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NATIONAL DEFENSE RESEARCH COMMITTEE

OF THE

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Report on

"Investigation of Oxygen Supply"

to

May 31, 1942

by

E. R. Gilliland

OSRD No. 613

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NATIONAL DEFENSE RESEARCH COMMITTEE

OF

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Quarterly Progress Report of

"Investigation of Oxygen Supply"

May, 1942

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1262413

TABLE OF CONTENTS

		Page
I.	Abstract	1
II.	Life-Activity Studies	3
III.	High Temperature Absorption and Desorption	7
IV.	Adiabatic Unit	10
V.	Naval Research Unit	13
VI.	Miscellaneous Experimental Work	14
	A. Effect of Tube Diameter	14
	B. One-inch Tube with Brass Grids	14
	C. Absorbent with Copper Powder	15
	D. Diffusion Experiment	16
	E. Pellets Containing Talc	17
VII.	Program	18

1262414

I ABSTRACT

A number of tests measuring the deterioration of the CO-Sa-En absorbent have been carried out. In one run the material was carried through 4,400 absorption and desorption cycles employing air at 80 lbs. per sq.in. and using steam at atmospheric pressure. The activity and saturation capacity of the absorbent was tested periodically. It was found that both the activity and capacity deteriorated at the rate of about 2 per cent of the original value per hundred cycles. Other tests indicate this deterioration increases more or less proportionally with the amount of air employed during the absorption period. It also increases rapidly with increased pressure. Two units were tested in series in order to check the possibility of some undesirable constituent in the entering air. However, both units lost activity at about the same rate. The absorbent from the test that extended 4,400 cycles has been analyzed by both Professors Calvin and Diehl. The analytical results are not completely conclusive as to whether selective stripping has occurred, but they do indicate that something other than carbon, hydrogen, nitrogen or cobalt was taken up during the test.

A number of absorption runs have been carried out at temperatures in the region from 45° to 77°C. and air pressures up to 800 lb. per sq.in.gage. Desorption runs were also made in this same temperature region using desorption pressures between 1/4 and 1 atmosphere. These runs were carried out in an attempt to evaluate the feasibility of operating a normal cycle unit in a temperature range less than the 20° to 100°C. range previously adopted, and to evaluate the possibilities of adiabatic operation.

An adiabatic unit was constructed and operated. The preliminary results indicate that such a system may be operable but that it would be necessary to do considerable development work in order to reduce the volume of the voids to a minimum. This is due to the fact that the time necessary to remove the air from the voids is long enough that a considerable portion of the oxygen is desorbed and lost.

The Naval Research Unit has been completely assembled. The initial tests were unsatisfactory chiefly due to the magnetic valves. These valves have been replaced by air operated valves which appear to function as desired. Preliminary tests have been carried out and the unit appears

1262415

to be producing oxygen at about the calculated rate. At present testing devices are being installed such that the total quantity of oxygen produced in a given time can be measured. In addition arrangements have been made for measuring pressures and vacuums as well as gas compositions in the various beds as a function of the time. It is believed that these tests will give valuable engineering information.

A number of miscellaneous problems have also been studied including (A) the effect of tube diameter; (B) the inclusion of metal gauzes to improve heat transfer in larger tubes; (C) incorporating fine copper powders with the absorbent; and (D) diffusion experiments through membranes of the CO-Sa-En absorbent.

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II. LIFE-ACTIVITY STUDIES

A considerable portion of the work has been directed to a study of the deactivation of the Co-Sa-En material. An extended life-activity test has been carried out in one of the 1/2" i.d. tube units. The unit was packed with 40.7 grams (oxygen saturated material) of 10 to 20 mesh Co-Sa-En material produced by the Rumford Chemical Company. The cycle employed involved an absorption period of 5-1/2 minutes with air at 75 lbs./sq. in. ga., followed by a short purging period, then a desorption period of six minutes, and finally a cooling period of 1-1/2 minutes. The desorption was carried out at atmospheric pressure and steam at atmospheric pressure was employed in the jacket. An air flow rate of 3 cu. ft./hr. (standard conditions) was employed during the absorption period. Periodically the continuous operation was interrupted in order to check the deterioration. This deterioration has been expressed as the per cent of the original activity, where activity is defined as the amount of oxygen produced in a given test cycle. This test cycle was identical with the continuous cycle given above with the exception that the cooling period was 4-1/2 minutes instead of 1-1/2 minutes. The results of this test are given in Fig. 1. It will be noted that the activity decreases almost linearly with the number of cycles and has dropped to 20 - 25% at the end of 4,400 cycles. This corresponds to a loss in activity of roughly 2% per 100 cycles. This result was rather unexpected in that a logarithmic type of decay would have been expected due to the inactivation of a constant fraction of the active material present. There are certain wobbles in the experimental points, and they suggest a possible flattening of the curve around 400 to 600 cycles and around 1800 to 2500 cycles. It seems likely that these are purely experimental inaccuracies, but it should be mentioned that the air purification bed was changed at the 574th cycle and at the 2,141th cycle, and it may be that these changes had some effect. The air purification employed in these studies involved passing the inlet gas at atmospheric pressure through a large calcium chloride dryer. It was then compressed by a reciprocating type compressor, filtered through glass wool, dried again with calcium chloride, filtered through glass wool, dried with silica gel, refiltered through glass wool, and then introduced into the unit.

The saturation capacity of the absorbent was checked a few times during the life study and the results indicated that the decrease in capacity more or less paralleled the

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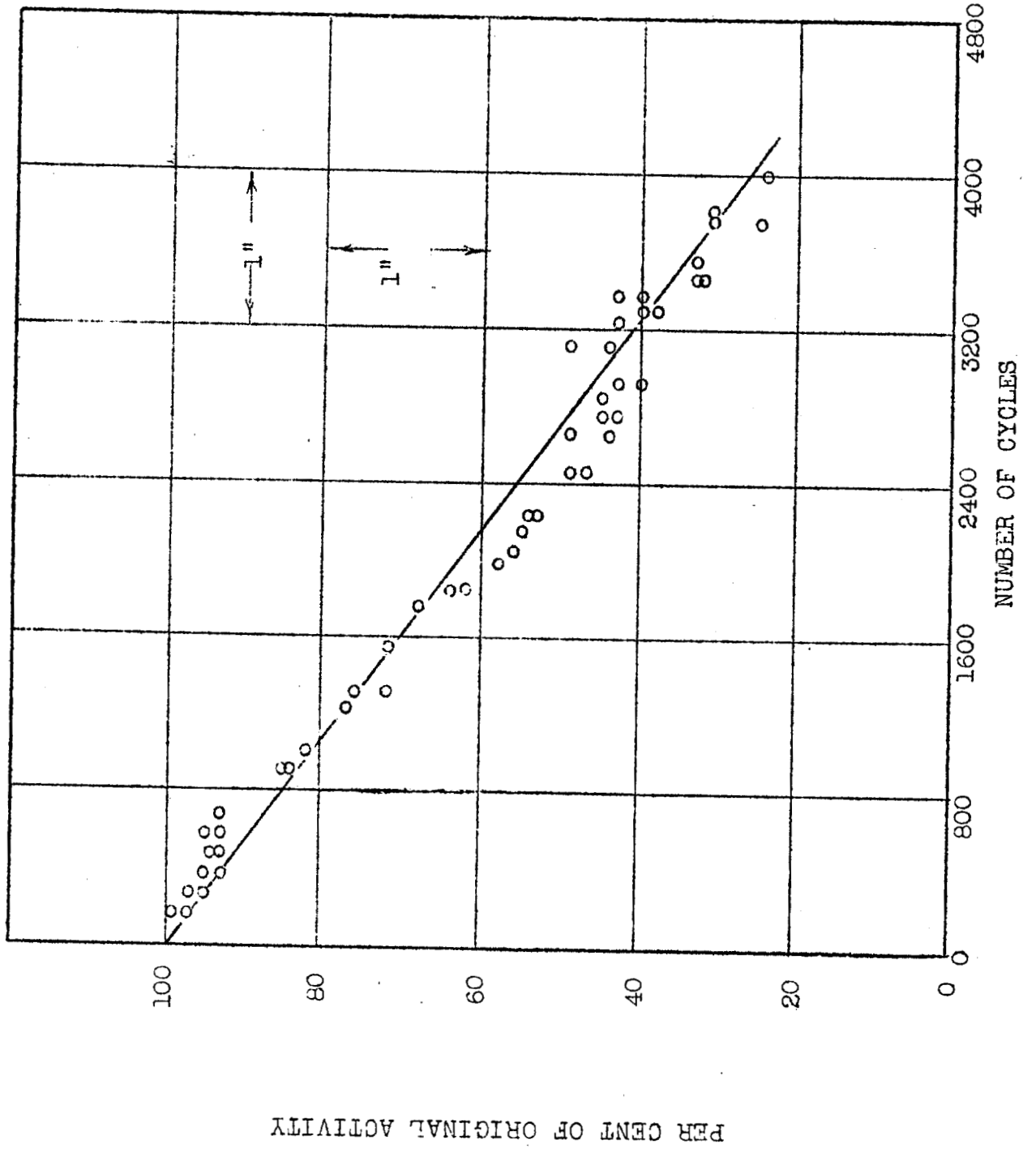
FIGURE 1



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decrease in activity.

Other activity studies have been carried out and in another case, this long time test was duplicated except that a flow rate of 8 CFH was used during absorption instead of the 3 CFH. It was found that the deterioration increased about proportionally to the flow rate. These results are compared in Fig. 2. Since this loss was more or less proportional to the flow rate, it was thought that deterioration might be due to something brought in or stripped but by the air during the absorption period. If such were the case, the material at different levels in the unit should have deteriorated with different rates. In order to check this hypothesis, two units were operated in series and it is found that both units deteriorated at approximately the same rate, indicating that the decay is not something peculiar to the inlet air. A short life-activity test was also carried out with a similar cycle employing 3 cu. ft. of air per hr. but with an average absorption pressure of about 250 lbs./sq. in. While this run was not as satisfactory as was desired, it did indicate that the rate of deterioration was several-fold greater at the higher pressures.

The deteriorated material from the 4,400 cycle run was divided into several portions and samples were sent to Professor Calvin at the University of California and Professor Diehl of Iowa State College. Both Professors Diehl and Calvin analyzed the deteriorating material and their analytical results are summarized in the following table:

	I (Calvin) Dried 45 min. in 110°C. oven	II (Calvin) Dried 1 hr. at 120° in vacuum	III (Diehl) Dried at 100°C. in vacuum	IV Theor.
C	53.75, 53.44	53.31, 53.28		59.0
H	3.66, 3.52	3.87, 3.79		4.31
N	8.67, 8.39	8.67, (Kjeldahl-6.03, 5.95)	7.70, 8.06	8.62
Co	17.22, 17.25	17.13, 16.97	16.46, 17.01	18.15
N/Co	2.13	2.22	1.99	

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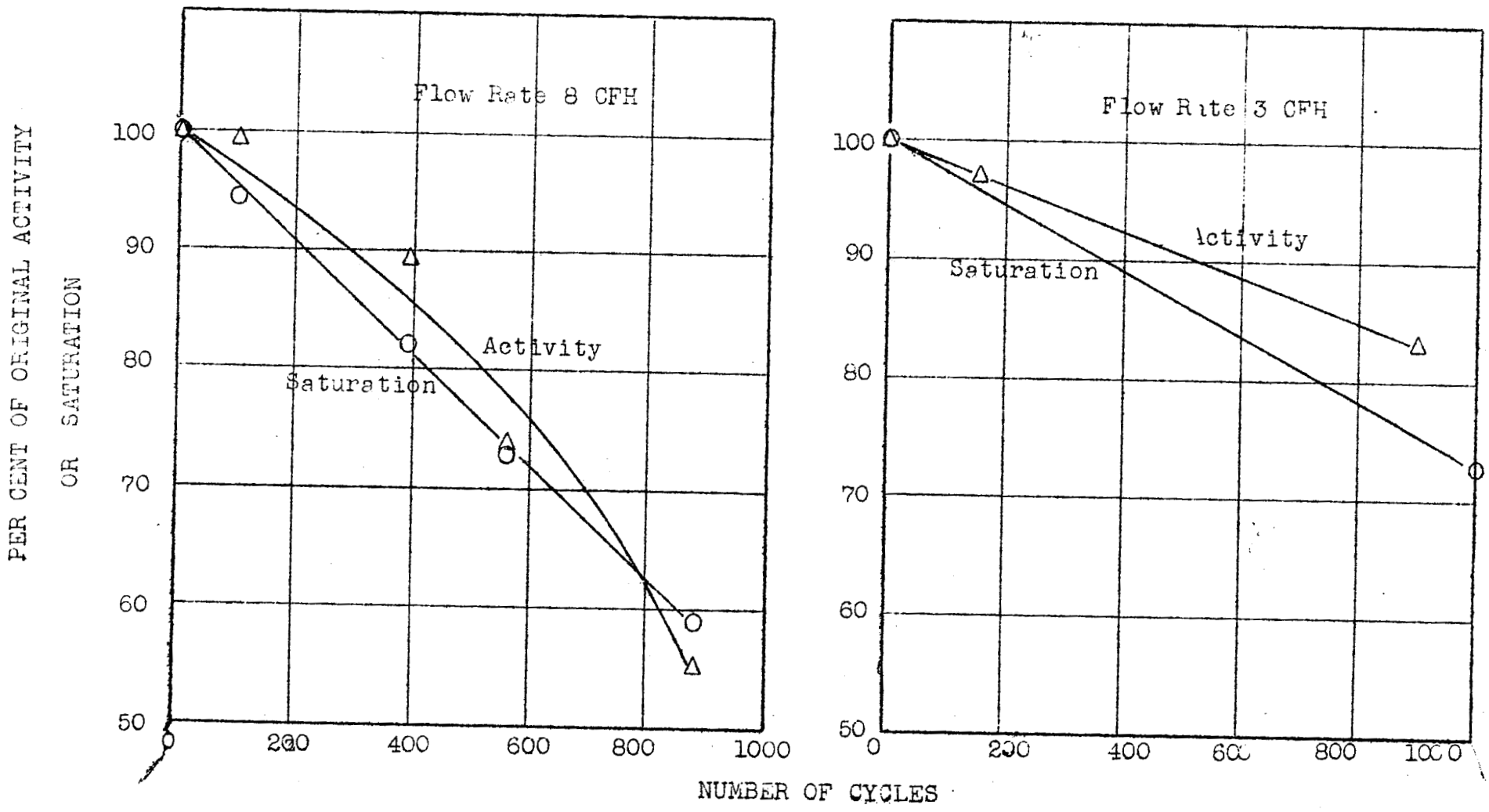
FIGURE 2



Analyses 1 and 2 are those reported by Professor Calvin. Analysis 3 is that reported by Professor Diehl, and the fourth column indicates the theoretical value. Professor Calvin reports nitrogen values obtained by both the Dumas method and the Kjeldahl method. While there are some differences between the analytical results obtained by Professors Diehl and Calvin, they both give the indication that the nitrogen to cobalt ratio is approximately the same as or perhaps higher than in the original, and they indicate that something other than carbon, hydrogen, nitrogen or cobalt has been added to the material. This latter conclusion is reached due to the fact that the weight per cent of essentially all of these elements have decreased. Professor Calvin also indicates that "the deteriorated material contains a large amount of cobaltic cobalt."

A number of reasons for the deactivation have been proposed and they will be summarized briefly. It has been suggested that oil vapor or entrainment from the compressors was responsible for the loss in activity. It is felt that Professor Calvin's analyses rule out this consideration due to the decreases in both carbon and hydrogen. It has also been suggested that the water vapor content of the entering air was either too high or too low. Again, Professor Calvin's analyses would indicate that the absorption of water is not a controlling cause. Professor Diehl has suggested that the removal of essential water from the compound might cause deactivation and that less drying of the air might be desirable. If this is true, something else would have to account for the increase in weight. Other possibilities suggested for the increase in weight were the absorption of CO_2 or oxygen. Several tests were made contacting the absorbent with pure CO_2 at atm. pressure both at room temperature and at 100°C. In neither case was there any appreciable loss in absorption capacity. However, this does not necessarily rule out the carboxylation theory since the material was not passing through a regular cycle. Professor Calvin's results indicate that oxidation may be taking place and the added oxygen may account for the decreased weight per cents of the other elements.

Other causes for the deterioration that have been suggested include disruption of the crystal lattice due to the oxygen absorption and desorption. It is suggested that the degree of disruption is a function of the rate at which oxygen is added or removed. Dr. Prentiss has suggested that the calcium chloride employed may give off small quantities of hydrogen chloride which poison the absorbent.

Additional life tests are being carried out in an attempt to reach a definite conclusion. Runs underway or under consideration include controlling the concentration of water vapor and carbon dioxide in the entering air, lower desorption temperatures, various absorption pressures, absorption with pure oxygen at atmospheric pressures, absorption cycle employing pure nitrogen at atmospheric pressure, various flow rates, and controlled rates of absorption and desorption.

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III. HIGH TEMPERATURE ABSORPTION AND DESORPTION

It has been suggested that the operation of an adiabatic unit might be feasible. If such a unit were to be operated, the temperature region would have to be relatively high in order to obtain satisfactory desorption rates. In order to obtain an orientation at these higher temperatures, a series of runs were carried out in the usual 1/2" tube units at temperatures of 55°, 66°, and 77°C. Desorption pressures of 1/4, 1/2, and 1 atmosphere were employed. The desorption tests were made by saturating the compound using air under pressure at cooling water temperature, and the desorption was carried out by passing hot water through the jacket around the tube. The rate of hot water flow was such that the inlet and outlet temperatures were essentially the same. The residual air was removed from the voids by evacuation prior to regeneration. The desorption results are summarized in Figs. 3, 4, and 5. Fig. 3 indicates results obtained at 55°C. At this temperature, the per cent of oxygen desorbed at a given time is a very definite function of the desorption pressure. In fact, the curve for 1 atmosphere indicates very strongly that equilibrium is a limiting factor at this pressure and temperature. The lower pressures do not show this same flattening but probably would with longer desorption times. Fig. 4 is a similar curve for 66°C. These curves indicate that the increased temperature has very decidedly increased the rate of desorption and in addition the equilibrium partial pressure apparently is much higher since the desorption curve at 1 atmosphere is not nearly so limited. A further increase in temperature to 77°C. gives still higher rates, especially at the higher pressures. These curves indicate that practical desorption rates can be obtained in a temperature region 55° to 77°C. At 55°C. the rate of desorption at 1 atmosphere pressure is undoubtedly too slow to be of practical importance and, in fact, Fig. 3 indicates that the maximum amount that could be desorbed under these conditions would be very small. At this temperature even with desorption pressures of 1/4 or 1/2 atmospheres the rates are so slow that very long cycles would have to be employed. This would probably make the operation at this temperature undesirable. Still lower pressures could probably give further increases in absorption rate but it is questionable whether they would be justified.

The rates of desorption at 66°C. are probably fast enough to be of practical importance. This is particularly true if the desorption pressure is 1/4 or 1/2 atmosphere.

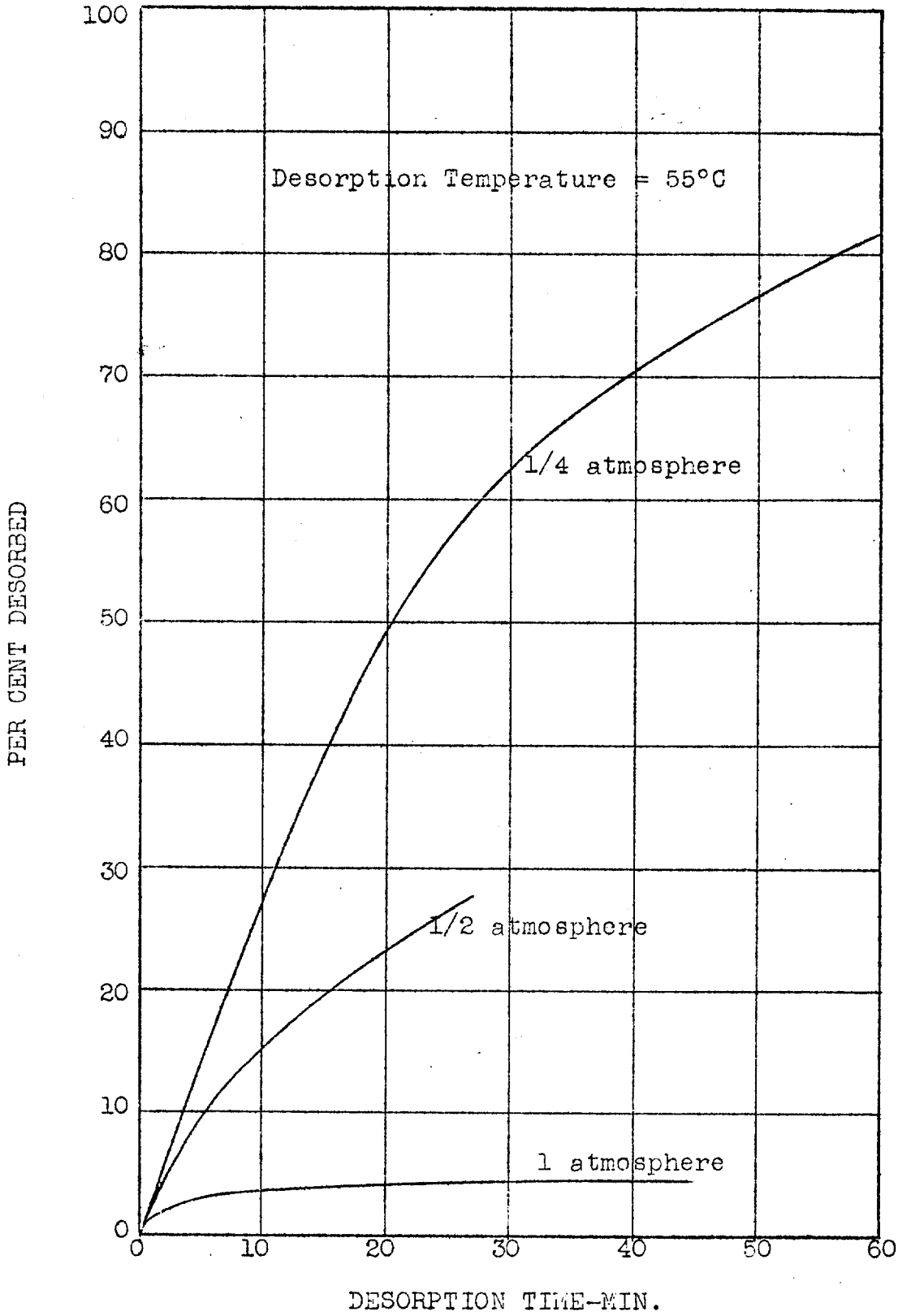

FIGURE 3

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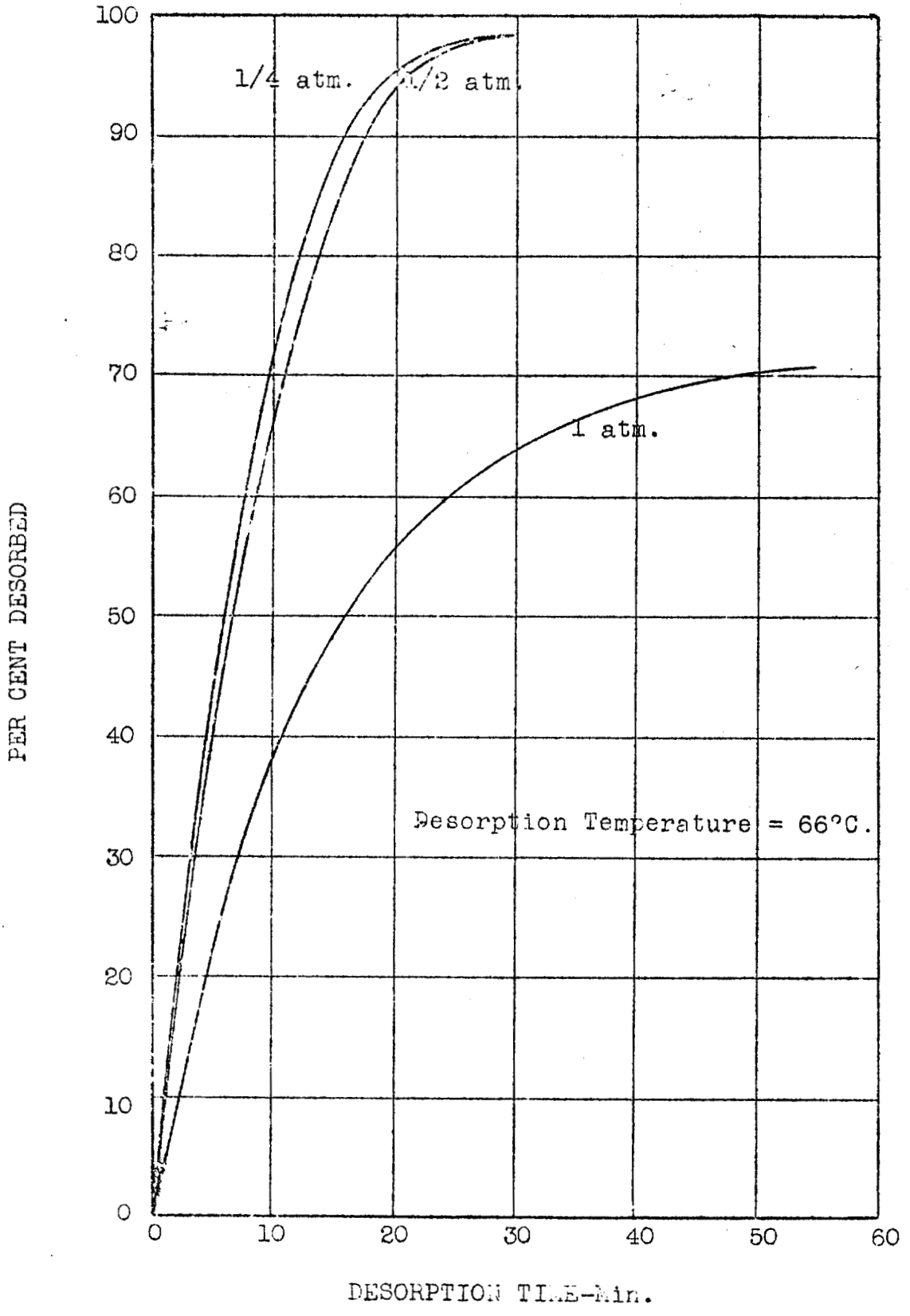

FIGURE 4

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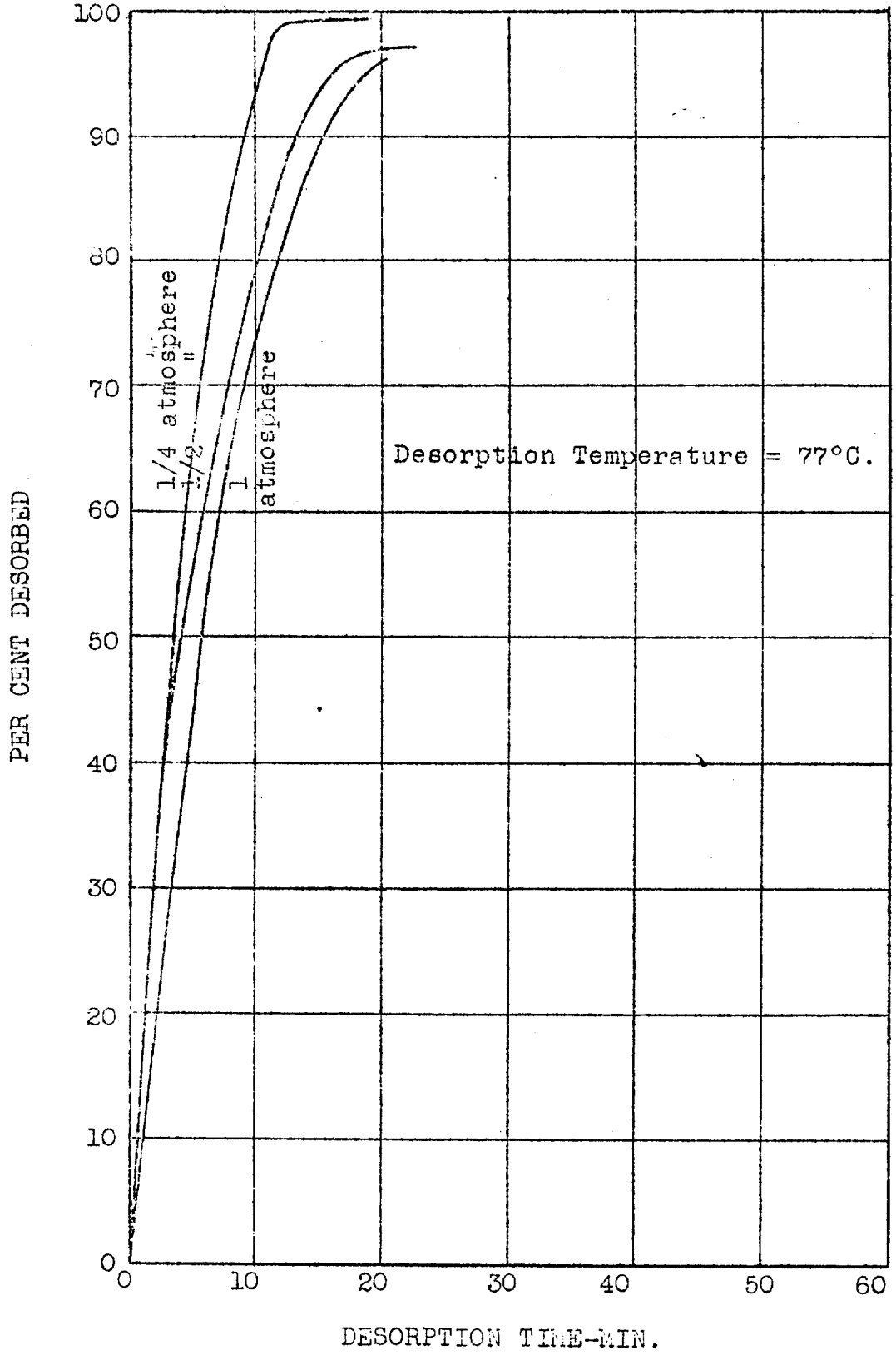

FIGURE 5

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At a temperature of 77°C. the desorptions are relatively rapid, but the initial desorption rate is so fast that difficulty would probably be encountered in removing the air from the voids without a serious loss of oxygen. These results would indicate that the adiabatic unit should probably operate somewhere in the temperature region of 60 to 70°C. if employing the present Co-Sa-En material.

Absorption runs were made in this high temperature region in order to check on the possibility of oxygen removal under these conditions. Again the unit was the usual 1/2" i.d. setup with 40.7 of the oxygenated Co-Sa-En material. The particle size was 10 to 20 mesh, and the particular sample was material produced by the Rumford Chemical Company. The major portion of the absorption runs was made with air pressures of 600 and 800 lbs./sq. in. ga., and with an absorption temperature of 65°C. These results are summarized in Table I and Figs. 6 to 12. Figs. 6 to 9 indicate the absorption results obtained with air at 600 lbs./sq. in. and with cooling water at 65°C. and correspond to different rates of exit air flow. They indicate that reasonably good oxygen absorption can be obtained under these conditions. Fig. 10 is for an absorption pressure of 800 lbs./sq. in. ga. and shows appreciably better absorptions than those obtained at 600 lbs./sq. in. ga. Fig. 11 illustrates the effect of absorption temperature for conditions of 800 lbs./sq. in. ga., 4 minutes absorption time, and 0.87 CFH of exit gas. Fig. 12 gives the effect of pressure at 65°C. on the amount of absorption. This figure indicates that pressures of the order of 600 lbs. will be necessary in this temperature region.

In addition to the runs at 65°C. Mr. Roberts of the Kellogg Company requested that isothermal runs be carried out with absorption at 45°C. and an absorption pressure of 550 lbs./sq. in. The unit employed in this test was identical with those previously described. The accuracy of the results is not as high as for runs made at lower pressures. This is due to the fact that the amount of air necessary to fill the voids under these conditions is quite large, and an accurate calculation of this quantity is difficult and therefore makes an uncertainty in the result. The cumulative mol per cent oxygen removal from the air and the weight per cent O_2 in the compound obtained in these runs are given in Figs. 13 to 17 and in Table II. In the case of the runs of Fig. 13, no exit gas flow was employed. The unit was simply charged to the desired pressure and maintained at this condition during the run. The theoretical oxygen available for

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TABLE I

Pressure lb/sq.in.ga.	Temperature °C.	Flow Rate C.F.H. **	Sorption Time Minutes	Wt. % O_2 in Compound	Cumulative Mol % O_2 Removed from Air
100 *	12	1	30	4.0	---
200	65	3	5	0.04	0.7
350	65	3	5	0.65	11.5
400	65	0.87	4	0.40	20.0
600	65	0.87	2	0.52	28.2
"	"	"	4	0.97	38.9
"	"	2	1	0.32	17.5
"	"	"	2	0.70	26.9
"	"	"	4	1.25	30.6
"	"	"	7	1.79	29.6
"	"	"	15	2.74	24.2
"	"	4	1	0.51	19.9
"	"	"	2	0.90	23.9
"	"	"	4	1.79	26.9
"	"	6	1	0.50	15.7
"	"	"	2	0.99	19.0
800	"	0.87	4	1.15	39.4
"	"	"	7	1.78	45.9
"	"	"	10	2.21	45.9
"	"	2	4	1.86	41.3
"	70	0.87	4	1.00	33.8
"	78	"	"	0.30	10.7

* Saturation Run
**Measured at room temperature and pressure (40.7 grams absorbent)

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Figure 6

600 Lb./sq. in.
2 C.F.H.
65°C.

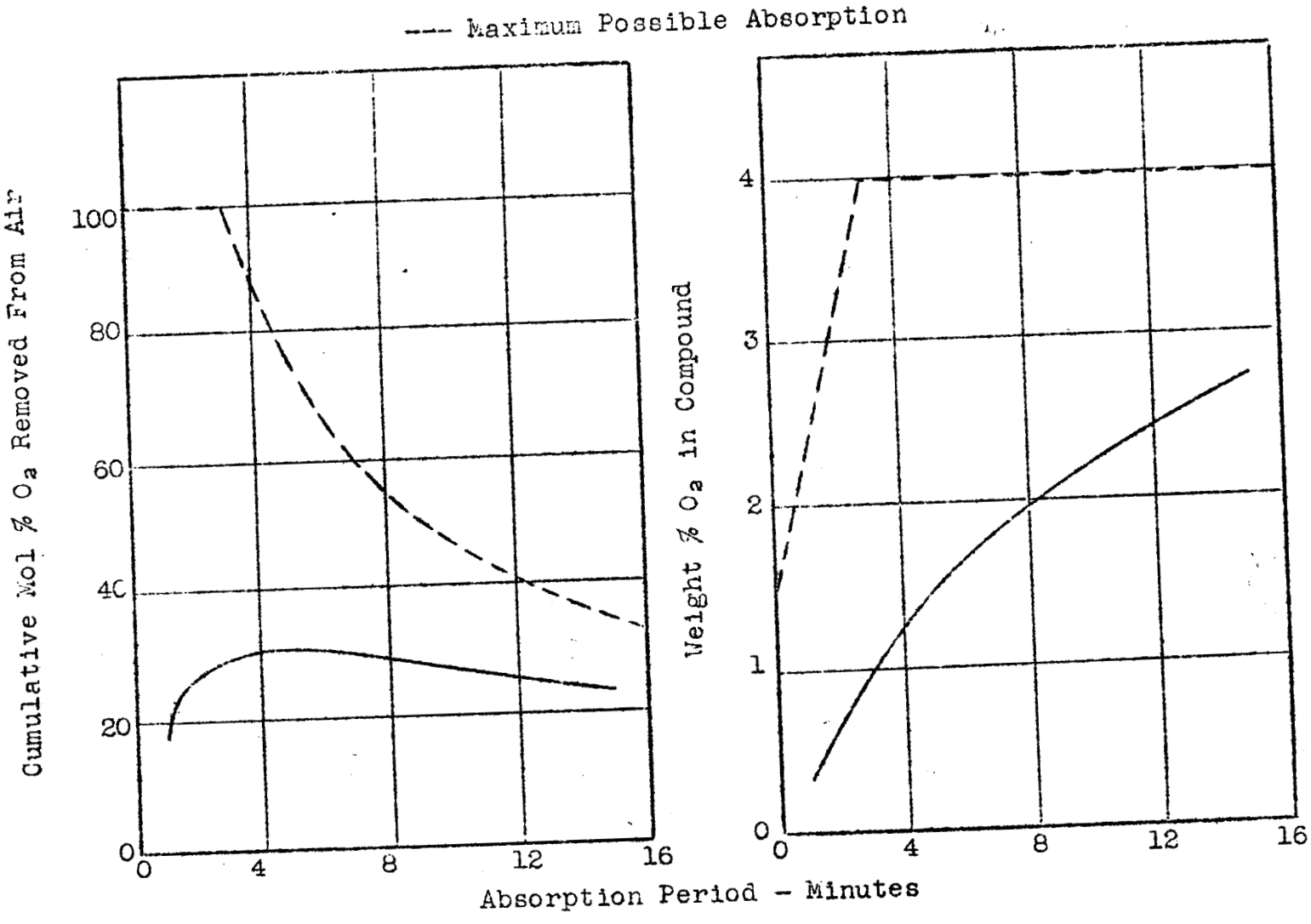

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Figure 7

600 Lb./sq. in.
4 C.F.H.
65°C.

--- Maximum Possible Absorption

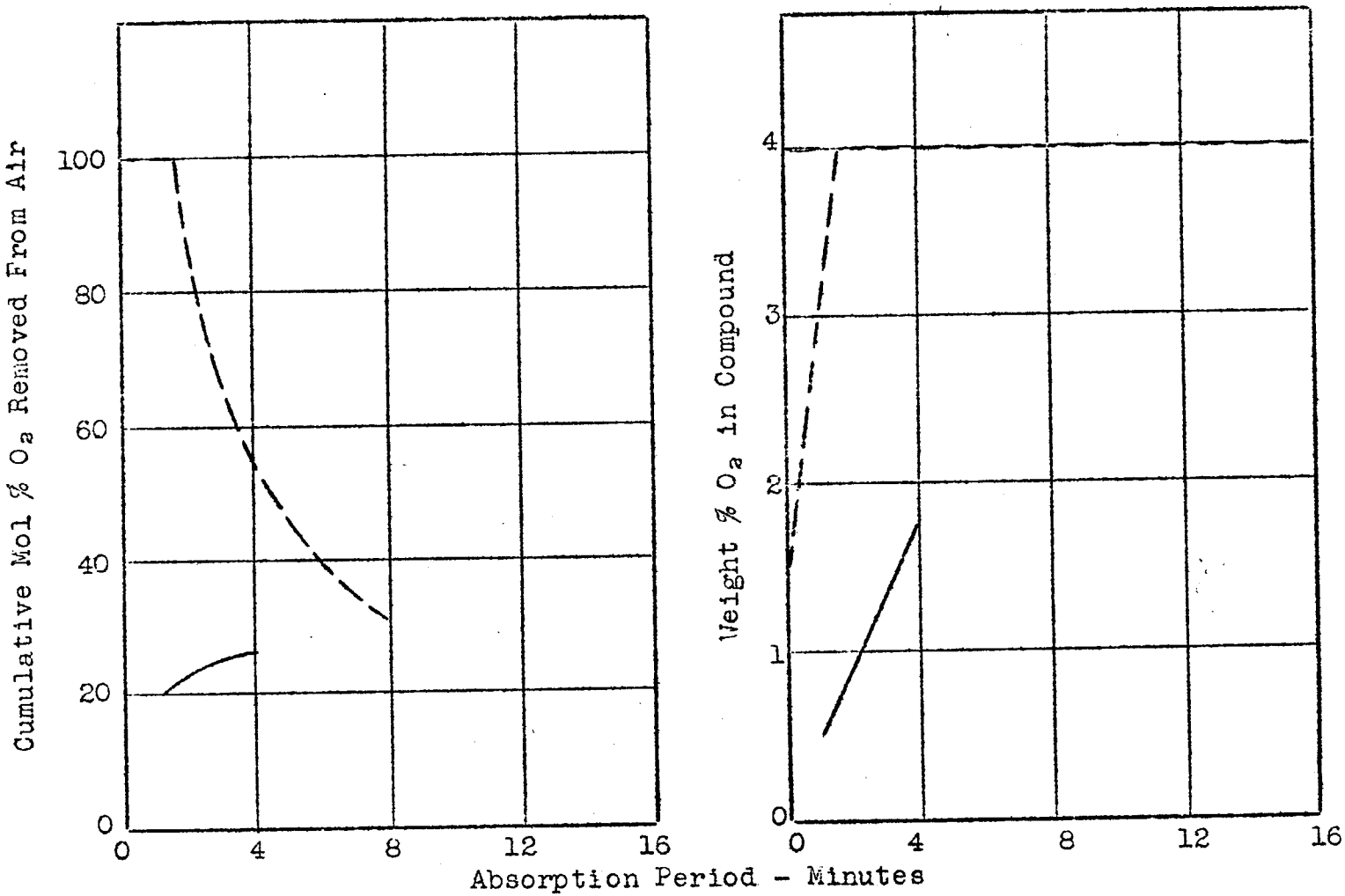

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Figure 8

600 Lb./sq. in.
6 C.F.H.
65°C.

---- Maximum Possible Absorption

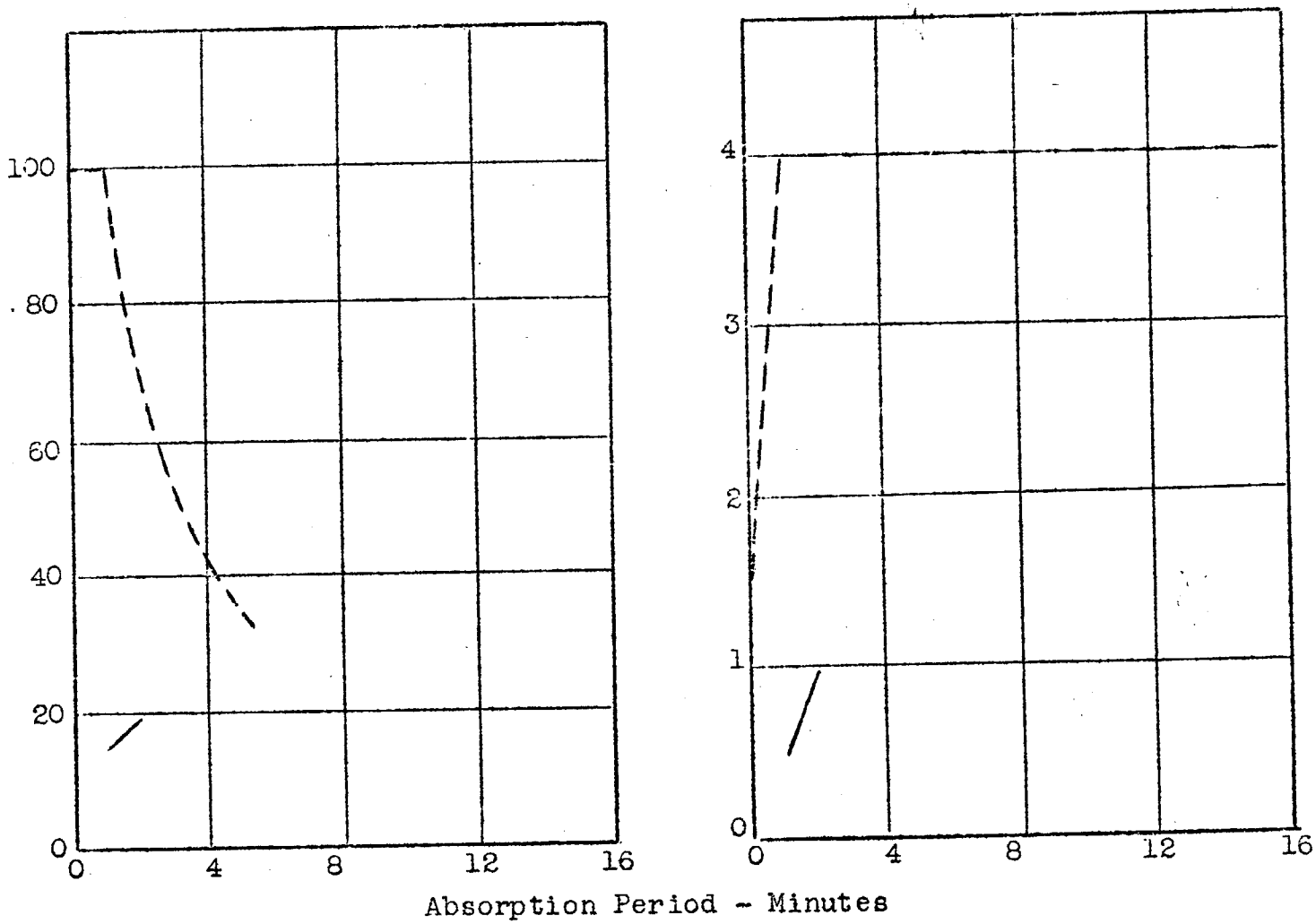

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Figure 9

600 Lb./sq. in.
0.87 C.F.H.
65°C.

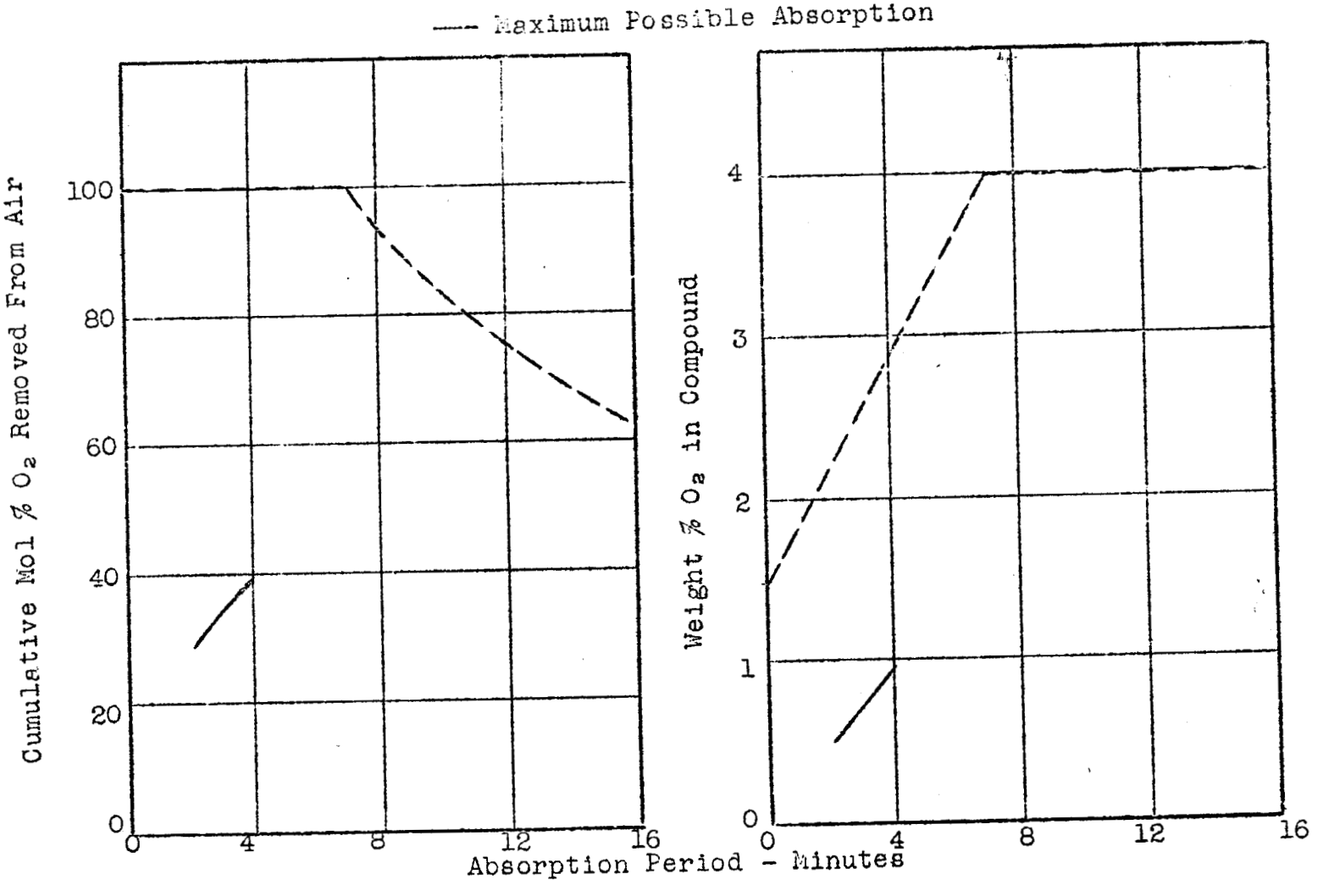

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Figure 10

800 Lb./sq. in.
0.87 C.F.H.
65°C.

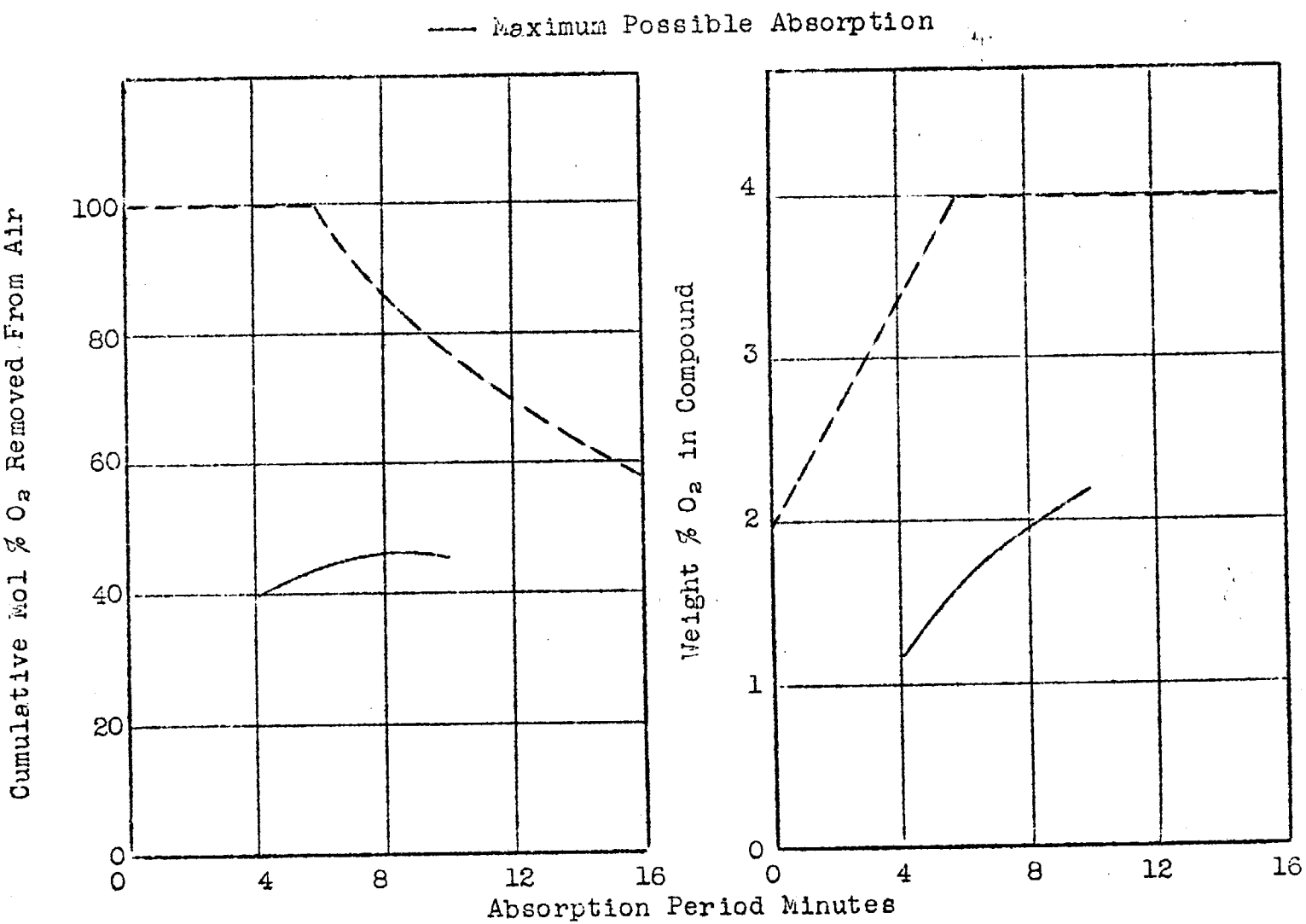

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Figure 11

0.87 C.F.H.
800 Lb./sq. in.
4 Min. Absorption Period

---- Maximum Possible Absorption

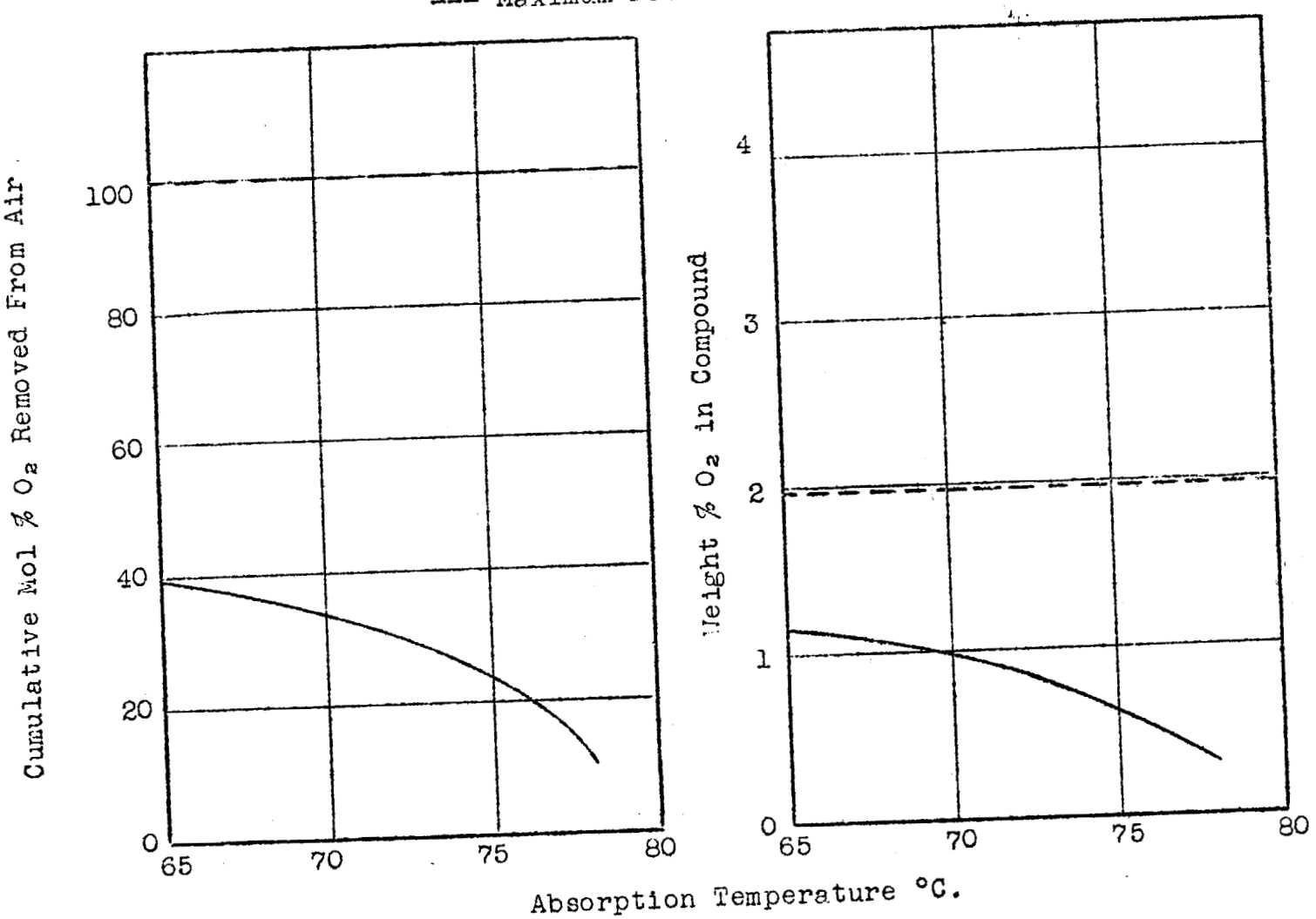

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Figure 12

0.87 C.F.H.
65 °C.
4 Min. Absorption Period

--- Maximum Possible Absorption

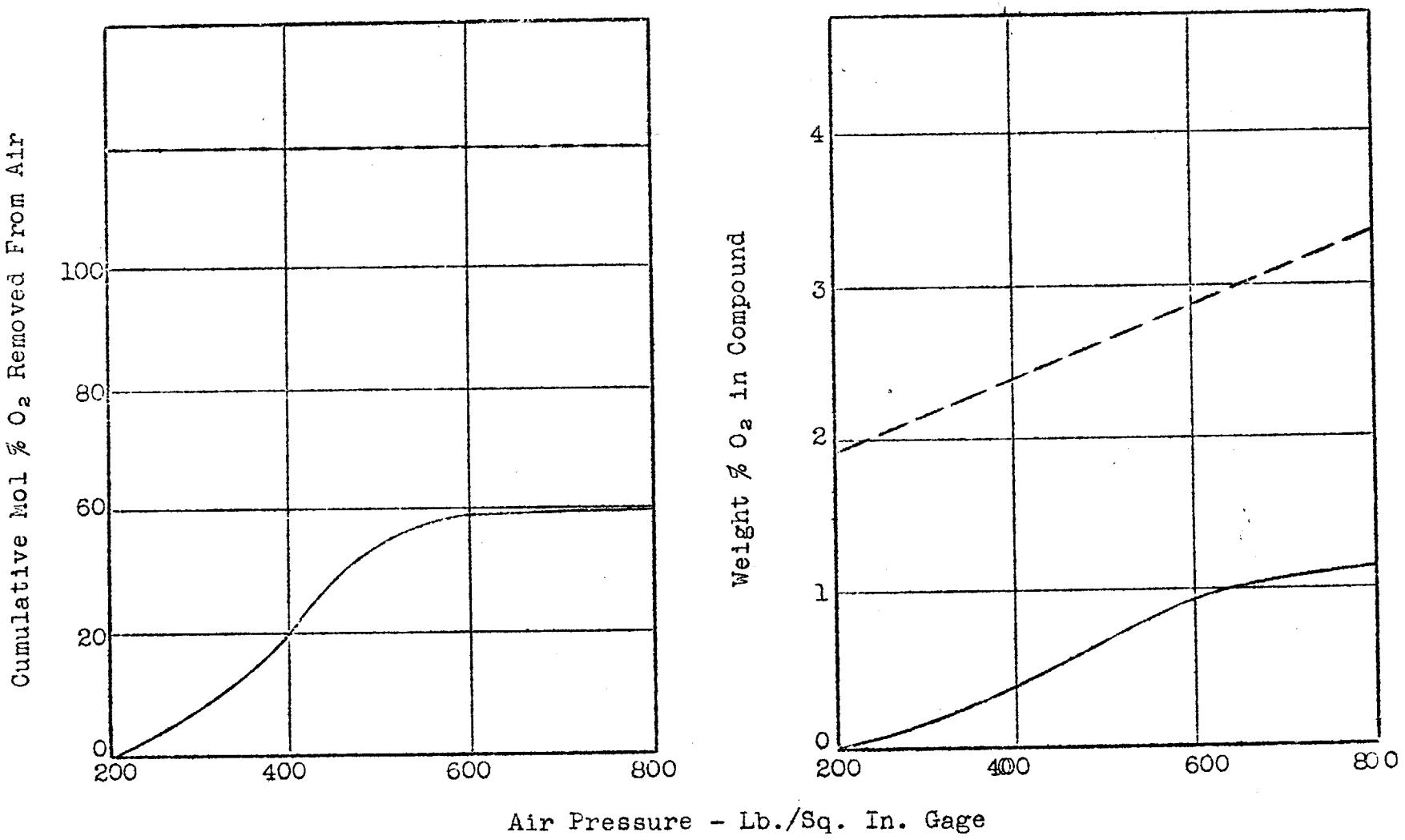

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TABLE II

Table of Data

550# Pressure

45°C. Absorption Temperature

Flow Rate C.F.H.*	Absorption Period Minutes	Cumulative Mol % O_2 Removed From Air	Weight % O_2 in Compound
0	1	62.6	0.83
0	2	84.1	1.17
0	4	99	1.44
0.475	1	66.6	0.97
0.475	2	80.2	1.41
0.475	4	82.8	1.78
0.475	7	77.5	2.13
0.475	10	77	2.49
0.87	1	65.2	1.09
0.87	2	72.8	1.50
0.87	4	76.3	2.09
0.87	7	75.2	2.82
0.87	10	66.1	3.1
1.40	1	58.1	1.07
1.40	2	62.8	1.49
1.40	4	64	2.22
1.40	7	67.2	3.1
1.40	10	56.6	3.71
2.00	2	61.4	1.75
2.00	4	61	2.66
4.00	2	48.3	2.04

*Exit gas rate at room temperature and pressure.

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FIGURE 13

Absorption Pressure - 550 lbs.
Flow rate - 0.0 CFH
Temperature - 45°C.
- - - - = Mass Possible Absorption

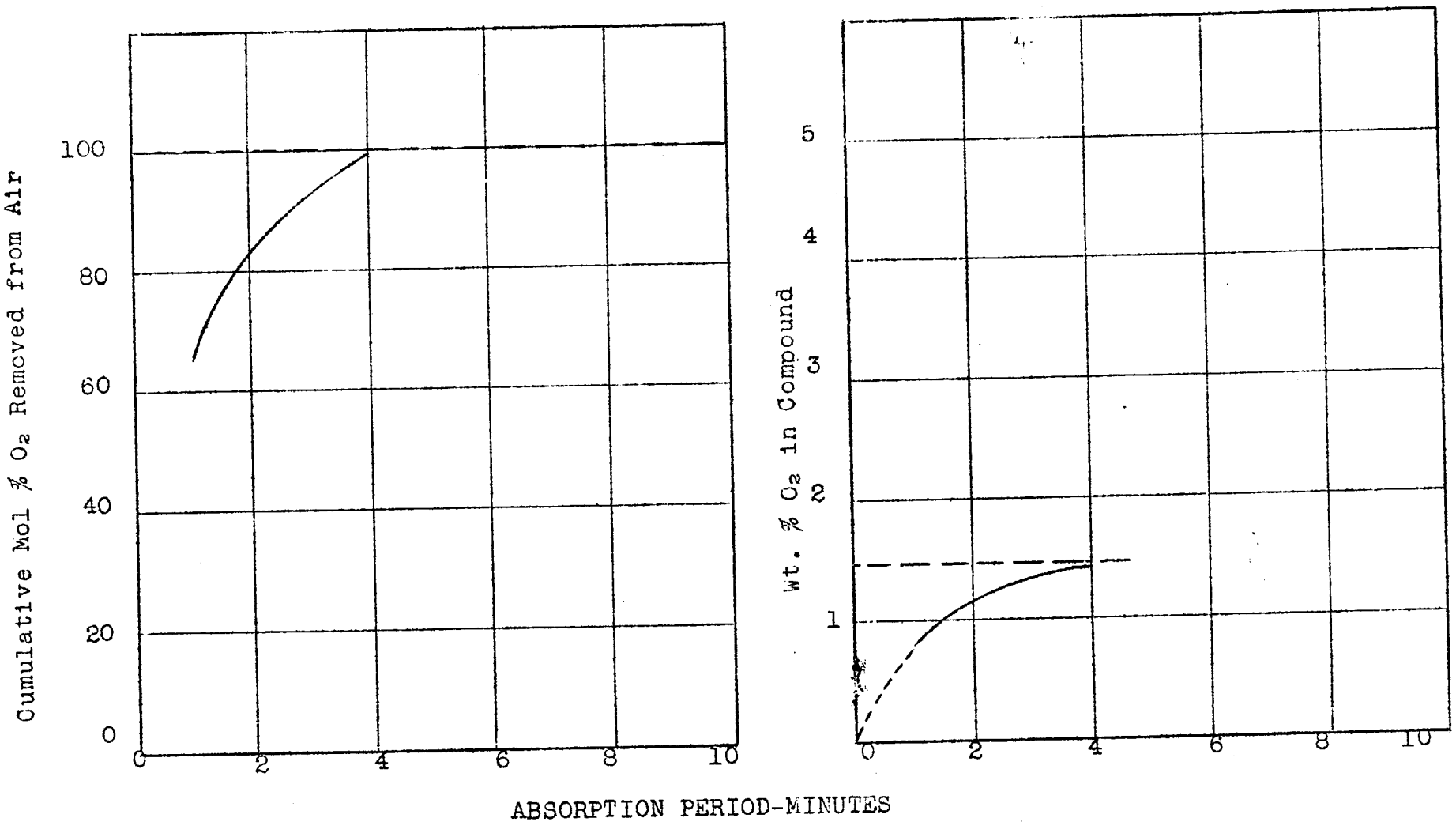

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FIGURE 14

Absorption Pressure - 550 Lbs.
Flow rate - 0.475 CFH
Temperature - 45°C.
- - - - - - = Maximum possible absorption

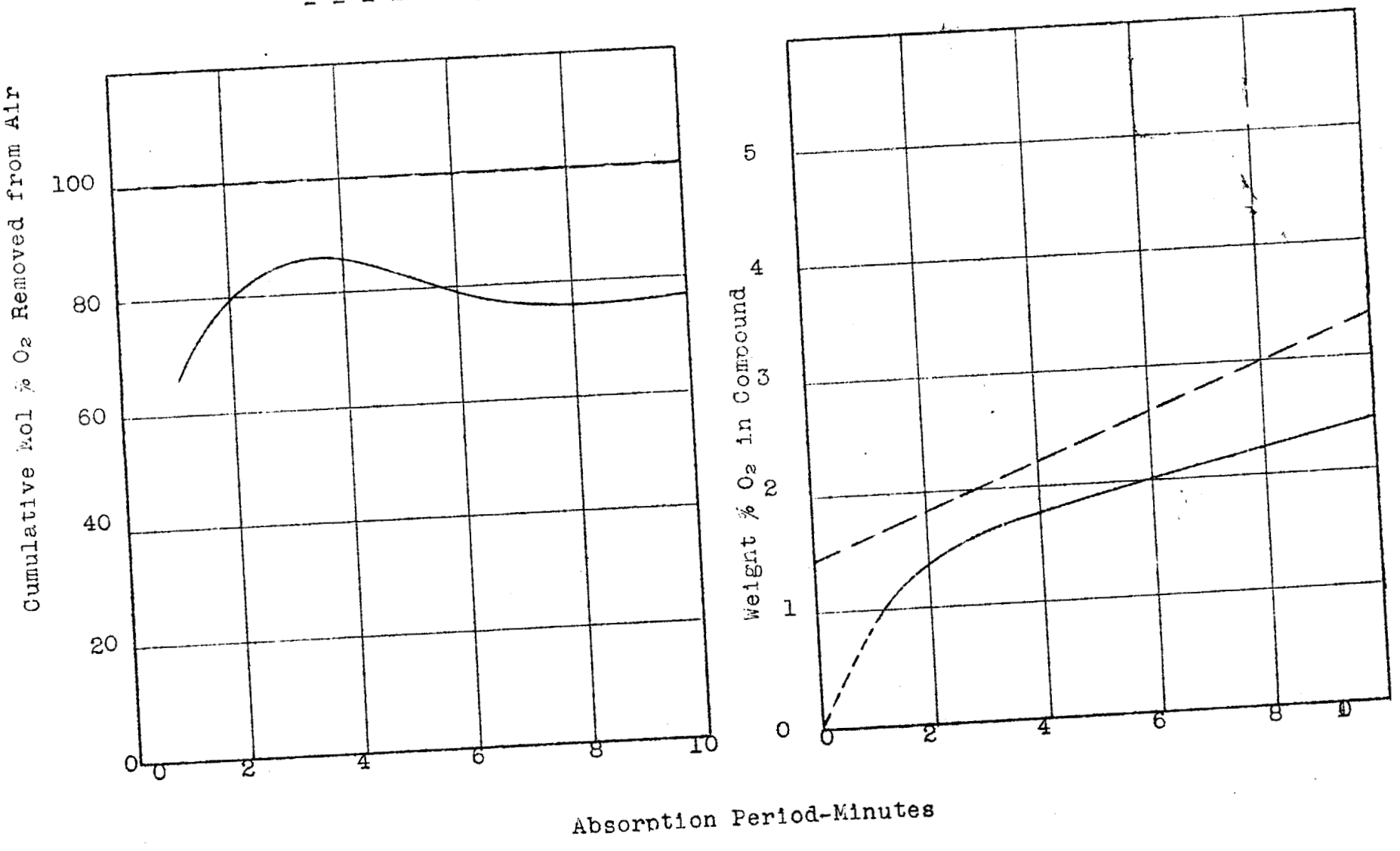

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FIGURE 15

Absorption Pressure - 550 lbs.
Flow rate - 0.87 CFH
Temperature - 45°C.
- - - - - - = Maximum possible absorption

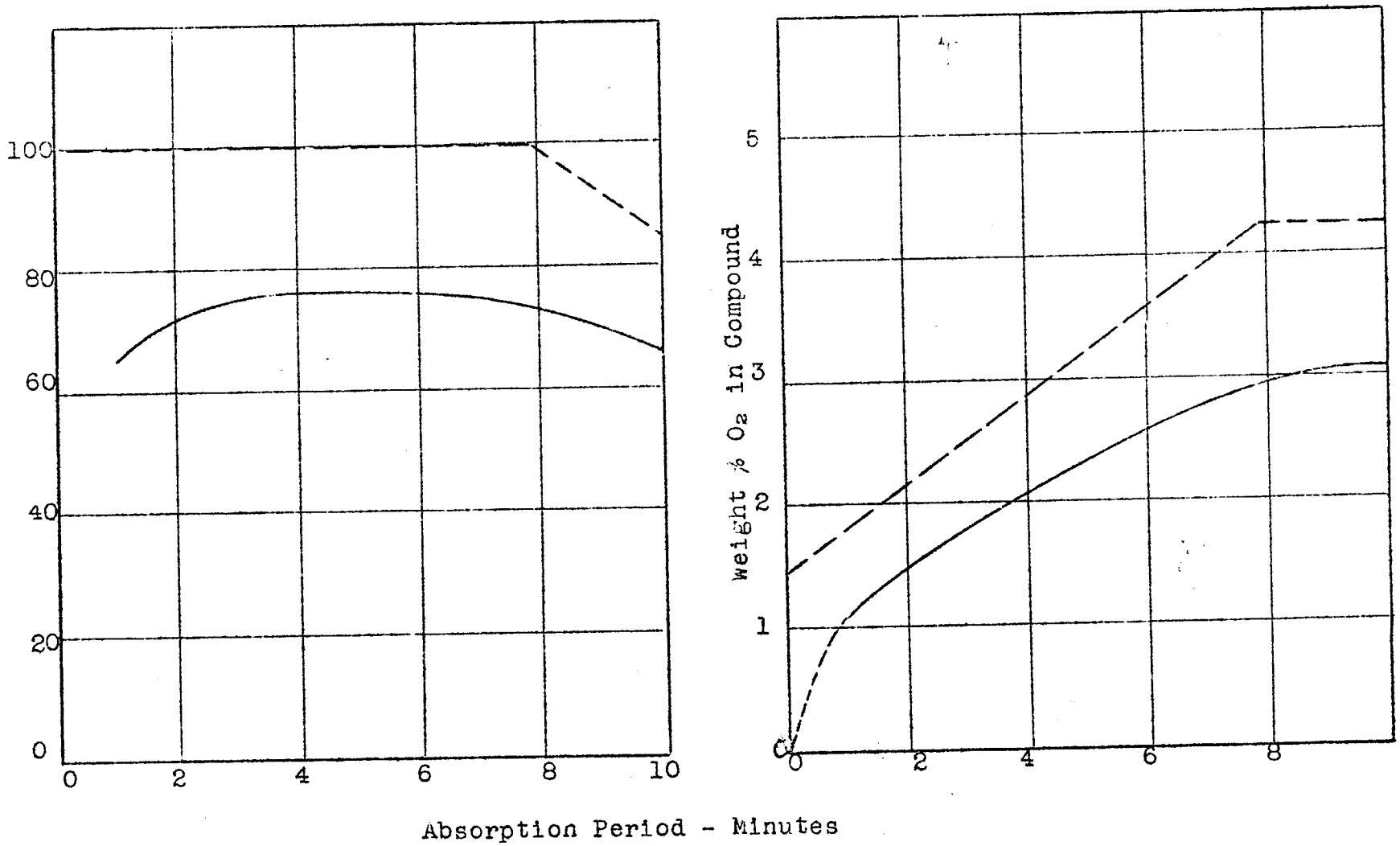

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FIGURE 16

Absorption Pressure - 550 Lbs.
Flow rate - 1.4 CFH
Temperature - 45°C.
- - - - - - = Maximum possible absorption.

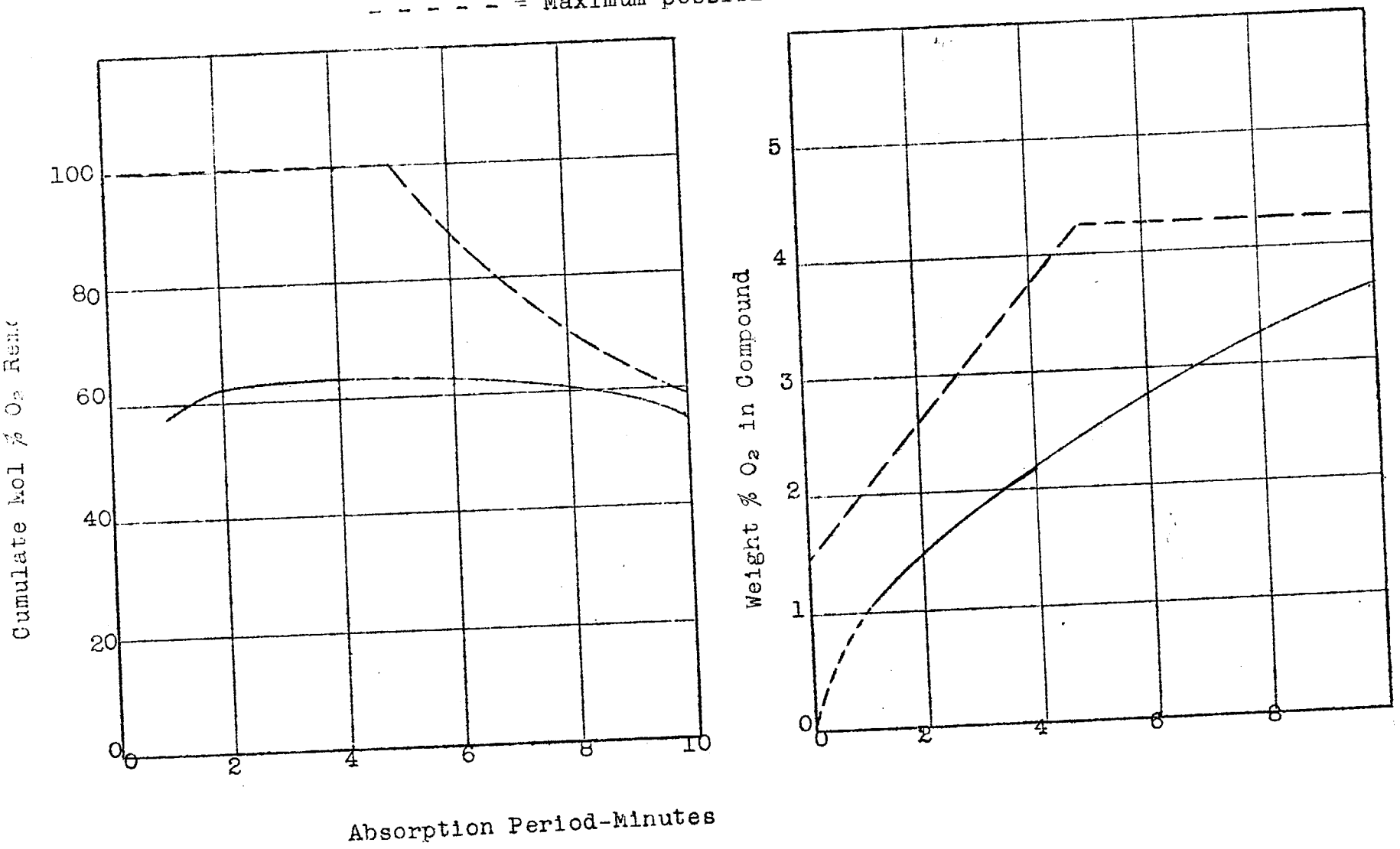

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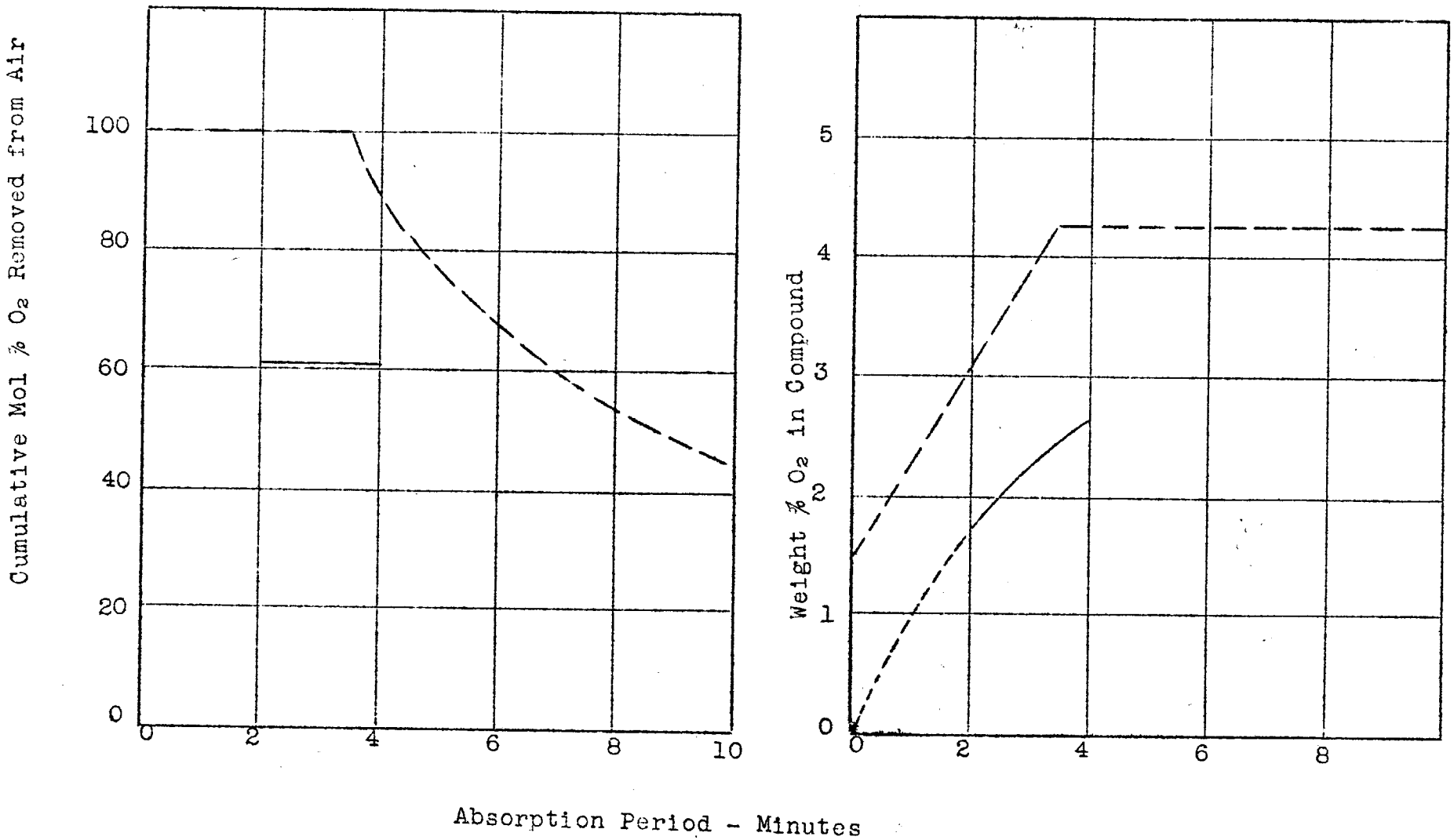
FIGURE 17

Absorption Pressure - 550 lbs.
Flow rate - 2.0 CFH
Temperature - 45°C.
- - - - - - = Maximum possible absorption.



absorption was calculated as that in the air filling the voids plus the amount equivalent to the air that flowed in to replace the oxygen absorbed. In the case of the rest of the figures, the calculations were similar except that the oxygen equivalent to the exit gas was included. These curves indicate that it is difficult under these conditions to obtain both a high saturation and a high percentage oxygen recovery unless a slow flow rate and a long absorption time are employed. These results were obtained in order to evaluate the possibilities of operating the cycle at temperatures between 45°C. and some higher desorption temperatures. They do not appear very promising and if a cycle with temperature variation is to be employed, somewhat lower absorption temperature is probably more favorable.

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IV. ADIABATIC UNIT

On the basis of the results obtained at the higher temperatures an adiabatic unit was constructed. This unit consisted of a steel reactor, 4-3/4" i.d. by 8" long. Originally, an attempt was made to place a layer of insulation inside the reactor, such as to leave an inner space 3" in diameter. This insulation was to make the unit adiabatic and isolate it from the surroundings. Insulating layers of transite and plaster of Paris were employed, but both of these apparently contained so many fine voids that large quantities of gas were stored up and then evolved slowly during the desorption period. This action was observed with nitrogen so that it was apparently a straight hydrodynamic phenomena. This slow gas evolution completely ruined the results and this type of construction had to be abandoned. The final construction consisted in forming a copper gauze tube 3" in diameter, and the space between this tube and the reactor was filled with carefully sized sand. This arrangement had an undesirable feature in the fact that there was a rather large volume of voids around the sand, but it did serve as fairly effective thermal insulation.

The space within the 3" id. gauze tube was filled with a mixture of 160.7 grams of oxygenated, 10 to 20 mesh Rumford Co-Sa-En material together with 1,285 grams of copper chips, the latter material being added for the extra heat capacity. This amount of absorbent filled the space 3" in diameter for about 7-1/2" and corresponds to a little less than half the absorbent that could have been placed in the same volume if it had been used alone.

This unit was operated by charging to an initial pressure of 600 lbs./sq. in. with no additional flow. The absorption period was allowed to proceed at constant pressure after which the bed was rapidly exhausted and the desorption period initiated. Fig. 18 gives results of 2 runs made with an initial temperature of 60°C. In one case the absorption period was 2 minutes and the temperature rose to 65°C. An oxygen saturation of about 1.1 per cent by weight was obtained. In the other case an absorption period of about 6 minutes was employed giving a temperature rise to 69°C. and a saturation of 1.5 per cent. The 2-minute run corresponds to 26% oxygen removal from the air around the material and the 6-minute absorption period corresponds to 36% removal. Fig. 19 illustrates the effect of desorption pressure. It will be noted that in all cases the rate of desorption is very

FIGURE 18

EFFECT OF ABSORPTION TIME

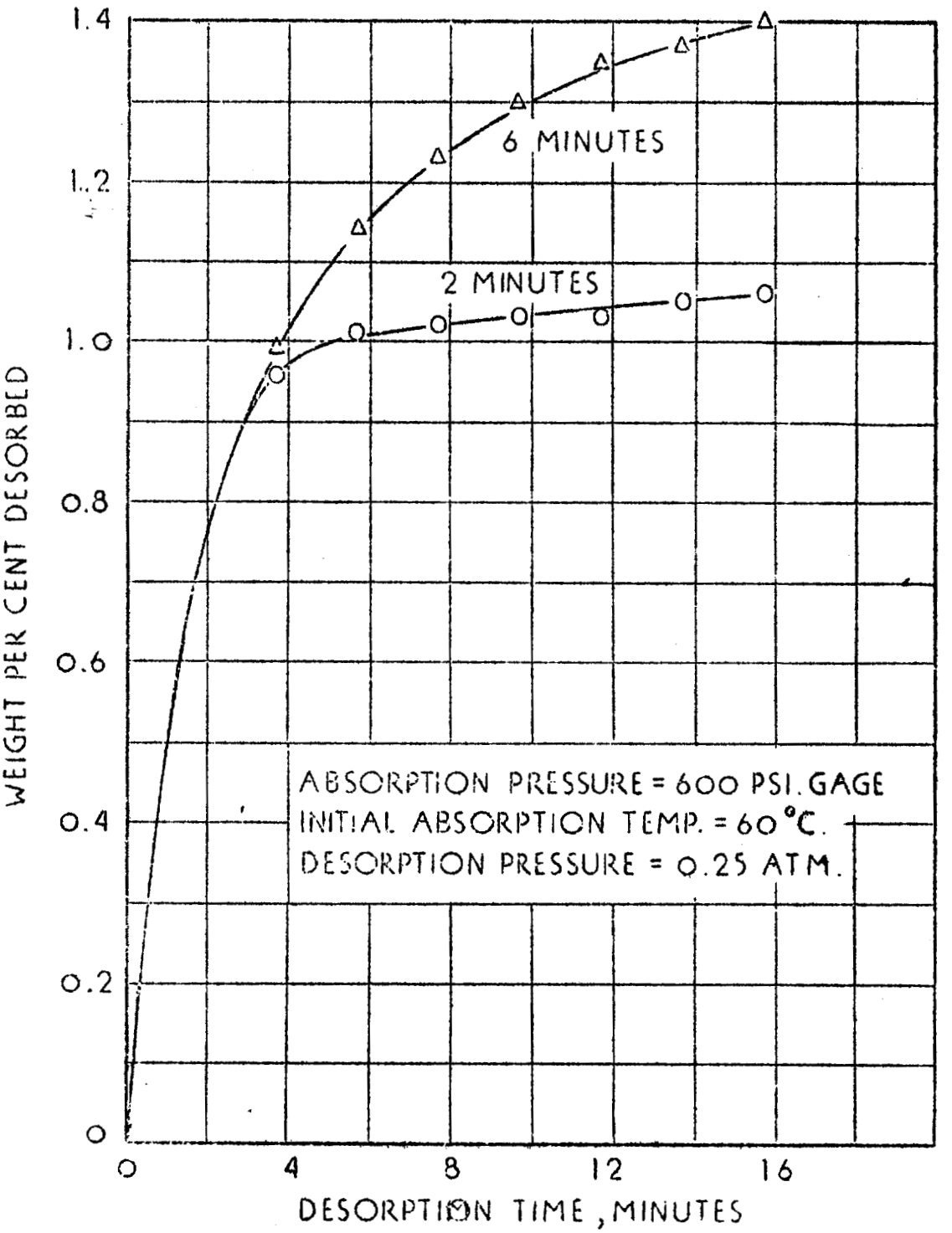

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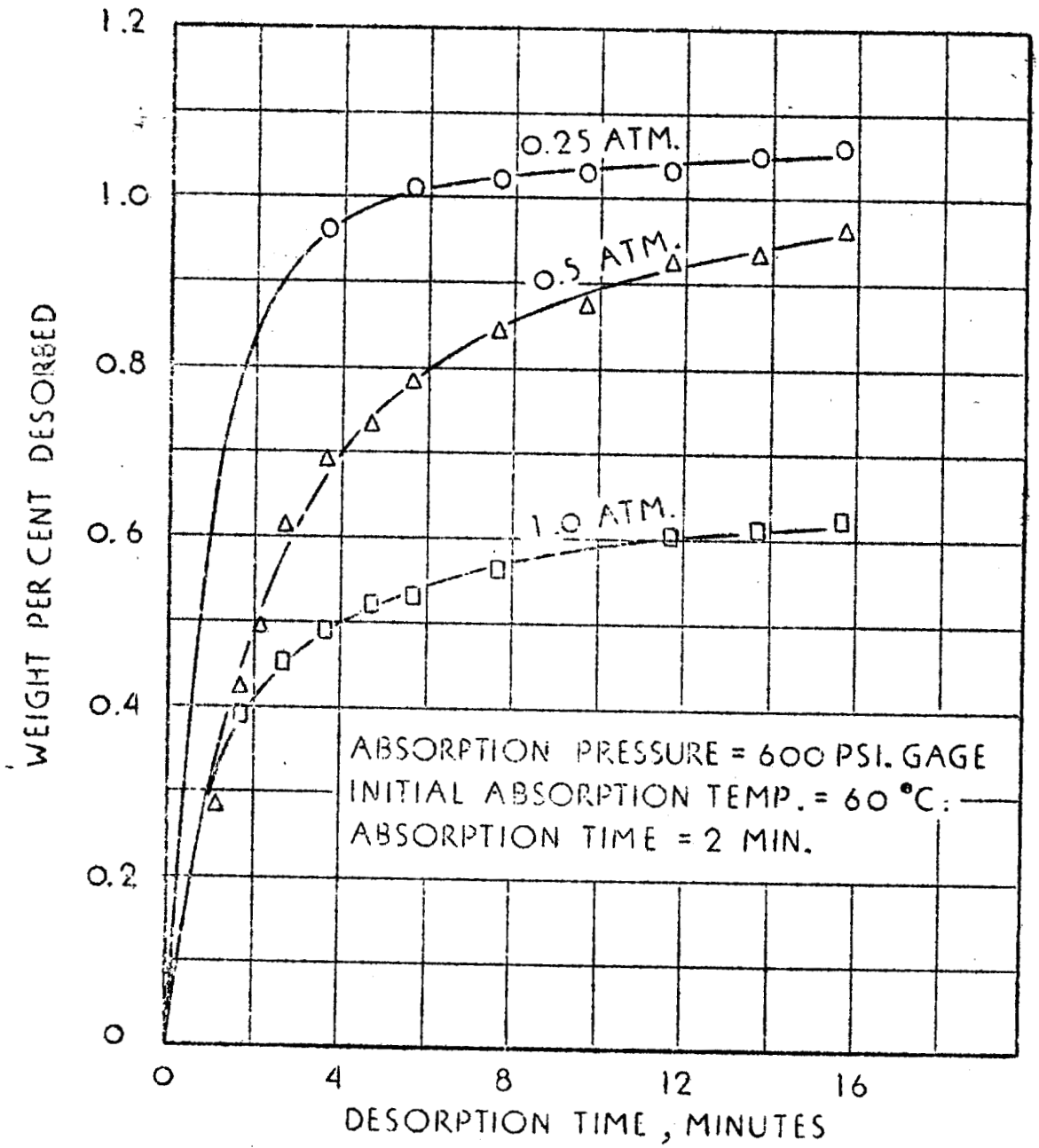
FIGURE 19

EFFECT OF DESORPTION PRESSURE



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rapid for the first portion of the period and this will make purging of the air from the voids difficult.

Fig. 20 compares desorption curves for adiabatic absorption runs carried out with initial temperatures of 50° and 60°C.

Fig. 21A represents the results obtained in a series of adiabatic runs made with a 1/4-minute pressure buildup period, an absorption period of 2 minutes at 600 lbs./sq. in. ga. (no flow) followed by a 1/4-minute blowdown and then a 4-1/2-minute desorption period at 1/4 atmosphere. At the end of this period, the cycle was repeated immediately. This type of operation was employed in an attempt to attain steady state conditions. These steady state conditions would not correspond to complete absorption or desorption but simply would give the operation where conditions would balance. However, this set of runs was not entirely satisfactory due to the fact that the temperature of the inlet air was not properly controlled and resulted in a progressive cooling of the bed amounting to about 1°C. over the seven cycles, indicated by temperature readings at corresponding times in each cycle, given in Fig. 21B.

These results on the adiabatic unit were discussed with the M. W. Kellogg people, and it was agreed that it would be almost impossible to design a unit operating with the large amount of voids present when the granular absorbent is mixed with a granular heat-absorbing material. This is due to the fact that the time necessary to remove the residual air after the absorption period would be so long that a large portion of the absorbed oxygen would be desorbed and lost. This effect is particularly serious due to the fact that the unit is at its highest temperature and thus has its highest desorption rate during the time the air is being removed from the void volume. It was therefore agreed that an adiabatic unit involving an arrangement having much less void space should be employed. The form finally agreed on was to consist of thin cakes formed by pressing a mixture of copper powder and Co-Sa-En material onto copper screens. These thin discs would have projections to permit air flow between successive layers and would be provided with means for making the air pass alternately back and forth across the absorbent bed. This unit has not been completed and the work is curtailed at present because of more urgent problems. A few of the pressed layers were formed and looked very promising; they are hard, strong, and very dense, giving the appearance of being almost metallic. The absorption properties of such dense mixtures of copper and an absorbent have been checked

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FIGURE 20

EFFECT OF INITIAL ABSORPTION TEMPERATURE

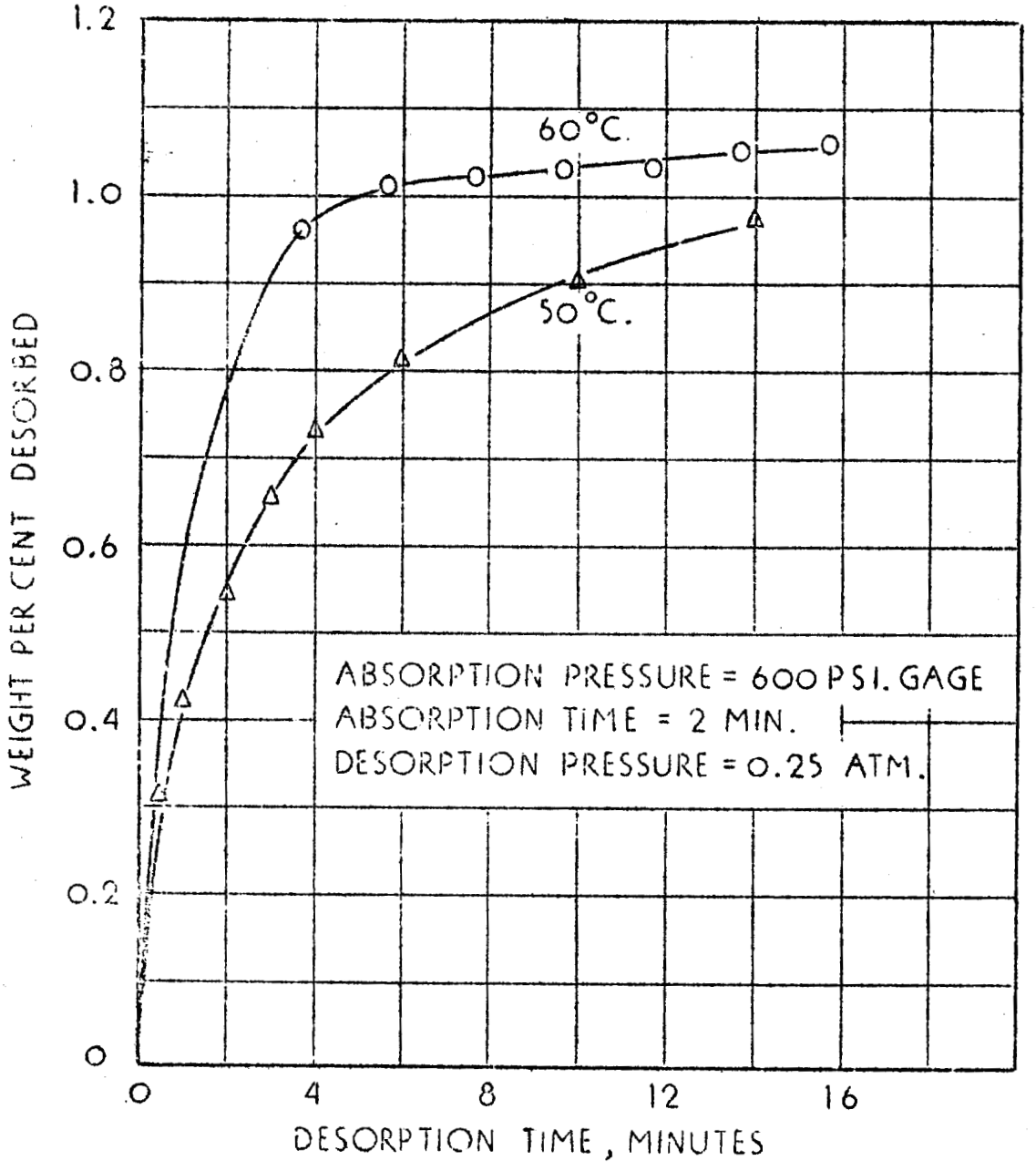

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FIGURE 21A

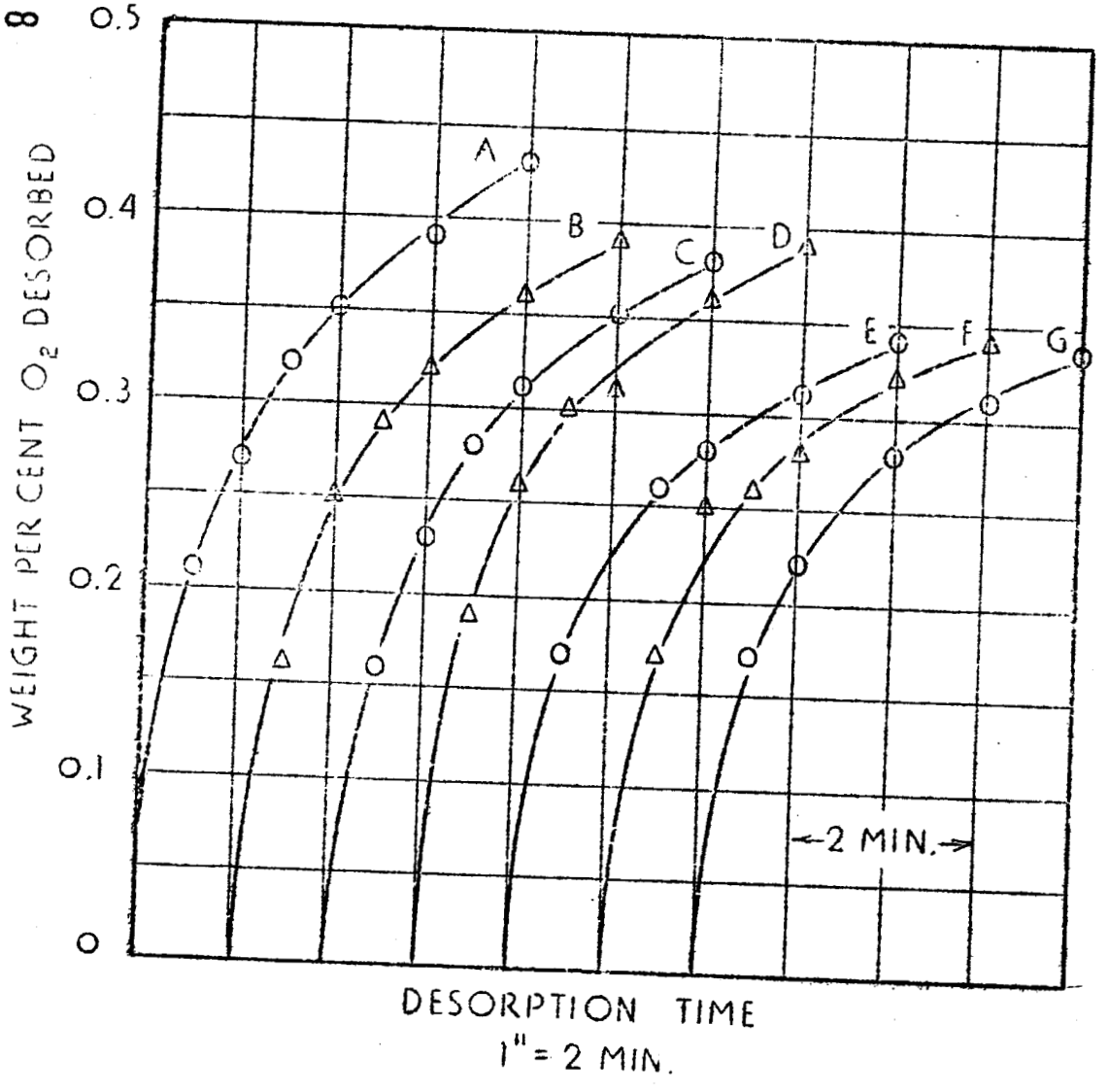
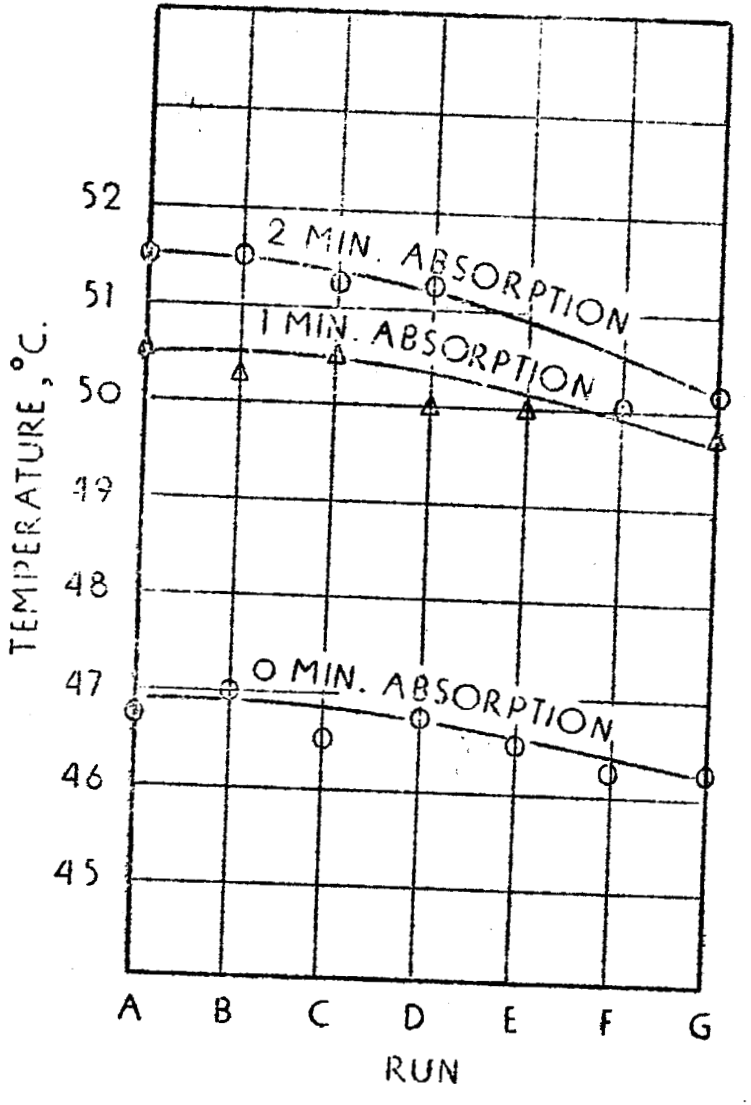


FIGURE 21B



in the 1/2" i.d. units and will be discussed in a later section.

The only serious drawbacks that appear for adiabatic operation are (1) the problem of purging air from the voids without an appreciable loss of oxygen and (2) the weight of the heat absorbent. These problems may be quite difficult, and for the first the most likely solution appears to be in the reduction of the voids. It might be possible to work an arrangement in which the air is swept out by oxygen while maintaining a pressure sufficiently high to prevent desorption but this would probably require very fancy timing and might be unsatisfactory due to the fact that there would be some mixing of the air and the oxygen.

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V. NAVAL RESEARCH UNIT

The Naval Research Unit has been completely assembled and a few preliminary tests carried out. The finned arrangement of the cooling surface and mechanical construction in general appear to be satisfactory. The introduction of the absorbent material into the beds was a real job. It was made particularly difficult by the fact that the absorbent material gives off considerable quantities of fine dust while it is being handled. Respirators were worn by all of the workers during the packing but sufficient powder passed through the mask to cause irritation of the nose and throat. There were no particular physiological effects noticed by any of the men, but it was chiefly a matter of inconvenience.

In its initial form, the unit did not perform satisfactorily. As far as could be ascertained, essentially all the difficulties were related to the operation of the magnetic valves. These valves offered too much resistance to flow in most cases and in addition frequently failed to seat properly. They have been replaced by larger air-operated valves.

These valves appear to operate satisfactorily and in a few tests carried out since they were installed, the rate of oxygen production appears to be about that which was calculated from the laboratory data. The unit is being equipped with meters to indicate the oxygen production for any given period of time and these will serve not only to check the output of the unit but will also make it possible to determine the rate of deterioration. These meters indicate that the pressure drop for the air flow through the bed is almost negligible and that with the original 30 seconds of purging and evacuation, a vacuum of about 25 inches of mercury was obtained on the vacuum end of the bed and about 17 inches vacuum on the other end. These evacuations were obtained while the ejector was operating at below rated pressure and under reduced capacity. Better vacuum will probably be obtained with more favorable operating conditions for the ejector. By increasing the evacuation time to one minute it was possible to bring the whole bed down to a 25 inch vacuum. This pressure was the limit of the vacuum pump.

The cycle operates to produce the oxygen at about 20 lbs. per sq. in. gage. Thus when the cooling period begins the bed is under this oxygen pressure. It is observed that during the cooling period this oxygen is reabsorbed and a vacuum of about 10 in. of mercury is produced before the absorption period begins. The unit is also being equipped with a

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manifold sampling device such that the composition of the various gas streams can be followed closely during the cycle.

A number of tests are planned in order to obtain engineering data on the unit and a detailed report on the design, construction, and operation will be presented in the near future.

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VI. MISCELLANEOUS EXPERIMENTAL WORK

A. Effect of Tube Diameter

Several runs have been carried out comparing the operation of a 1/2" tube and a 1" diameter unit. In both cases the tubes were packed with 40.7 grams of the oxygenated material. The runs were made in the usual manner and the effect of tube diameter on absorption rate is given in Table III. It will be noted that in general, the amount absorbed by the 1" tube under comparable conditions is about 70 to 80 per cent of that obtained with the 1/2" i.d. tube.

The effect of tube diameter on the desorption rate is given in Table IV for an initial saturation of 4.4 weight per cent oxygen. These results indicate that a desorption period about 3 times as long is required to obtain a given per cent desorption for the 1" pipe as compared to the 1/2" tube, and this relation hold approximately over most of the region. Table IV also gives the rate of regeneration obtained with the 1" pipe when the steam pressure in the jacket was held such that the condensation temperature was 115.5°C. The increase resulting from this higher temperature is not very great, presumably indicating that a low temperature difference is not the limiting factor in the rate of desorption.

B. 1" Tube with Brass Grids

Since the results obtained with the 1" pipe were so unfavorable in comparison with the 1/2" tube, particularly during desorption, it was felt that poor heat transfer must be the limiting factor. In an attempt to improve this rate of transfer the 1" pipe was repacked with cup-shaped brass grids. These brass cups were formed from 70-mesh brass gauze in such a way that the cup sides would spring out and fit snugly against the wall. In the packing, about six of these cups were used per inch of tube length. The desorption rates obtained with this construction when employing atmospheric pressure steam in the jacket are given in Table V. Two runs are given: one for a compound about 50 per cent saturated with oxygen and the other for a completely saturated absorbent. These two runs do not check very satisfactorily since the more saturated material indicates a higher per cent desorbed for a given time than does the other sample. However, if the values for either sample are compared with the results of Table IV, it will be noted that the rate of desorption is quite good. In fact, it appears to be equal to,

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TABLE III

Effect of Tube Diameter on Absorption Rate

Abs. Pressure psi. ga.	Abs. Time Min.	Cool. Time Min.	Exit Gas Rate C.F.H.	Wt. % O_2-Absorbed 1" std. pipe*	1/2" i.d. tube	Percentage Ratio of Absorptions
100	4.0	30.0	4.0	1.93	2.86	68.0
"	6.0	30.0	2.0	2.23	2.96	75.3
250	2.0	30.0	4.0	2.05**	2.68	76.5
300	1.0	30.0	8.2	1.57	2.20	71.3

* i.d. = 1.049"

** 7°C. instead of 20°C.

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TABLE IV

Effect of Tube Diameter and Desorption

Temperature on Desorption Rate

(Compound saturated to 4.40 wt. per cent oxygen)

Desorption Time Min.	Percentage Desorbed At 100°C. 1/2" tube	At 100°C. 1" std. pipe	At 115.5°C. 1" std. pipe
0	0	0	0
1	32	14	17
2	56	22	31
3	76	29	39
4	90	35	48
6	99	45	60
8	100	53	70
10		61	78
15		76	92
20		86	98
25		93	99
30		97	100

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TABLE V

100°C. Desorption in Tube Unit with Brass Screens

(1" std. pipe with 6 screens per inch)

Desorption Time Minutes	Percentage Desorbed 2.3 Wt. % Absorbed	4.2 Wt. % Absorbed
0	0	0
1	21.6	37.5
2	60.5	82.2
3	84.0	97.0
4	92.5	97.7
5	94.5	98.0
6	95.0	98.5
8	98.6	99.0
10	99.5	---
15	100.0	100.0

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if not better than, that obtained in the 1/2" tubes. Other heat transfer arrangements could be employed in a similar way. In fact, as was indicated under the section on adiabatic operation, it is possible to press the absorbent directly onto the wire gauze. Forms of these types in tubes of this diameter should allow the absorbent to be introduced and removed by a cartridge type of arrangement.

One absorption run was also made with this copper grid arrangement, and with a four-minute absorption period at 100 lb./sq. in. ga. and an exit gas rate at 4 CFH, a saturation of 2.36 weight per cent O_2 was obtained. This compares with a value of 1.93 for the 1" tube without the grid, and 2.86 with the 1/2" tube. It is believed that these results are not strictly comparable due to the fact that the 1/2" tube experiments were made with a different batch of absorbent and it has been found that the material used in the 1" tube shows a rate of oxygen absorption as much as 20 per cent lower. This 20 per cent difference would make the 1" tube with grids compare closely with the 1/2" tube. It is planned to make runs with both arrangements employing the same absorbent but the work has been curtailed for more pressing operations.

C. Absorbent with Copper Powder

In order to check the effect of incorporating a heat-abosrbing material such as copper with the absorbent, a mixture of precipitated copper powder and the Co-Sa-En material was pressed to 20,000 lb./sq. in. in a hydraulic press. It is estimated that the particle size of the copper powder was around 100 mesh. Two mixes were made, one employing 8 parts of copper by weight per part of absorbent, and the other 4 parts of copper per part of absorbent. With a pressure of 20,000 lb./sq. in. the cake formed was hard and had a shiny copper appearance; in fact, the cake was of about the same consistency as when the copper powder alone was pressed. A pressure of 3,000 lb./sq. in. had been tried with the 8 to 1 mixture but it did not give an adherent cake. These pressed cakes were crushed and screened to 10 to 20 mesh. For the 8 to 1 mixture, 200 grams of these particles filled the 1/2" i.d. tube for about 27-1/2". This corresponds to a bulk density for the Co-Sa-En material of about 0.27 and for the copper-absorbent mixture as a whole of 2.42. This packing resulted in a tube containing only 22.2 grams of absorbent. The results of absorption runs made with this arrangement are given in Table VI. In Runs 1 and 2 it will be noted that the

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TABLE VI

100 psi Absorption with Copper-Co-Sa-En Mixture

Run No.	Exit Gas Rate CFH*	Absorption Time Minutes	Cooling Time (air in voids)	Cooling Water Temp. °C.	Weight % O_2 Absorbed	Cumulative Mol % O_2 Removed from air
1	3	30	2	10	1.21	2.2
2	3	15	2	10	1.15	4.2
5	3	5	2	10	3.42	33.5
6	3	5	2	10	3.39	33.2
7	3	30	2	10	4.01	7.2
8	4	4	15	20	3.25	30.2
9	2	6	15	20	3.54	42.0

*Based on 22.2 g Co-Sa-En (oxygenated)

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activity of this absorbent was very poor. During Runs 3 and 4 no data were collected. However, on the subsequent runs the activity of the system appears to be excellent. Just what made this marked improvement between Runs 2 and 5 is not known. While it is difficult to compare these data with those obtained with the usual arrangement containing 40.7 grams of absorbent, Runs 5 to 9 indicate activities that are probably as good as would have been obtained without the copper powder present. These results would indicate that incorporating the copper powder does not seriously harm the rate of absorption and that such pressed cakes could be used with the adiabatic operation to give a unit containing relatively small voids.

Table VII illustrates the per cent desorption as a function of time for these copper powders. This table can be compared with results for the regular 1/2" tube given in Table IV. It will be noted that the desorption rate is considerably improved, but this may be due in part to the fact that less absorbent is present in the unit containing the copper powder or it may be an actual improvement in the rate of heat transfer.

D. Diffusion Experiment

Professor Furnas suggested that it should be possible to form thin membranes of the Co-Sa-En absorbent which could be used as diaphragms semi-permeable to oxygen. It was felt that by pressing the absorbent into a hardened sheet that the passage of nitrogen could be almost completely restricted but that oxygen would still be able to diffuse through due to its reaction with the absorbent. A small amount of experimental work was carried out along these lines in which thin discs of the absorbent were made. These discs were studied with an atmosphere of either oxygen or nitrogen on one side and a moderate vacuum on the other side. In all cases the passage of nitrogen through the membrane was as rapid as that of the oxygen. However, the amount of effort expended on preparing these diaphragms was relatively small, and it still seems possible that suitable ones might be made. Such diaphragms if they would operate at a practical rate, would completely eliminate the heat transfer problem. There would be a temperature gradient across the diaphragm but no net heat would be added or removed. Further work on this idea was discontinued in order to obtain information on adiabatic operation. It is hoped that a study of this problem can be resumed in the near future.

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TABLE VII

100°C. Desorption of Copper-Co-Sa-En Mixture

(4.13 Weight per cent O_2 absorbed)

Desorption Time Minutes	Percentage Desorbed
0	0
1	37.2
2	79.0
3	95.8
4	98.0
5	99.2
9	100.0

1262459

E. Pellets containing talc, prepared by the Rumford Chemical Co.

The Rumford Chemical Co. has prepared some pellets containing a small amount of talc which we understand was used as a lubricant for the pilling machine. These pellets were compressed to 5000 lb/sq. in. and were 0.2" in diameter by 0.13" thick. They packed in the 1/2" tubes to a bulk density of 0.823. As they were initially received they contained 3.76 weight O_2 based on the absorbent material (excluding the talc). Absorption tests were carried out with air at 100 lb./sq. in. ga. and an exit gas flow rate of 3 cu. ft./hr. The cooling water temperature was 15°C. and the absorption time was 30 minutes. Only 0.99 weight per cent oxygen on the absorbent was obtained. With the usual Rumford material, i.e., 10 to 20 mesh granules, these conditions give essentially complete saturation. It appears that these pellets are decidedly inferior with respect to rate of absorption.

Desorption experiments were also carried out for these same pellets, and for the material with 0.99 weight per cent oxygen the following results were obtained:

Desorption Time - Minutes	0	5	10	20	40	70
Per cent desorped	0	23	36	60	86	100

These desorption rates are very much slower than would normally be obtained. In general complete desorption is obtained in 5 minutes. It is not known whether the slower rates of absorption and desorption are due to the inclusion of the talc or due to the pill size.

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VII. PROGRAM

1. The work on the life-activity of the absorbent is being pushed, and it is hoped that the flow of experimental results will be accelerated in the near future.

2. The unit for the Naval Research Laboratory is being altered to obtain satisfactory operation and after a certain amount of testing in our laboratory, it is planned to ship the unit to the Naval Research Laboratory.

3. Additional information under various absorption and desorption conditions is being obtained to aid the M. W. Kellogg Company in their design calculations.

4. It is planned to resume work on the diffusion apparatus, copper grid arrangements, and adiabatic units as soon as possible.

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