapolis illuminating gas which has the following composition:

CO ₂	3.75
C ₆ H ₆	2.73
C ₂ H ₂	9.44
O	1.14
CO	19.40
H	26.75
CH ₄	25.02
N	<u>11.77</u>
	100.00

The amount of ore used was one pound. The ore contained a considerable amount of moisture, and to get rid of this, before starting the experiments,

the temperature was raised sufficiently high to drive it all off. During this process air was passed through the furnace, which had been passed through caustic potash and then through two large calcium chloride towers. When a temperature of about 400° C. was reached no more moisture came off.

The apparatus for collecting the moisture and carbon dioxide formed during the reduction was arranged so that it rotated on the 3/8" pipe which extended from the end of the furnace. The gas passed out at the end of the furnace into a weighed flask kept cool by ice water. Most of the water formed was collected in this flask. It then passed into a calcium chloride tube in order to remove the remainder of the water, then into two 12" U tubes 1 1/2" in diameter, which were filled with caustic potash in sticks about 1/2" long, moistened with water for the purpose of removing the carbon dioxide. It then passed into soda lime to remove the last traces of carbon dioxide. Finally it passed through another tube of soda lime

which was not weighed, but arranged so as to prevent carbon dioxide from entering the apparatus through back pressure.

The apparatus was then thoroughly tested at every joint so as to be sure there was no leakage at the temperature and pressure which I was using.

In the first few experiments several minor difficulties were experienced and changes made to overcome them.

Experiment I

The temperature was first raised in order to drive out all moisture. The flow of gas was then started, with the following results:

Ore! 1 lb. crushed to 60 mesh

Length of experiment: 1 Hr.

Temperature of " : 600° to 650° C.

Gas	H ₂ O	CO ₂
22 liters	6.209 gms.	lost

Experiment II

The conditions were the same as in experiment I.

The results were as follows:

Ore: 1 lb. crushed 60 mesh.

Length of experiment: 1 hr.

Temperature: 650° to 715° C.

Gas	H ₂ O	CO ₂
27	9.97 gms	16.68 gms.

Assuming that the iron was reduced from Fe₂O₃, and calculating for the amount of iron, would give the following:

Fe from H ₂ O	Fe from CO ₂	Total Fe
20.62 gms	14.12 gms	34.74 gms

These figures would then show a reduction of 12.30 % of the iron present.

Experiment III

The method of procedure was changed somewhat. The same amount of ore was used as before, but the temperature was raised until it was constant while

the dry air was passing through, then the flow of gas allowed to pass through for one hour. The flow was stopped, and the absorption apparatus weighed and changed. This method was continued for ten hours, the temperature remaining constant during the entire time. The results were as follows:

Hr.	Gas	H ₂ O	CO ₂
1	20 liters	7.15 gms.	9.15 gms.
2	8	3.59	6.65
3	9	2.28	6.56
4	19	3.54	12.00
5	22	4.11	12.17
6	27	4.57	8.45
7	1271	1.71	4.78
8	9	1.18	2.95
9	16	1.84	4.04
10	<u>19</u> 181	<u>3.67</u> 32.64	<u>3.80</u> 70.55

Ore: 1 lb.

Temperature! 725° to 735° C

Experiment III (Con.)

Hr	Gas	Fe from H ₂ O,	Fe from CO ₂	Total Fe
1.	20	14.44 gms.	7.743 gms.	22.183 gms.
2.	8	7.419	5.627	13.046
3.	9	4.712	5.551	10.263
4.	19	7.316	10.150	17.466
5.	22	8.495	10.300	18.795
6.	27	9.445	7.151	16.596
7.	12	3.534	4.045	7.596
8.	9	2.439	2.496	4.935
9.	16	3.803	3.419	7.222
10.	<u>19</u>	<u>5.518</u>	<u>3.216</u>	<u>8.734</u>
	161	67.460	59.700	127.160

Assuming as before that the iron is reduced from Fe₂O₃, the above results would give a reduction of 45.02 % of the iron present.

On examination of the residue it was found to consist of free iron and ferrous oxide. No satisfactory method of obtaining the amount of the ferrous oxide in the presence of the free iron, was found. The

Experiment III (Con.)

method adopted was to determine the total iron by taking a weighed sample and igniting it to burn out any carbon, then getting it into solution by hydrochloric acid, reducing with stannous chloride, and titrating with potassium permanganate.

The free iron was then determined by measuring the amount of hydrogen liberated on treating the residue with dilute hydrochloric acid. The apparatus used for this was that of Frnkforter and Frary (Journal of the Amer. Chem. Soc. Vol. 27 pp. 744.) for determining the hydrogen equivalent of zinc.

The analysis of the residue by the above method gave the following results:

Free iron	41.96 %	118.77 gms.
Ferrous oxide	55.04	164.33

The residue in the above experiment, as are those in the later experiments, was cooled in an atmosphere of the reducing gases.

Experiment III (Con.)

During the fifth hour a sample of the escaping gas was taken, and the examination of this showed that all the benzine and the unsaturated hydrocarbons had been decomposed.

Experiment IV

In the previous experiment it appeared that the amount of reduction depended to a considerable extent on the amount of gas passed in, consequently in this experiment the gas was passed in faster.

The results were as follows:

(Next page)

Experiment IV (Con.)

Ore: 1 lb. crushed 60 mesh

Length of experiment: 11 hrs.

Temperature: 705° to 725° C.

Hr.	Gas	H ₂ O	CO ₂
1.	32 liters	10.69 gms.	20.65 gms.
2.	27	6.04	12.61
3.	40	8.74	12.46
4.	41	8.60	4.09
5.	38	8.30	9.96
6.	44	5.93	7.09
7.	50	8.17	6.58
8.	45	3.45	3.50
9.	55	4.31	4.12
10 & 11	<u>---</u> 372	<u>9.81</u> 74.04	<u>----</u> 81.06

It appears that part of the carbon dioxide escaped during the fourth hour, and the weight during the tenth and eleventh hour was not obtained.

Experiment IV (Con.)

Hr.	Gas	Fe from H ₂ O,	Fe from CO ₂ ,	Total Iron
1.	32	22.09	17.08	39.17
2.	27	12.48	10.67	23.15
3.	40	18.06	10.54	28.60
4.	41	17.78	3.46	21.24
5.	38	17.15	8.24	25.39
6.	44	12.26	5.99	18.85
7.	50	16.89	5.57	22.46
8.	45	7.12	2.96	10.08
9.	55	8.89	3.49	12.38
10 & 11		<u>20.27</u>	<u>-----</u>	<u>20.27</u>
		372	68.60	221.62
		153.02		

Calculating as before, this gives a reduction of 78.10 % of the iron present.

The analysis of the residue gave the following:

Free iron	48.76 %	132.40 gms.
Ferrous oxide	53.24	150.70

Experiment V.

Metallic Copper as a Catalytic Agent

In this experiment the system of collecting the water and carbon dioxide was changed somewhat. Calcium chloride towers were substituted for the large U tubes and arranged so that they rotated horizontally as shown in plate III.

The conditions were the same as in the previous experiment with the exception that a strip of copper gauze 2" wide was placed in the furnace pipe, so that the ore sifted through it as the pipe rotated.

The results were as follows:

Ore 1 lb. crushed 60 mesh

Length of experiment: 11 hrs.

Temperature: 722° to 735° C.

(over)

Experiment V (Con.)			
Hr.	Gas	H ₂ O	CO ₂
1.	34	9.33	8.68
2.	20	4.43	11.29
3.	17	3.46	9.49
4.	23	3.74	8.48
5.	26	3.99	7.18
6.	30	6.55	9.44
7.	35	6.18	8.33
8.	11	1.21	2.36
9.	30	3.61	6.05
10.	39	1.11	5.79
11.	<u>31</u>	<u>6.50</u>	<u>5.54</u>
	298	50.11	82.62

Experiment V (Con.)				
Hr.	Gas	Fe from H ₂ O	Fe from CO ₂	Total Iron
1.	34	19.28	7.35	26.63
2.	20	9.16	9.55	18.71
3.	17	7.15	8.03	15.18
4.	23	7.73	7.18	14.91
5.	26	8.25	6.08	14.33
6.	30	13.54	7.99	21.53
7.	35	12.77	7.05	19.82
8.	11	2.50	1.99	4.49
9.	30	7.46	5.12	12.58
10.	39	2.29	4.90	7.19
11.	<u>31</u>	<u>13.43</u>	<u>4.69</u>	<u>18.12</u>
	296	103.56	69.92	173.48

The above results would give a reduction of 61.29 % of the iron present.

The analysis of the residue gave the following:

Free iron	70.90 %	200.71 gms.
Ferrous oxide	29.10	82.39

Experiment VI

In order to find the influence of time on the reduction, it was decided to pass the gas through r rapidly.

The absorption apparatus was removed, and the temperature raised until it was constant. The flow of gas was then started with the following results:

Ore: 1 lb. crushed to 60 mesh

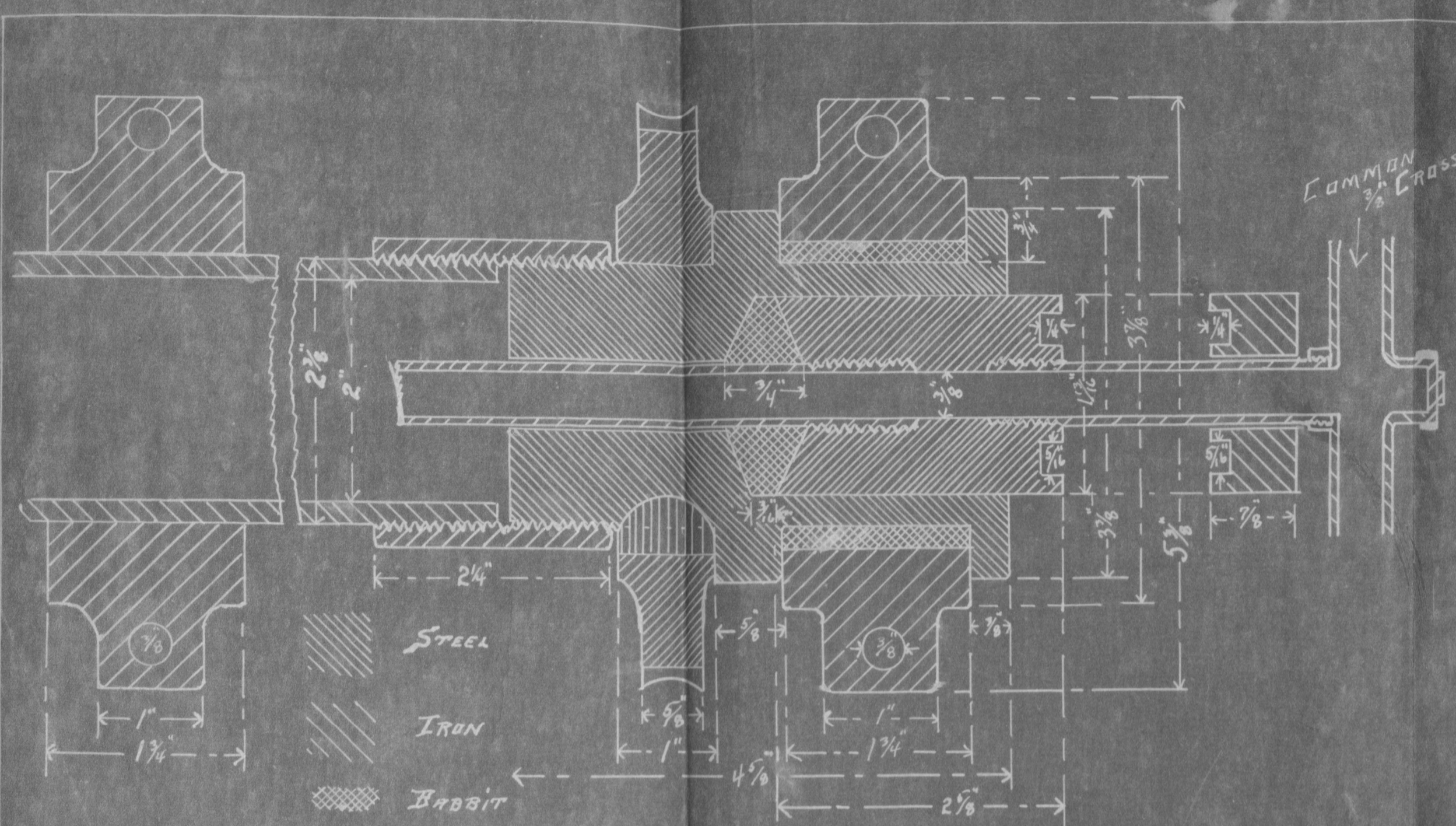
Length of experiment: 2 1/2 hrs.

Temperature: 725° to 735° C.

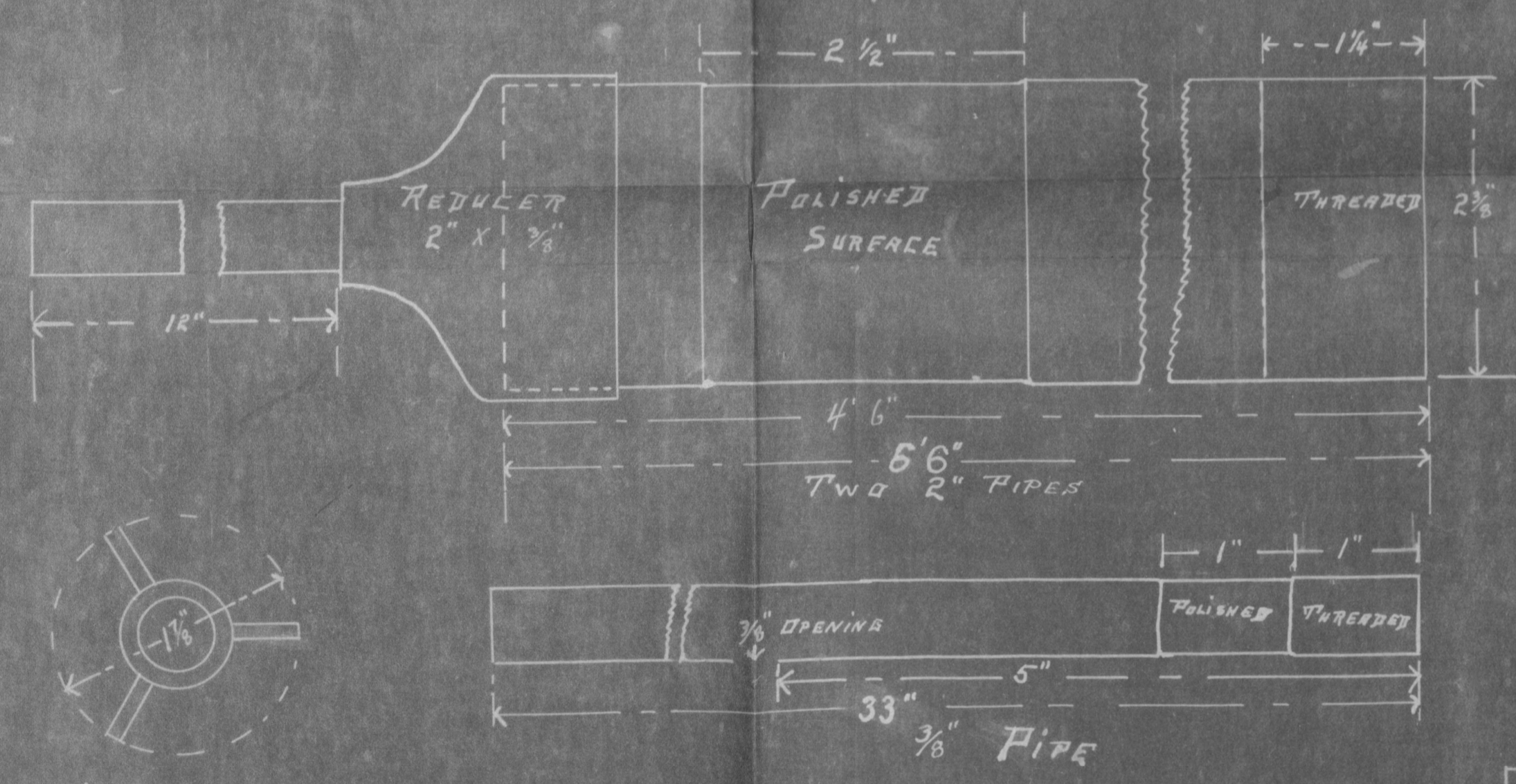
Gas passed through: 450 liters

The analysis of the residue showed the following:

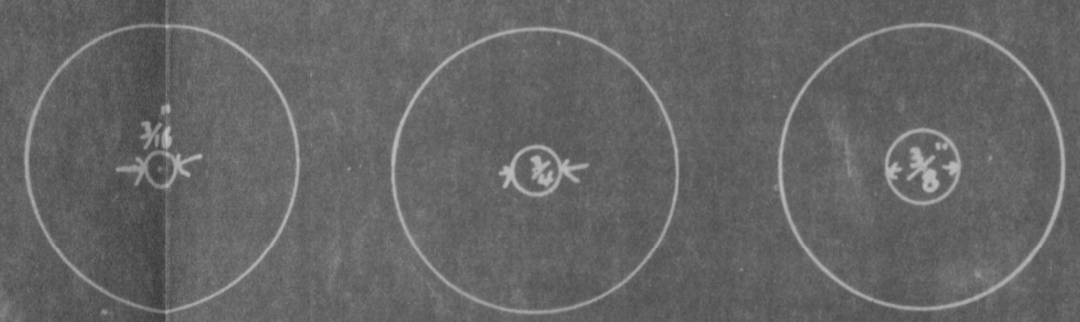
Free Iron	43.96 %	124.45 gms.
Ferrous oxide	56.04	158.65



ROTATING JOINT

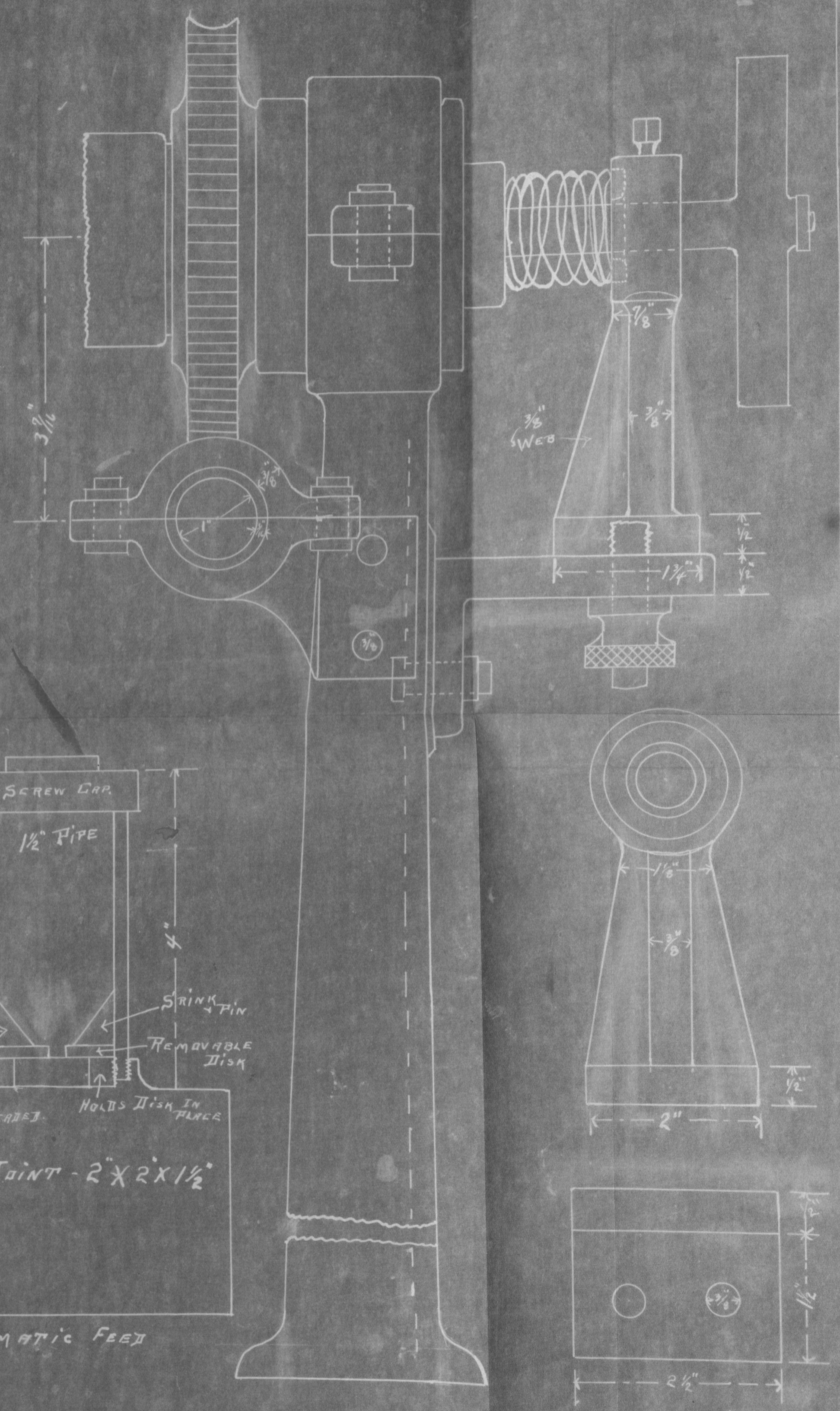
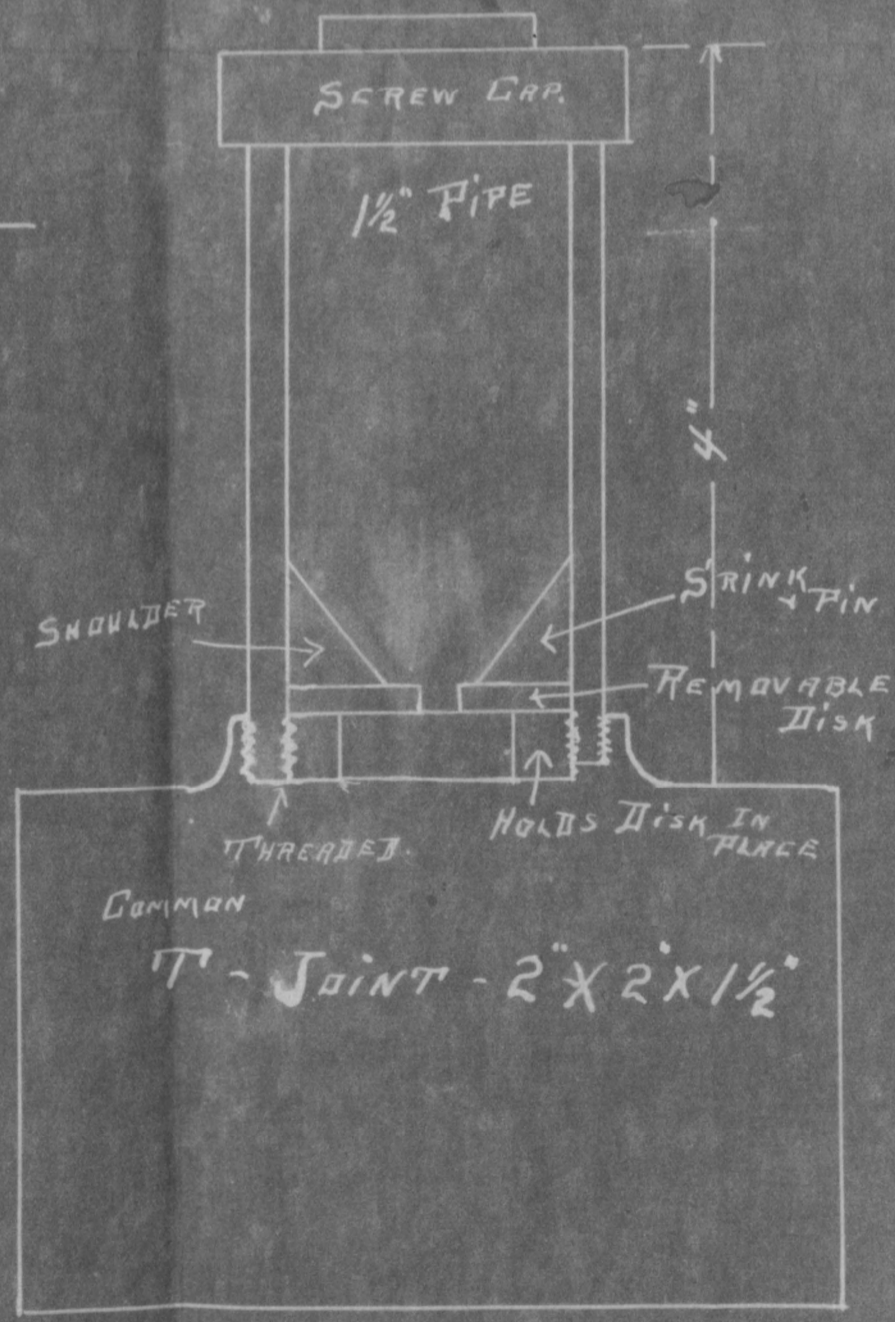


PIPE SUPPORT
WIDEN 1/2" DEEP



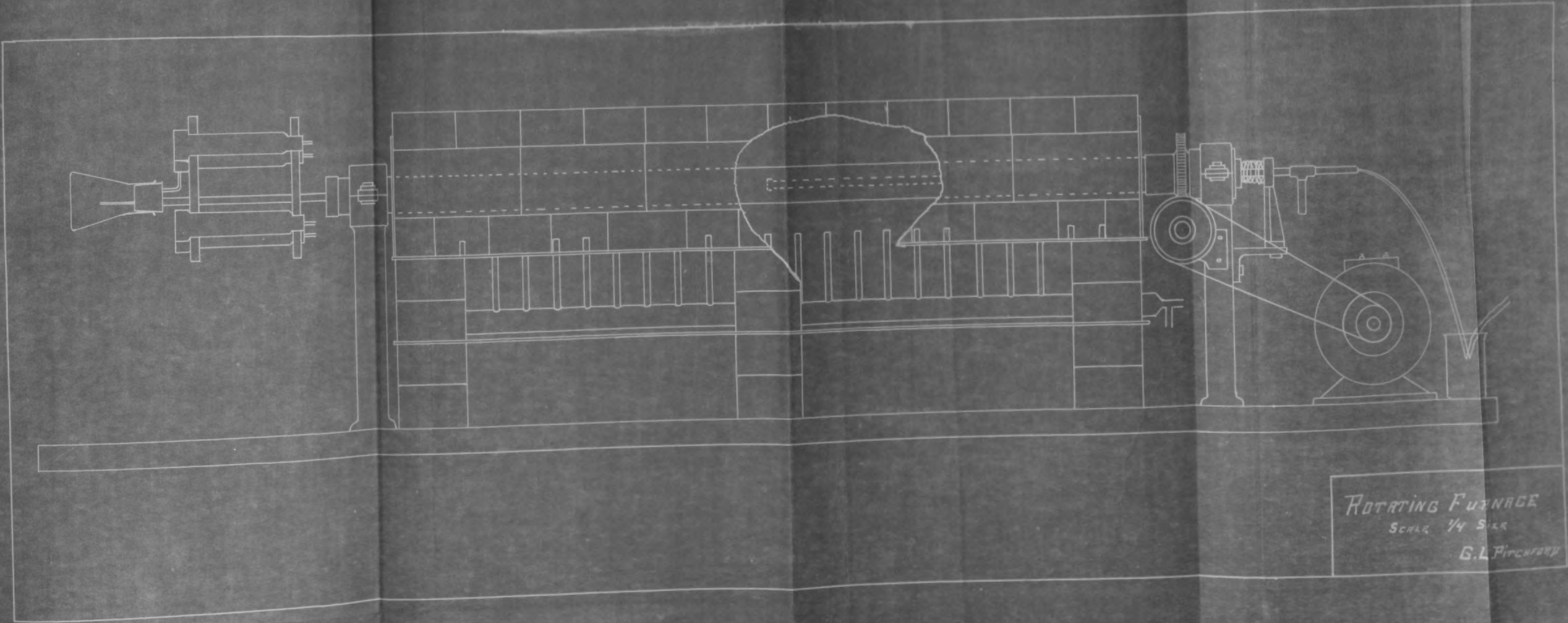
1/8" METAL DISKS FOR FEED

PLATE I
ROTATING FURNACE
SCALE - FULL SIZE
G. L. FITCHFORD

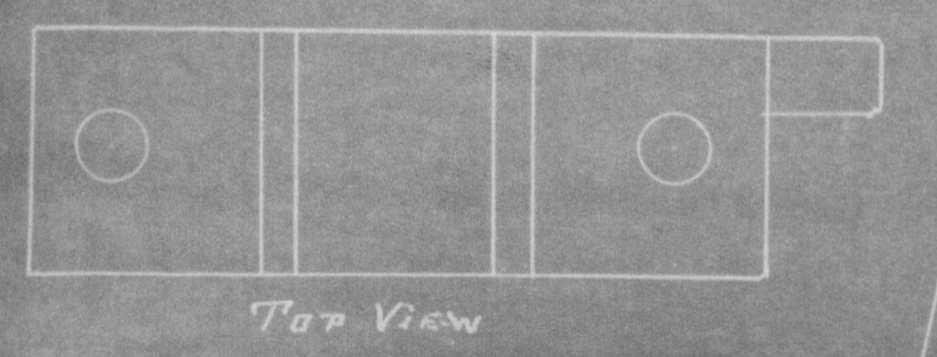
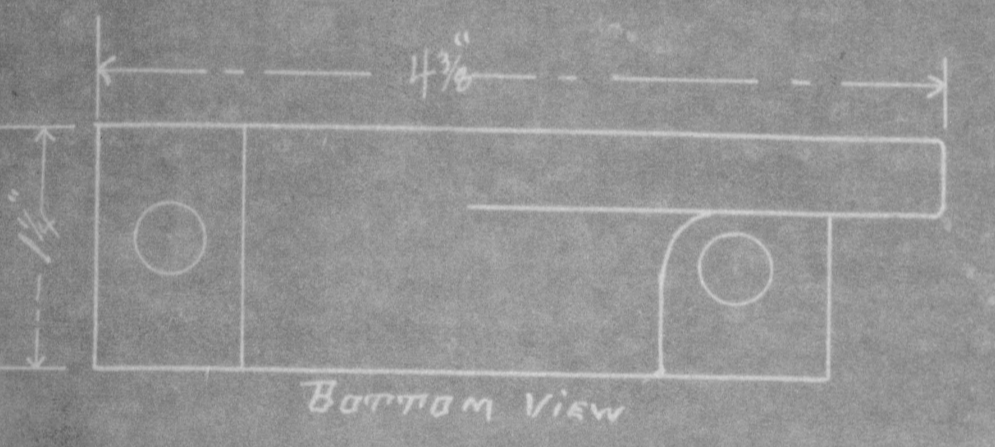
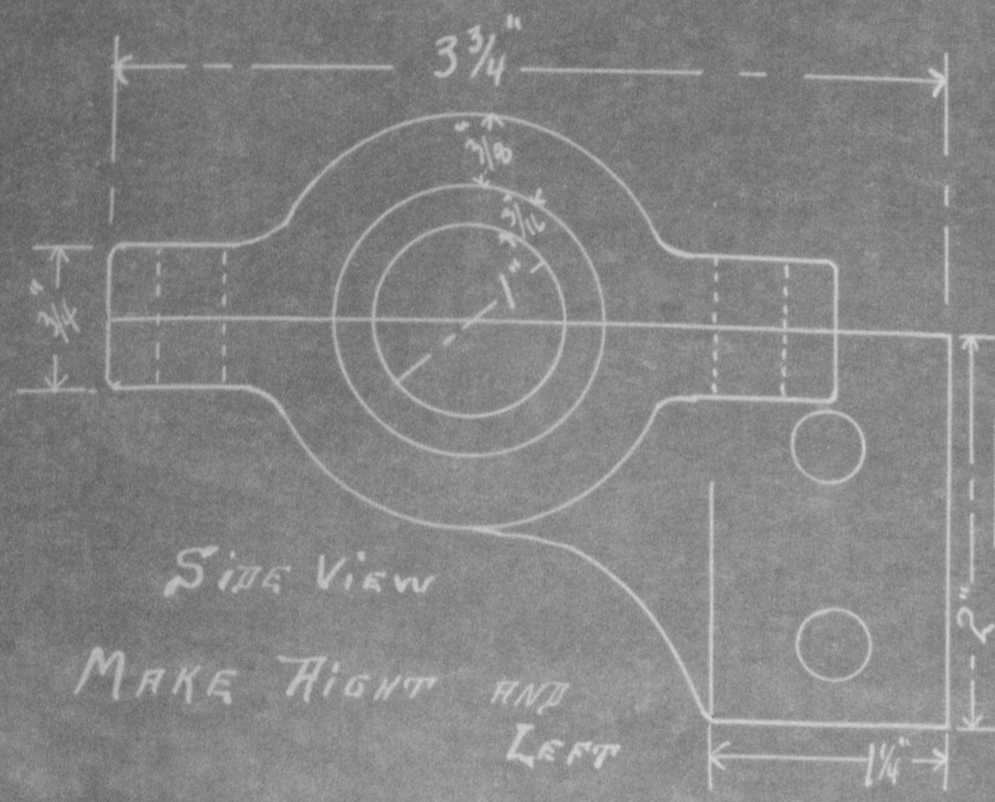


From the above experiments the following conclusions are drawn:

1. At a temperature of about 725° C. hydrogen is a more active reducing agent than carbon monoxide.
2. Iron ore can be completely reduced to iron by gaseous reducing agents at a temperature of 725° C.
3. Metallic copper acts as a catalytic agent and accelerates the process of reduction.
4. The rate of reduction is almost proportional to the rate at which the gaseous reducing agents are brought in contact with the iron ore.



ROTATING FURNACE
SCALE 1/4 SIZE
G.L. FITCHER



MOTOR SPEED 1750
 WORM REDUCTION 66:1
 PULLEY " 3:2
 SPEED APPROX. 17.5 R.P.M.
 BASE 2" X 14" X 9'6" FRANK

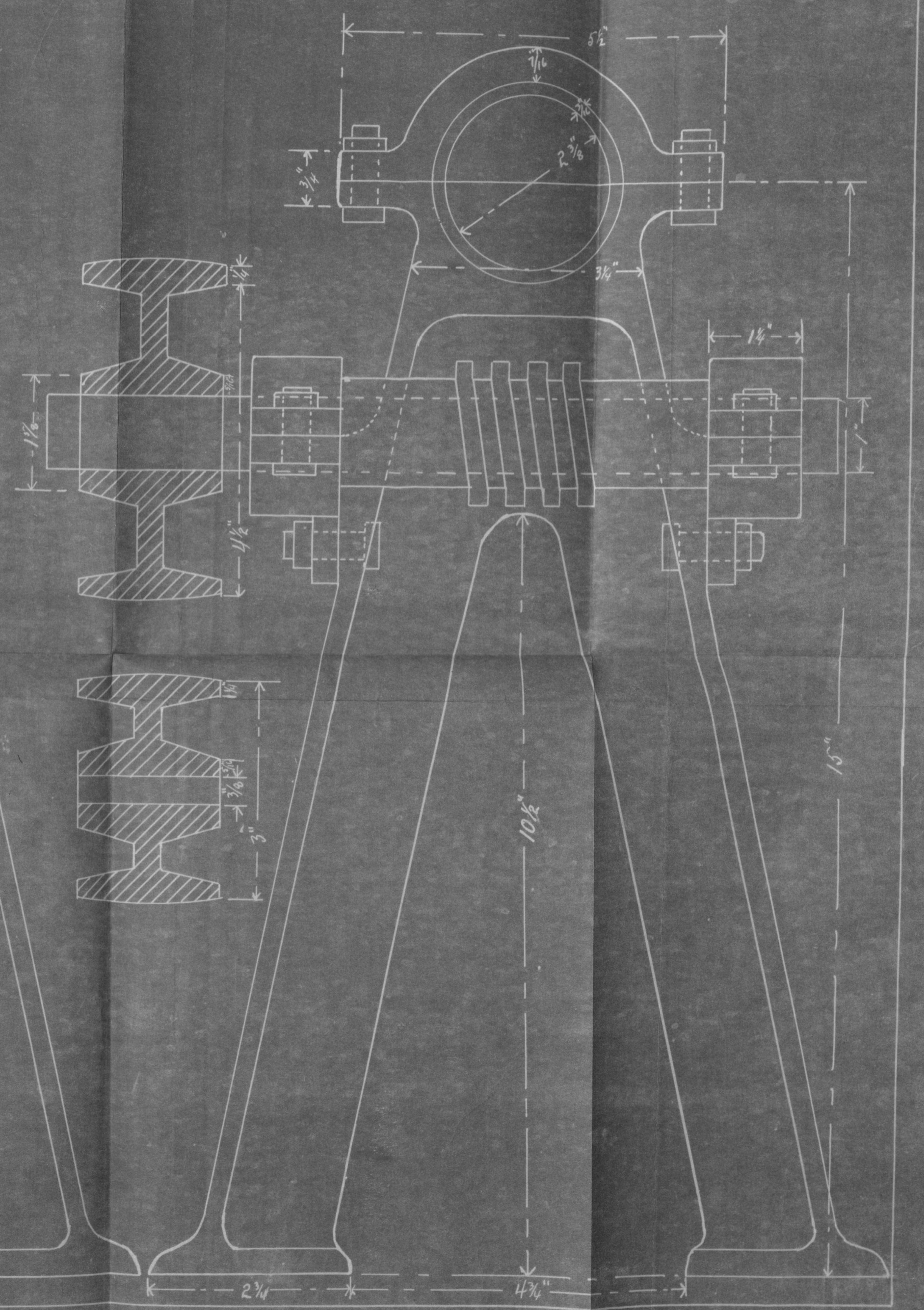
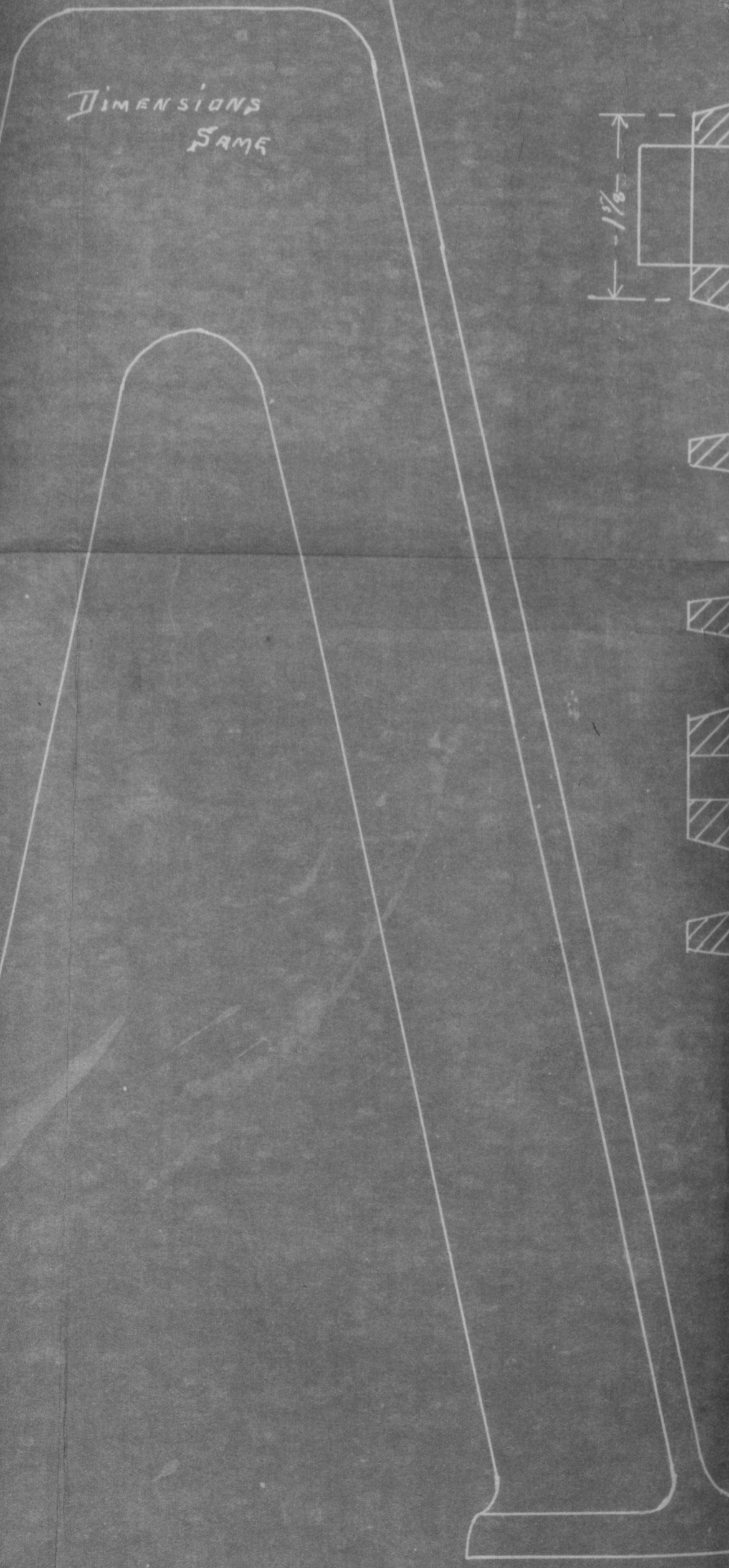
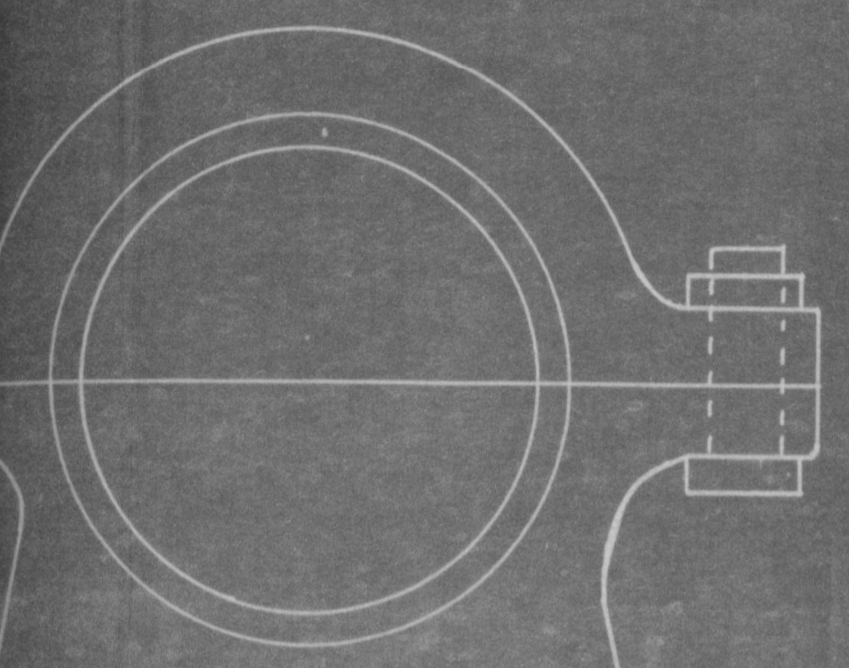


PLATE II
 HOT TILING FURNACE
 SCALE - FULL SIZE
 B. L. FINEBARD

Conversion °C

100° 200°

Temperature

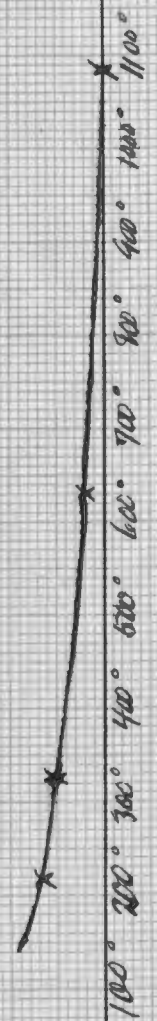


Plate IV