1-1-1969

The Production of Activated Carbon From North Dakota Leonardite

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THE PRODUCTION OF ACTIVATED CARBON
FROM NORTH DAKOTA LEONARDITE

by

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B.S. in Chemical Engineering, University of North Dakota 1967

A Thesis

Submitted to the Faculty

of the

Graduate School

of the

University of North Dakota

in partial fulfillment of the requirements

for the Degree of

Master of Science

Grand Forks, North Dakota

January
1969

This thesis submitted by Donald E. Schroeder, Jr. in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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Title   The Production of Activated
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Date   *November 19, 1968*

ACKNOWLEDGEMENTS

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ABSTRACT

The utilization of leonardite for the production of granular
activated carbons was investigated. In granular activated carbons it
is desirable to have hard dense granules to permit use without exces-
sive disintegration. Two methods were used to modify the leonardite
structure in order to obtain better granules. In one method the
leonardite was put into colloidal suspension with certain alkalis.
Chemicals were then added to the suspension. The additives used were
calcium hydroxide, phosphoric acid, and calcium carbonate. This mate-
rial was then granulated by drying. The second method for preparing
granules consisted in pelletizing powdered leonardite in a rotary drum
using a fine spray of sodium hydroxide solution. The chemical addi-
tives used in this method were pitch, zinc chloride and phosphoric
acid. These granules were then dried, carbonized and activated.
Activation was carried out in a rotary tube furnace using steam as an
activating agent. For leonardite char fed at 534 grams per hour the
optimal activation conditions for methylene blue adsorption were found
to be 950° C. with a steam rate of 300 grams per hour. Methylene blue
and heat of wetting tests indicated that leonardite char when activated
generally had more adsorptive power than the colloidally prepared car-
bons and had less adsorptive power than the pelletized carbons. The
carbon with the greatest adsorptive capacity was a pelletized carbon
with a zinc chloride additive. For methylene blue adsorption it was

equal to Darco grade S-51 and about 60 per cent as efficient as .

Columbia grade G. The hardness and abrasion resistance of the pre-

pared carbon were inferior to that of the commercial carbons.

CHAPTER I

INTRODUCTION

Leonardite is a naturally oxidized lignite having a high percentage of humic acids. It occurs in lignite outcrops and in beds under alkaline soils which are permeable to water. Due to its abundance and low cost many attempts have been made for the utilization of this resource. One possible way to use this resource is as a base material for the production of activated carbon.

There are two types of activated carbons, granular and powdered. Granular activated carbons demand a price of at least two to three times that of powdered carbons depending on the type of application (10). Therefore, there is more economic incentive to utilize leonardite as a raw material for granular activated carbons. This work concerns the use of leonardite for the production of granular activated carbon.

In granular activated carbons it is very important that the supporting walls of the granules be dense or firm, that the granules have a high density, and that the granules possess the necessary structural strength to permit their use in filter columns or beds without excessive disintegration.

The purpose of this research was to explore the possibility of producing a granular activated carbon from leonardite by modifying the structure, carbonizing and activating. The initial interest in using leonardite as a raw material arose from the fact that leonardite could

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be put into colloidal suspension with certain alkalis, and that the precipitation and drying of the suspension would yield hard dense granules. Many chemical additives, such as metallic chlorides and phosphoric acid, have been used to enhance the adsorptive power of activated carbons in other processes. Some of these chemical additives were used in this research to determine their effect on the activation of leonardite.

A second method of modifying the structure of leonardite consisted of pelletizing powdered leonardite in a rotary drum. A five per cent solution of sodium hydroxide was sprayed onto the powdered leonardite while the drum was rotating until pellets formed. Here again various chemicals were added to the leonardite to determine their effect in activation. These activated granules had a weak structure and were easily powdered. The granules were also less dense than the colloidally prepared granules.

After the pellets and granules were dried, they were carbonized at a temperature of 560° C. During the carbonization process most of the volatile constituents of the carbon were removed. The carbonized granules were then screened and the 6 to 16 mesh portion was activated in a 1.625 inch by 42 inch rotary tube furnace at 950° C using steam as an activating agent.

Three methods were used to determine the activity (adsorptive power) of the activated carbons produced. They were the service time test, the heat of wetting test, and the methylene blue adsorption test. The results of these tests indicated that raw leonardite when carbonized and activated had equal if not superior adsorptive power to

those active carbons prepared using colloidal suspensions and additives.
The bulk density of the 8-14 mesh activated carbon prepared from raw
leonardite was approximately 0.50 grams per ml., whereas the 8-14 mesh
activated carbons prepared from colloidal suspensions had a bulk density
of approximately 0.55 grams per ml. Possibly the internal porosity of
the activated carbons prepared from colloidal suspensions was reduced
considerably when the suspensions were precipitated. The pelletized
activated carbons generally had more adsorptive power than activated
carbons prepared from raw leonardite. The bulk density of the pellet-
ized activated carbons was approximately 0.40 grams per ml. The
greater adsorptive power of the pelletized activated carbons was probboth
ably due to greater porosity of the structure. The bulk density of
Columbia grade G was 0.48 grams per ml., and the bulk density of Darco
grade S-51 was 0.40 grams per ml. These two commercial activated car-
bons, Columbia and Darco, were selected for comparison with the acti-
vated carbons produced in this work. Darco was selected because it is
made from Texas lignite, and Columbia grade G was selected because of
the superiority of coconut chars for gas adsorption.

Of the carbons prepared the one with the greatest adsorptive
power was pelletized leonardite with a zinc chloride additive. The
heat of wetting value of this carbon was approximately 0.6 times the
heat of wetting value of Columbia activated carbon grade G, and approxi-
mately 1.2 times the heat of wetting value of Darco grade S-51. In the
methylene blue test this carbon was slightly less adsorptive than Darco
grade S-51 throughout the range of concentrations studied. And both
of these carbons were approximately 60 per cent as efficient for

methylene blue decolorization as Columbia Grade G throughout the range

of concentrations studied. The structural strength of most of the car-

bons prepared was poor when compared to Columbia activated carbon. The

source material for Columbia grade G activated carbon is coconut shells

(29).

The scope of this investigation consisted in determining the

optimum activation conditions for leonardite, and then under these con-

ditions activating and comparing the results of the various leonardite

granules with commercial granular activated carbon.

CHAPTER II

BACKGROUND INFORMATION

Commonly, activated carbon refers to carbonized materials which have been especially prepared to impart to them a high adsorptive capacity. The Condensed Chemical Dictionary, second edition by Turner describes activated carbon as follows:

> Activated charcoal (active carbon) . . . . A more or less pure carbon characterized by high adsorptive capacity for foreign molecules. This adsorptive power is due partly to the chemical nature of the carbon atom with its attendant free valencies and partly to the capillary structure of the charcoal which presents an enormous adsorbing surface. Other factors, such as condensation of gases and vapors in the capillaries, solid solution and chemical combination, also contribute to its adsorptive power. Activated charcoals cover a wide range of adsorptive power for various foreign molecules, depending primarily upon the size and chemical properties of the molecules to be adsorbed.

Thus, fundamentally an activated carbon can be referred to as a carbonaceous material which has adsorptive properties, but this does not include ordinary charcoal which has little or no adsorptive power. Activation is the process by which the surface area of the carbonaceous substance is increased, the hydrogen is removed, and the adsorptive capacity is produced.

C. W. Scheele is credited with the discovery of the phenomenon of adsorption as we understand it today. The phenomena was first mentioned in a letter of Scheele to P. J. Gahn on March 1, 1773 (26). In 1785 Lowitz observed that charcoal would decolorize many liquids. A few years later wood char was employed in a refinery to clarify cane

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sugar. In 1811 bone char was found to be superior to vegetable charcoal in decolorizing power, and subsequently it was adopted in the cane sugar industry. A number of attempts were made during the nineteenth century to prepare decolorizing carbons from other sources. Blood char was developed by Bussy by heating blood with potash. Blood char prepared as such had a decolorizing power of 20 to 50 times that of bone char and it was prepared extensively in laboratories until the introduction of modern activated carbons. In 1865 Hunter (11) discovered the great adsorptive capacity of coconut char for gases. Some of the outstanding properties of coconut char for gas adsorption have never been duplicated by other materials. Engineering difficulties encountered in the industrial production of activated carbons were almost insurmountable during this period of time. Special structural materials were not available then to withstand the corrosive action of the activation conditions required.

More recently, inventions patented by Ostrejko (12, 25) in 1900 and 1901 paved the way for the development of the modern commercial activated carbons. He patented a basic process in which metallic chlorides were incorporated with vegetable substances and then carbonized. Another patent described the use of carbon dioxide as an activating agent. Eponite in 1909 was the first commercially productive active carbon.

Early processes for the production of activated carbon employed heated vertical tubes. The carbonaceous material was placed in the tubes and the activating gas was passed upward through the bed of carbon. This method of activation was found to be unsatisfactory since the product was not uniform. Large temperature gradients existed in the carbon

bed due to its poor thermal conductivity and the fact that the chemical reaction involving steam and the carbon was endothermic. In an attempt to solve these problems early investigators used larger particles. This allowed them to use a higher steam velocity through the bed and eliminated the temperature gradients in the bed, which in turn resulted in a more uniform reaction throughout the bed. This method was unsuccessful though since only the outside of the large particles was activated. Subsequent methods of activation involved the use of continuous systems to overcome the problems of activating carbon by the stationary bed method.

Wickenden and Okell (13) developed a method by which the activating gases were passed upward through the bed of carbon at sufficient velocity to suspend the bed of carbon. The advantages of this method were that a uniform distribution of temperature existed, the entering steam contacted different particles, and as the particles were activated their density decreased so that they could be continuously floated away as they reached the desired activity.

In 1962 Robert Thelen (38) investigated the possibility of producing activated carbon from North Dakota lignite using the fluidized bed technique. The active carbon produced in this manner compared favorably with Darco activated carbon. Amick and Lavine (45) prepared an activated carbon from carbonized North Dakota lignite that compared favorably with the equivalent Darco product. On a pilot plant scale using a rabble-type furnace Cooley (46) prepared an activated carbon from North Dakota lignite which compared favorably with commercial products from water purification.

Presently the Atlas Powder Company Darco plant is the only com-
mercial plant in the United States known to be manufacturing activated
carbon from lignite. This plant has been operating since 1922 at
Marshall, Texas. In 1952 it had a capacity of some two million pounds
per month of activated carbon (47).

In the course of the literature survey much information con-
cerning the activation of various carbonaceous materials was found,
but no published literature was found concerning the activation or
use of leonardite as a basic starting material for producing activated
carbon. Since leonardite is a naturally oxidized lignite the activa-
tion of lignite can be considered to a certain degree analogous to the
activation of leonardite.

CHAPTER III

THE PROCEDURE FOR PRODUCING GRANULES

Material

The leonardite used in this experimentation was a portion of the leonardite prepared by Philip H. Tufte for his Master's thesis. This leonardite was found and screened to -325 mesh. The proximate and ultimate analysis of the leonardite as obtained from Tufte's thesis (39) is given in Table 1.

TABLE 1

PROXIMATE AND ULTIMATE ANALYSIS OF LEONARDITE*

Item	Moisture Free	Moisture Ash Free
Proximate Analysis Per Cent		
Moisture		
Volatile Matter	44.31	51.18
Fixed carbon	42.28	48.82
Ash	13.41	
Ultimate Analysis Per Cent		
H	3.29	3.80
C	56.51	65.26
N	1.18	1.37
O	25.08	28.96
S	0.53	0.61
Ash	13.41	
Heating Value-BTU per pound	8,720	10,070

*Run by U. S. Bureau of Mines Laboratory at Pittsburgh.

Procedure for Colloidally Prepared Granules

The general procedure involved in making of the granules from the powdered leonardite was as follows:

1. An alkali, either ammonium hydroxide or sodium hydroxide, and water were used to make a colloidal suspension of leonardite. A mixing time of approximately fifteen to twenty minutes was required to do this.

2. After the colloidal suspension was thoroughly mixed, the chemical additive, either as a slurry or as a solution with a limited amount of water, was added to the suspension. The mixture was again thoroughly mixed.

3. The mixture was poured into pans and dried. In most cases tray drier was used to dry the material, but some of the mixtures were allowed to dry at room temperature.

Not all of the mixtures made in this manner were carbonized and activated, since in some cases the granule structure after drying was very poor. A listing of the composition and method of preparation of all the mixtures is given in Table 2.

Procedure for Pelletized Granules

The −325 mesh leonardite used for preparing granules from colloidal suspensions was too fine for pelletizing. Therefore, raw leonardite was ground in a rotary grinder until the material was less than 60 mesh.

The procedure used for adding chemical additives consisted of first mixing the chemical, water, and leonardite in a sigma blade mixer.

TABLE 2 GRANULES PREPARED FROM COLLOIDAL SUSPENSIONS

Mixture Code No.	Ingredients Added Step 1			Ingr. Added Step 2		Drying Method	Comments
	lbs. Leon	H_2O	Alkali	lb. Additive	lb. H_2O		
1	6 lbs.	15 lbs.	160 gm.NaOH	None	None	Tray Drier Low Air Flow	Mixture too fluid.
2	6 lbs.	15 lbs.	160 gm.NaOH	None	None	Tray Drier No Heat	
3	10 lbs.	20 lbs.	0.8 lbs.NaOH 2.0 lb. H_2O	.2 lbs. $Ca(OH)_2$	.5 lb.H_2O		Mix was too dry. More H_2O required. Very lumpy before adding $Ca(OH)_2$.
4	10 lbs.	23 lbs.	1.25 lb. 28% NH_3	.2 lb.$Ca(OH)_2$	.5 lb. H_2O		Mixed 30 min. Too fluid. Mixture is foamy.
5	10 lbs.	20 lbs.	1.9 lb. NH_3 28% by wt.	.2 lb.$Ca(OH)_2$	.5 lb. H_2O	Tray Drier	
6	15 lbs.	25 lbs. + 4 lbs.	1.2 lbs.NaOH 3.0 lb. H_2O	.4 lb. $Ca(OH)_2$	.5 lb. H_2O	Tray Drier	Produced hard granules.
7	15 lbs.	25 lbs. + 3 lbs.	1.2 lb. NaOH 3.0 lb. H_2O	.6 lb.$CaCO_3$ Suspension	3 lb. H_2O	Tray Drier Low Heat Low Air Flow	Mixed 20 minutes.
8	15 lbs.	27 lbs.	1.2 lb. NaOH 6.0 lb.H_2O	.2 lb. $CaCO_3$	None	Tray Drier No Heat Low Air Flow	Material lumpy.
9	15 lbs.	27 lbs.	2.7 lb. NH_3 28% Soln.	.2 lb. $CaCO_3$	6 lb. H_2O	Tray Drier No Heat Low Air Flow	Material lumpy.
10	10 lbs.	21 lbs.	1.9 lb. NH_3 3 lb. H_2O Slowly	.15 lb.$CaCO_3$	3 lb. H_2O	Tray Drier With Heat	Powdery structure.

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TABLE 2--Continued

Mixture Code No.	Ingredients Added Step 1			Ingr. Added Step 2		Drying Method	Comments
	lbs. Leon	H_2O	Alkali	lb. Additive	lb. H_2O		
11	10 lbs.	21 lbs.	1.9 lb. NH_3 $\sim$5 lb. H_2O Slowly	.15 lb. $CaCO_3$	2 lb. H_2O	Tray Drier Heat Low Air Flow	
23	10 lbs.	19.9 lb. H_2O	1.9 lb. NH_3	1.2 # 85% H_3PO_4	4.8 lb. H_2O	Set Overnite Dried in Morn. Tray Drier High Heat	Mixed well for 1 hour to get colloidal suspension. Then H_3PO_4 was added. Mixture became lumpy. Added more H_2O and mixed 20 min.

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Enough water was added to the mixture so that no dusting occurred. A portion of this additive mixture was then added to the leonardite used in pelletizing.

The equipment used for pelletizing the leonardite was a rotating airplane tire approximately thirteen inches in diameter. A hand sprayer which produced a fine mist, was used to spray the sodium hydroxide solution on the leonardite. The procedure used in preparing the pellets was as follows:

1. Two hundred grams of leonardite was placed in the rotating drum.

2. While the drum was rotating, approximately 200 to 250 ml. of a 5 per cent sodium hydroxide solution was sprayed in a fine mist onto the leonardite.

3. The drum was allowed to rotate until pellets of the proper size formed.

4. The pellets were dried in a tray drier. A listing of the various pellets made and their contents is given in Table 3.

TABLE 3 CONTENTS OF PELLETIZED GRANULES

Material Code No.	Additive Mixture	Amount of Additive	Amount of Leonardite	Pelletizing Agent and Comments
12	None	None	200 gm.	5% NaOH solution.
13	400 gm. leon. 173 ml. 10% H_3PO_4	20 gm.	200 gm.	5% NaOH solution. More Leonardite added slowly.
14	400 gm. Leonardite 178 ml. 10% $ZnCl_2$	20 gm.	200 gm.	5% NaOH solution. More Leonardite added slowly.
15	Spencer deashed lignite pitch	100 gm.	900 gm.	5% NaOH solution.
16	Spencer deashed' lignite pitch	200 gm.	800 gm.	5% NaOH solution.
17	Spencer deashed lignite pitch	100 gm.	900 gm.	Pelletized with pure H_2O and wetting solution.

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CHAPTER IV

THE CARBONIZATION PROCESS

Carbonization, or destructive distillation as it is sometimes called, is simply a process for removing the volatile matter from a carbonaceous material in the absence of air. Chaney and others report that temperatures below 600° C are desirable for carbonization in order to produce chars which are suitable for activation by steam, although this does not hold for all cases (1, 6, 14, 27). They consider that carbon liberated above 600 to 700° C is inactive and, moreover, cannot be activated. If the carbonization temperature is above this temperature cracking of the evolved gases occurs. Some of these cracked gases are apparently deposited on the parent carbon structure. Hence they maintain that it is important in activating charcoal to avoid decomposition of the hydrocarbons in such a manner as to deposit a coating of inactive carbon upon the surface.

Fieldner, Hall and Galloway (40) report that it is desirable to conduct the heating in such a manner as to allow the carbon sufficient time to evolve most of the volatile matter at as low a temperature as practicable. This is then followed by heating to a somewhat higher temperature (approximately 600° C) to free the surface of remaining smaller amounts of volatile matter. This procedure is of more value for materials, such as coal, which contains large amounts of tarry matter.

In this work the carbonization was carried out at 560° in a muffle furnace. Approximately one hour was required before the evolution of gases abated. The carbonized material was then removed from the furnace and was spread out to cool. In some cases it was necessary to spray a fine mist of water onto the granules to prevent oxidation of the granules.

Two typical carbonization temperature curves are shown in figure 1. The temperatures indicated in this graph are the center temperature of the muffle furnace. These two curves show that a portion of the volatile matter was driven off at lower temperatures before the desired temperature was reached as was suggested by Fieldner, Hall and Gallaway for tarry materials.
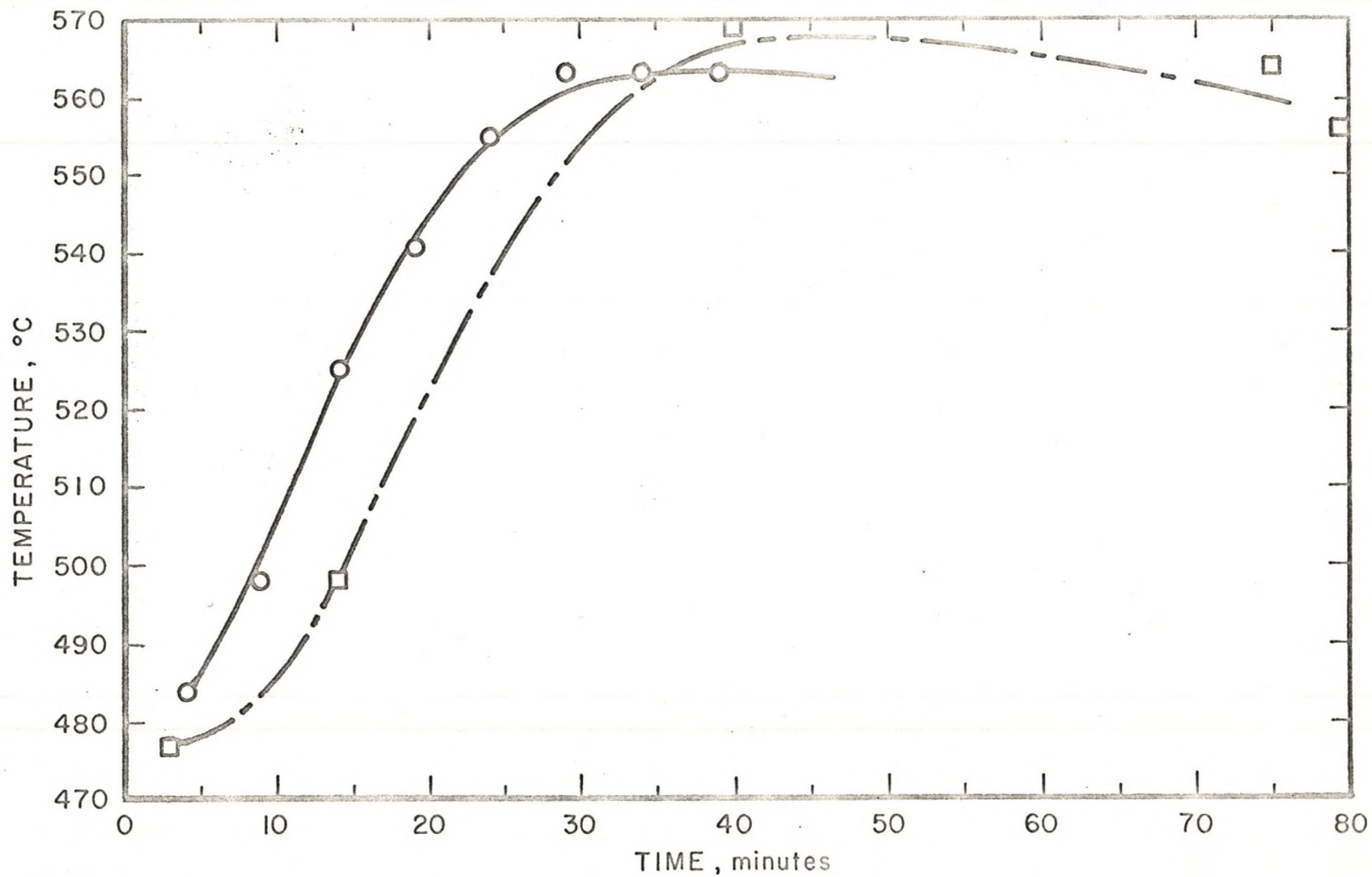
FIG I. Typical carbonization curves.

CHAPTER V

THE ACTIVATION PROCESS

In the activation process oxidation and subsequent removal of the adsorbed film of hydrocarbon complexes and part of the carbon structure occurs. Ray (3) states that there are four methods by which the various types of activated carbons may be prepared: (1) The hydrocarbons present in the chars prepared by low temperature carbonization can be removed by selective oxidation so as to leave the carbon in an active state. Air, steam, carbon dioxide, and chlorine have been used as activating agents. (2) The presence of inorganic chemicals has been used to prepare activated carbon. The carbonaceous material is impregnated with a solution of the chemical and then carbonized. The chemical is then dissolved out leaving an active carbon. (3) Carbonized residues can be activated by calcination alone. It appears that the activation is due to leakage of air into the heating chamber and not as a result of the heating. (4) Lenher and Dorsey claim that carbonized material can be activated by the action of selenium oxychloride, but evidently this method has not been too successful.

Bloomquist (4) states that inventors have found that steam is a better activating agent than carbon dioxide and that it is advisable to keep the percentage of carbon dioxide as low as possible when oxidizing gases are being used for activation.

After reviewing the various methods for activation it was decided that activation by the means of the oxidizing gas method with steam would be the most practical approach. The principal reaction (15) which occurs in the process of activation with steam is:

$$H_2O + C = H_2 + CO$$
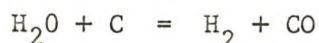
This is an endothermic reaction at the temperatures used in activation. Carbon dioxide (2) is also formed corresponding to the reactions:

$$CO + H_2O = H_2 + CO_2$$

and
$$2 CO = CO_2 + C$$
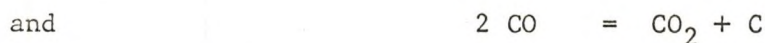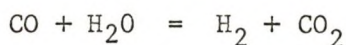
Fieldner, Hall and Galloway (41) in their work on the activation of various coals using steam maintain that the temperature during activation should be 925° C. For some very active materials they report 900° C is satisfactory. They also reported the analysis of the gases evolved by the activation of North Dakota lignite as follows:

$$CO_2 \ldots 14.4 \text{ per cent}$$
$$CO \ldots 27.6 \text{ per cent}$$
$$H_2 \ldots 58.6 \text{ per cent}$$

These results compare well with the ranges set by Williams (50) for gases evolved from the steam activation of coal. Williams also states that generally the degree of activation is largely affected by the homogeniety of the product, assuming that the temperature and steam treatments are constant.

Hassler (16) states four factors which determine the kind of adsorptive properties developed in activation by oxidizing gases. They are the amount and kind of mineral ingredients in the char, the extent to which the activation is conducted, the temperature of the reaction,

and the chemical nature and concentration of the oxidizing gas. He also states that the optimum activation conditions are specific for each situation and in a large extent depend on the history of the char.

Although steam was used as the principal activating agent in this work, the chemical additives used in some of the preparations would assist in the activation of the carbon. McKee and Horton (5) state that the added materials may be listed according to their chemical and physical effects in the following way: (1) Those that act as dehydrating agents and cause decomposition at low temperatures. These chemicals cause the decomposition products to be liberated as water rather than as hydrocarbons, as for example, zinc chloride, magnesium chloride, and sulphuric acid. (2) Those that have a chemical reaction on the products of the decomposition which makes them soluble or allows them to escape. This prevents the deposition of inactive carbon on the carbon structure. Compounds frequently used in this manner are sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. (3) Those that provide a framework upon which the carbon is deposited and protect the carbon structure from the products of decomposition. These materials when extracted leave a porous mass of activated char. Sodium chloride, sodium sulfate, calcium carbonate, calcium phosphate, calcium sulfate, and silicon dioxide are some materials which are used in this manner.

Equipment Used In Activation

The activation equipment (shown in figure 2) consisted of an electric rotary tube furnace fitted with a feed hopper and auger. The electric furnace was inclined at an angle of 4.7 degree from horizontal, so that the material would feed through the tube at the proper rate.

Reaction tube (slope .98 inch per foot)

Burrell electric furnace

Product collector

Feed hopper

Graphite washer

Steam generator

Feed auger

Stand
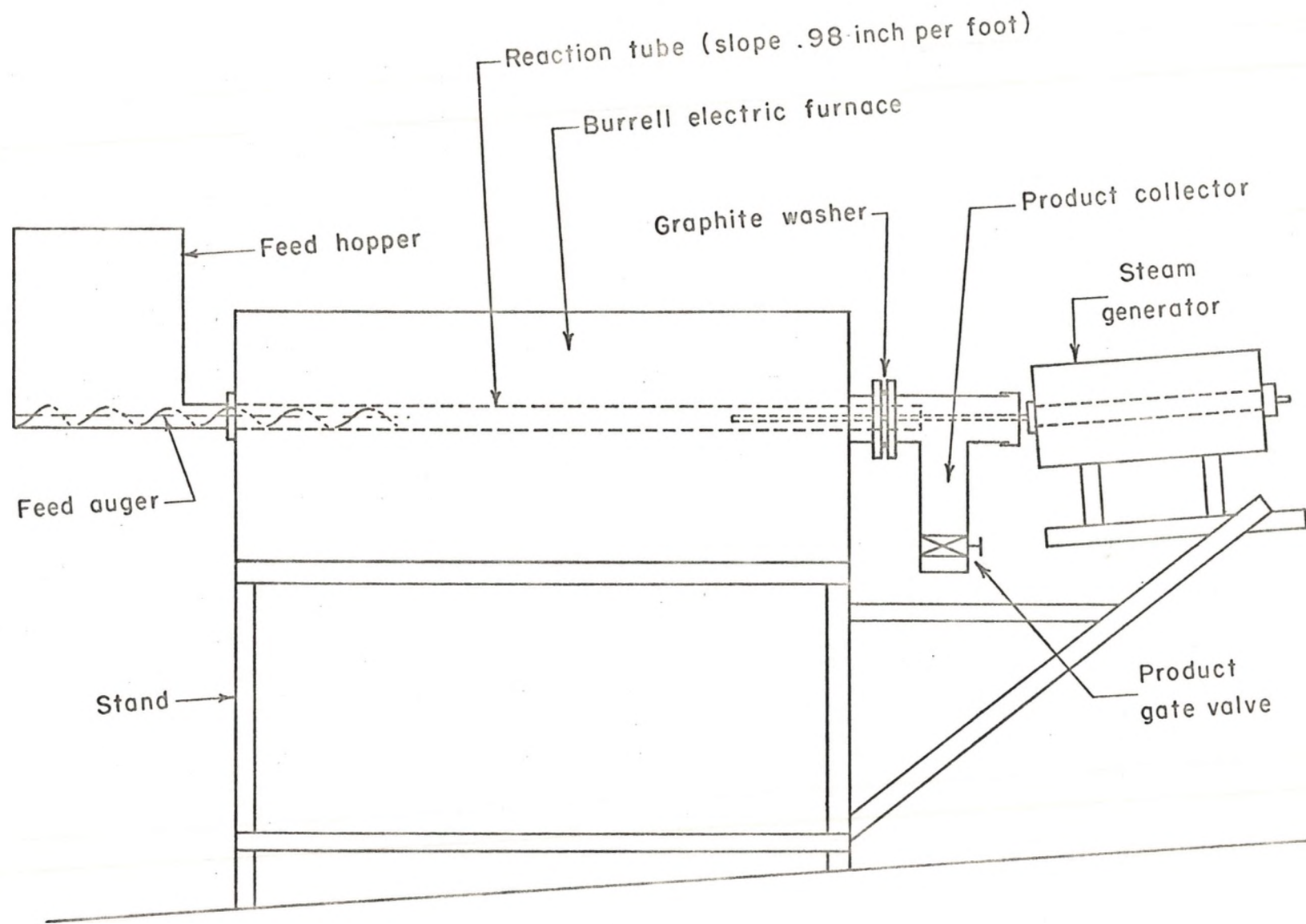
Product gate valve

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FIG 2. Activation equipment.

The reaction tube was 1.625 inches in diameter and about 42 inches long. It rotated at 5.75 rpm. The product was collected in a 2-1/2 inch pipe fitted with a gate valve. The collector was located at the lower end of the furnace with air tight fittings so that no reaction gases could escape through the collector.

The furnace was initially designed for activation with carbon dioxide gas. Modifications were made in the furnace so that steam could be used as the activating agent. A 220 volt electric tube furnace was used to generate steam. A one inch stainless steel pipe packed with broken porcelain was placed in this furnace. A small fitting was located at one end of the packed pipe to admit water. On the other end of the packed pipe a long 3/8 inch stainless steel tube was used to transport the steam to the reaction zone. The apparatus as constructed provided superheated steam of 400 to 500 degrees F. This steam generating apparatus was then attached to the activating furnace as shown in figure 2. Water was fed into the steam generator by means of a sigma pump. The calibration for this pump is given in Appendix E. Since the reliability of the sigma pump was questionable the amount of water consumed was determined at frequent intervals by weighing.

Condensation of steam in the product collecting pipe occurred during the initial run. To rectify this situation heating tape was wrapped around the collector pipe so that its temperature could be maintained above 100 degrees C.

When the granules were fed into the reaction tube by the auger approximately 20 to 22 minutes would pass before the granules would

appear in the product collector. The heated portion of the reaction tube was approximately two feet long, so this would indicate that the residence time in the reaction zone was approximately 12 to 13 minutes.

The feed rate was dependent on the granule size, shape, and the angle of repose. To obtain a uniform feed rate the material was screened to 6 to 16 mesh.

CHAPTER VI

METHODS OF EVALUATION OF ACTIVATED CARBON

The literature survey revealed that in practice many different methods of analyses are used in the evaluation of activated carbons. The majority of these methods are time consuming and are not overly indicative of the value of a carbon for a particular purpose. Each different application usually requires a different test. For example, the service time test is used to evaluate carbons used in gas adsorption, the phenol test is used to evaluate carbons used in water purification, or the methylene blue adsorption test is used to evaluate carbons used in decolorization. In industry the recommended procedure for the selection of a carbon for a process is to test a series of different carbons in the actual situation where it is to be used. Often times this procedure is shortened considerably by the use of screening tests to eliminate those carbons with less potential (17).

It has been pointed out by Chaney, Ray and St. John (33) that the most reliable analytical data pertaining to gas adsorbing active carbons are:

1. Service Time. This is the time required for a vapor to break through a bed of carbon under standard conditions. In this test, air with a known concentration of impurity (carbon tetrachloride) is passed through a bed of carbon

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until the impurity breaks through the bed. The bed
depth is specified along with the flow rate of the gas
per square cm. of bed.

2. Adsorption Value. This is the weight of vapor adsorbed
by an active carbon under conditions of saturation. The
test is an extension of the service time test. The passage
of the vapor-air mixture is continued, with weighings of
the adsorption tube each half hour, until no further gain
in weight is evident. The gain of carbon tetrachloride
in milligrams per gram of carbon is recorded as the ad-
sorption value.

3. Retentivity Value. This is the weight of vapor held by
a carbon by the secondary valence bonds, under standard
conditions. More simply, retentivity value is the amount
of vapor which is retained by the saturated carbon from
the adsorption value determination after it has been
heated and evacuated under standard conditions until no
more of the vapor can be removed. A sample of the
saturated carbon from the adsorption value determination
is transferred quickly from the adsorption tube to a
glass stoppered bottle and weighed. The glass stopper
is removed and the weighing bottle is placed in a vacuum
desiccator which in turn is placed in an oven maintained
at 90 to 100° C. The carbons are evacuated to 2 mm. Hg
pressure, with periodical weighings, until the weight
loss is less than 15 mg. over a half hour period. The

retentivity value is determined by graphing the percentage
weight of vapor retained against time, and extending the
portion of the curve representing low rate of vapor loss
back to the retentivity axis.

The main criticism of these methods (34) arises from the lack of
definition of terms and of precise descriptions of the procedures which
have appeared in the literature. Quantitative results can be achieved
and duplicated only by a rigorous standardization of the analytical
procedures.

Stone and Clinton (35) have suggested the use of heat of wetting
for the evaluation of gas adsorbent carbons. The advantages they cite
are extreme rapidity, satisfactory accuracy and suitable correlations
yield data on the other characteristics of the carbon.

In view of these considerations the heat of wetting test and
the service time test were selected for the evaluation of the carbons.
Since both of these tests are mainly for gas adsorbents, a third test
was also used on some of the carbons in order to determine their ability
to adsorb larger molecules from liquids. The test selected for this was
the methylene blue test.

Heat of Wetting Test

The heat of wetting test affords a measure of the decrease in
total surface energy of an activated carbon. (18) The heat of wetting
is determined by placing a dry weighed portion of activated carbon in a
liquid, such as benzene, and measuring the temperature rise. The re-
sults are reported as calories per unit mass of adsorbent.

For the determination of the heats of wetting a silvered cylin-
drical Dewar flask was used as a calorimeter. A Beckman thermometer
was used to record the initial and final temperatures of the liquid.
The liquid used in this testing was benzene, although Stone and Clinton
(36) recommend meta-toulene because of its relatively constant specific
heat over the temperature range used, and because of its lower volatil-
ity.

The heat capacity of the assembly was determined by the heat of
neutralization of dilute sodium hydroxide and hydrochloric acid solu-
tions using the value of the heat of neutralization, ΔH_n, of -13.70
kcal. per gram mole at 25° C (8). The heat capacity was found to be
3.725 cal. per degree C.

A 50 ml. portion of benzene was pipetted into the calorimeter
and when equilibrium was reached the temperature of the calorimeter was
recorded. A dried and screened sample (8 to 16 mesh) of carbon was
weighed to the nearest milligram and added rapidly to the calorimeter.
The thermometer was used to gently rotate the contents until the maxi-
mum temperature was reached. After recording this temperature the
benzene was filtered for reuse.

The temperature of the carbon was taken prior to its addition
to the calorimeter. This was done by simply placing a tenth degree
thermometer in the carbon for a few minutes before adding the carbon
to the calorimeter. If this differed from the initial benzene tem-
perature by more than 0.3° C a correction was made on the initial
benzene temperature. The temperature rise, Tr, was obtained by sub-
tracting the initial temperature from the final temperature. (See
Appendix A.)

Using this corrected temperature rise, T_r, the known heat capacity of the calorimeter, H, and the weight of carbon used, m, the corresponding heat of wetting, Q_x, of the carbon for benzene in calories per gram is given by the formula,

$$Q_x = (T_r/m)(H + 18.019 + .17m)$$

for a temperature of 26° C. The number 18.019 is derived from the weight and specific heat of the benzene, and the .17 is the approximate specific heat of the carbon.

Service Time Test

The service time test is a dynamic adsorption method which is designed to simulate the industrial process. A known mixture of gases is passed continuously at a constant rate through a definite volume of activated carbon. The depth of the carbon bed is specified, along with the flow rate per square centimeter of cross-sectional area of the bed. The time required for the adsorbable vapors to break through the bed and appear in the exit gas stream is recorded as the service time.

The apparatus used is shown in figure 3. Air is first passed through a rotameter at a rate of 650 ml. per minute. The calibration for the rotameter is shown in figure 4. From the rotameter the air passes through a concentrated sulphuric acid wash tower where any moisture present is removed. Next the dry air is passed through a carbon tetrachloride saturation tower which is maintained at 0° C by an ice bath. The carbon tetrachloride saturated air is then passed through a copper coil submerged in a 25° C constant temperature bath. After the coil there is a three-way stopcock which either passes the vapor-laden air out to the vent or to a U-tube containing the carbon sample.
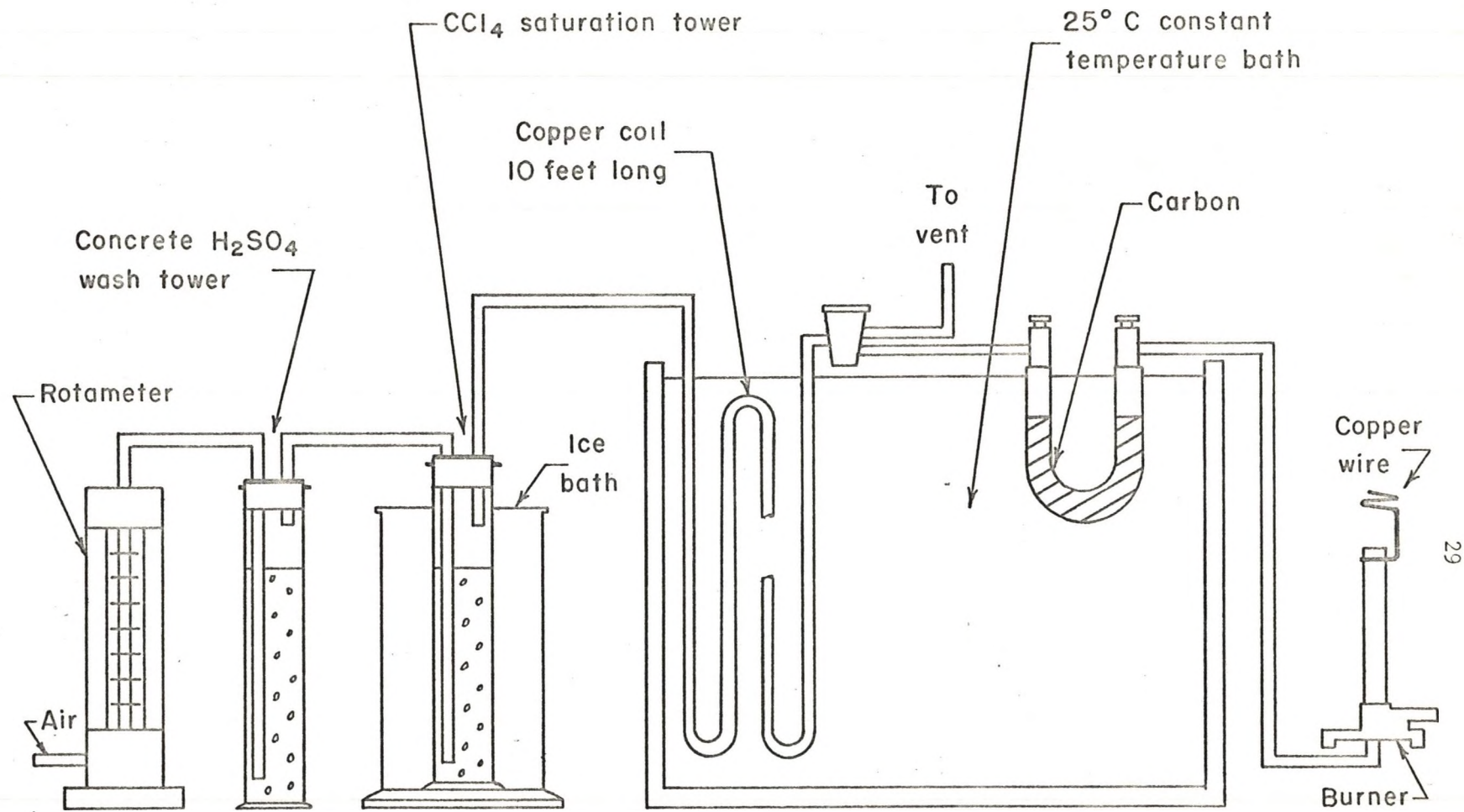
FIG 3. Apparatus for determination of service times.

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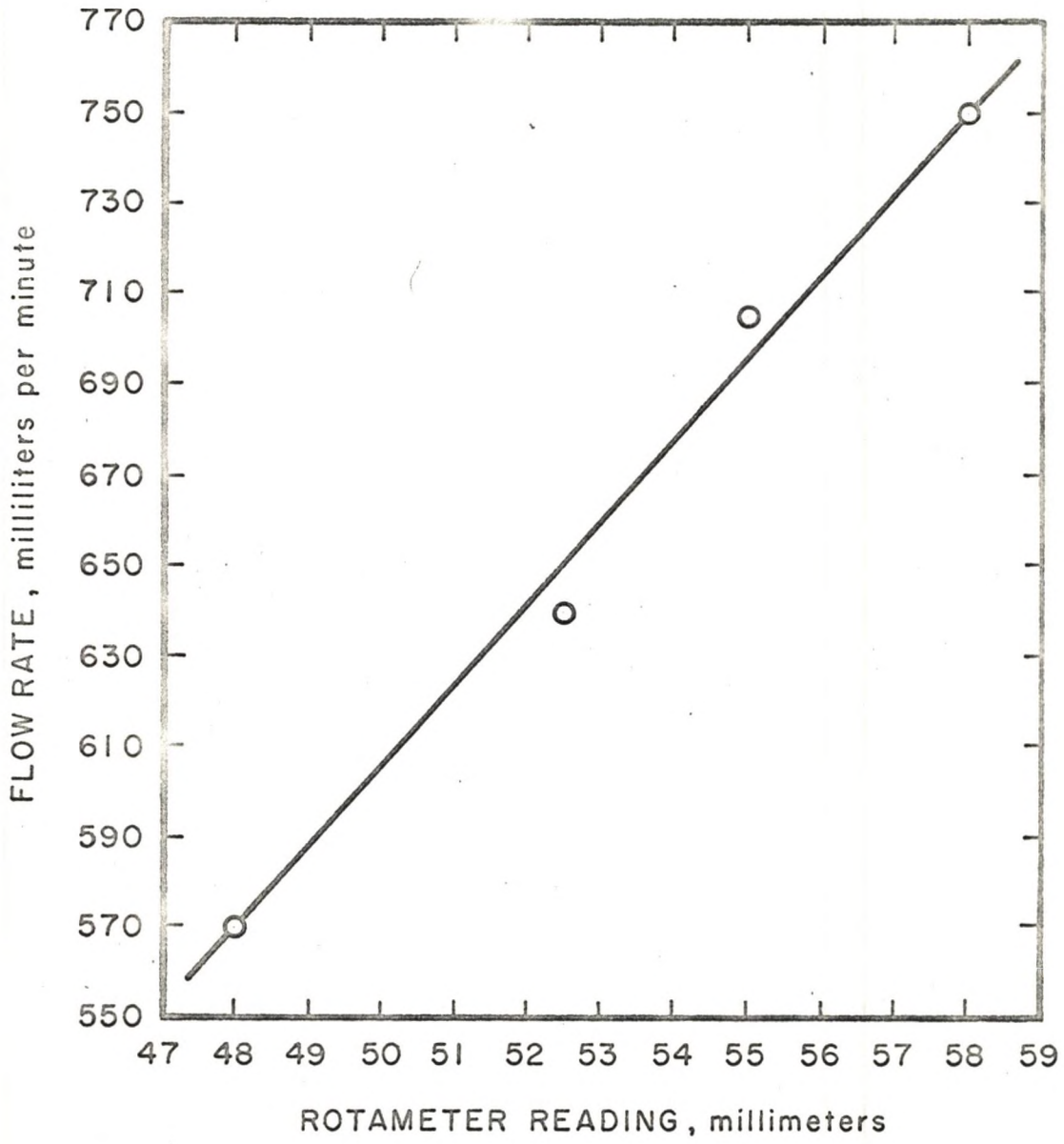
FIG 4. Rotameter calibration.

The exit gas from the U-tube is passed through a bunsen burner. A
copper coil is attached to the bunsen burner in such a manner that it
is in direct contact with the flame and about two cm. above the top of
the burner. When the gas was passed through the U-tube the carbon re-
moved most of the carbon tetrachloride for some time. When the carbon
tetrachloride finally breaks through the bed a green color appears when
the carbon tetrachloride makes contact with the coil. The first appear-
ance of a greenish tinge in the burner flame is taken as the break through
point. It is interesting to note a procedure developed by Coull, Engel
and Miller (7) in which the concentration of the exit stream was monitored
by a thermal conductivity cell and potentiometer. This allowed them to
continue the adsorption until the sample was saturated (would adsorb no
more). Tests conducted in this manner give a better indication of the
characteristics of a carbon.

The procedure used for the service time test is a modification
by Stone and Clinton (37) of the methods of Chaney and Fieldner. The
sample was screened and the 8 to 16 mesh portion was dried for three to
four hours at 140° C. After cooling, sufficient carbon was added to the
1.3 cm. I. D. (inside diameter) U-tube to give a tamped column length
of fifteen cm. The contents of the tube were weighed to the nearest
milligram and then retamped into the U-tube. The U-tube was placed in
the water bath and sufficient time was allowed for it to reach thermal
equilibrium.

The air flow rate of 650 ml. per minute was established through
the apparatus while the vapor-laden air was vented. The stopcock was
then turned so that the vapor-laden air would pass through the sample.

The initial time was noted and any adjustments to the flow rate were made. The break through point was noted and the elapse time was recorded as the accelerated carbon tetrachloride service time, although in this work it was called the service time.

It is very important that the temperature of the carbon tetrachloride in the ice bath be maintained at 0° C. The following table shows how the vapor pressure of carbon tetrachloride increases markedly for a slight temperature increase.

Temperature °C	Vapor Pressure mm. Hg
0	32.45
2	36.40
5	43.60

Precautions must also be taken in order to ensure a constant air-flow rate, since small deviations will introduce relatively large errors.

Methylene Blue Test

The methylene blue decolorization test generally requires the determination of an adsorption isotherm if an accurate comparison of activated carbons is to be made. In order to determine the isotherm equal volumes of a liquid containing an adsorbable impurity are contacted with different weights of an activated carbon. The distribution of the impurity between the adsorbed and solution phases will depend on the amounts of active carbon present. The graphical relationship between the amount of impurity in the solution phase at equilibrium and that in the adsorbed phase is termed an adsorption isotherm. The empirical Freundlich equation can be used to interpret these results.

$$X/m = k\ c^{(1/n)}$$

where,

m equals weight of carbon.

x equals amount of impurity removed.

x/m equals the concentration in the adsorbed state.

or the amount of color adsorbed per unit weight.

of carbon.

c equals the equilibrium concentration in solution.

after adsorption.

1/n and k are constants.

A linear relationship is obtained from this equation by taking
logs of both sides: $\log x/m = \log k + 1/n \log c$. When x/m is plotted
against c on log-log paper a straight line should be obtained. The
Freundlich equation will generally yield linear isotherms if the solu-
tions are dilute and the concentration range is limited (30).

Several factors must be considered when selecting the experi-
mental conditions. For the methylene blue tests Hassler (19) recommends
a 0.80 gram per liter solution of methylene blue. The suggested carbon
dosage given by Hassler was 0.15 to 0.50 grams per 100 ml. of the test
solution. Fornwalt and Hutchins (9) suggest pulverizing the granular
carbons so that everything passes through 325 mesh screen. They also
recommend using at least one hour contact time to allow the solution to
reach equilibrium.

A preliminary experiment was performed in order to determine
what length of contact time ensured a reasonable approach to equilibrium.
In this experiment fixed volumes of the methylene blue solution were
contacted with a fixed weight of carbon for one, two, three and four hour

periods. The per cent decrease in concentration was then plotted as a function of time (See figure 5). After examining the results and considering the amount of extra equipment which would be necessary for experimenting with the longer contact times it was decided that a one hour contact time was sufficient.

The effect of pH must be considered in liquid adsorption tests. The pH in adsorption systems can vary for two reasons:

1. Dissolution of inorganic constituents in the active carbon.
2. Preferential adsorption of basic or acid molecules from the solution.

Therefore, pH measurements were made on all samples before they were filtered. It should be noted that the pH does not have a pronounced effect on the color of methylene blue solutions.

A Beckman spectrophotometer was used to analyze the equilibrium concentrations of the solutions. Readings were taken at two wavelengths where the methylene blue absorbance was high and where the impurity (filter aid) adsorbance was low (28). The two wavelengths selected were 550 mμ. and 600 mμ. The calibration curves are shown in figures 6 and 7.

Procedure

1. The sample was pulverized with a mortar and pestle until a large portion of the sample would pass through a 100 mesh screen. The ground sample was oven dried for approximately three hours at 140° C.
2. Four different weights of carbon were placed in 600 ml. beakers.
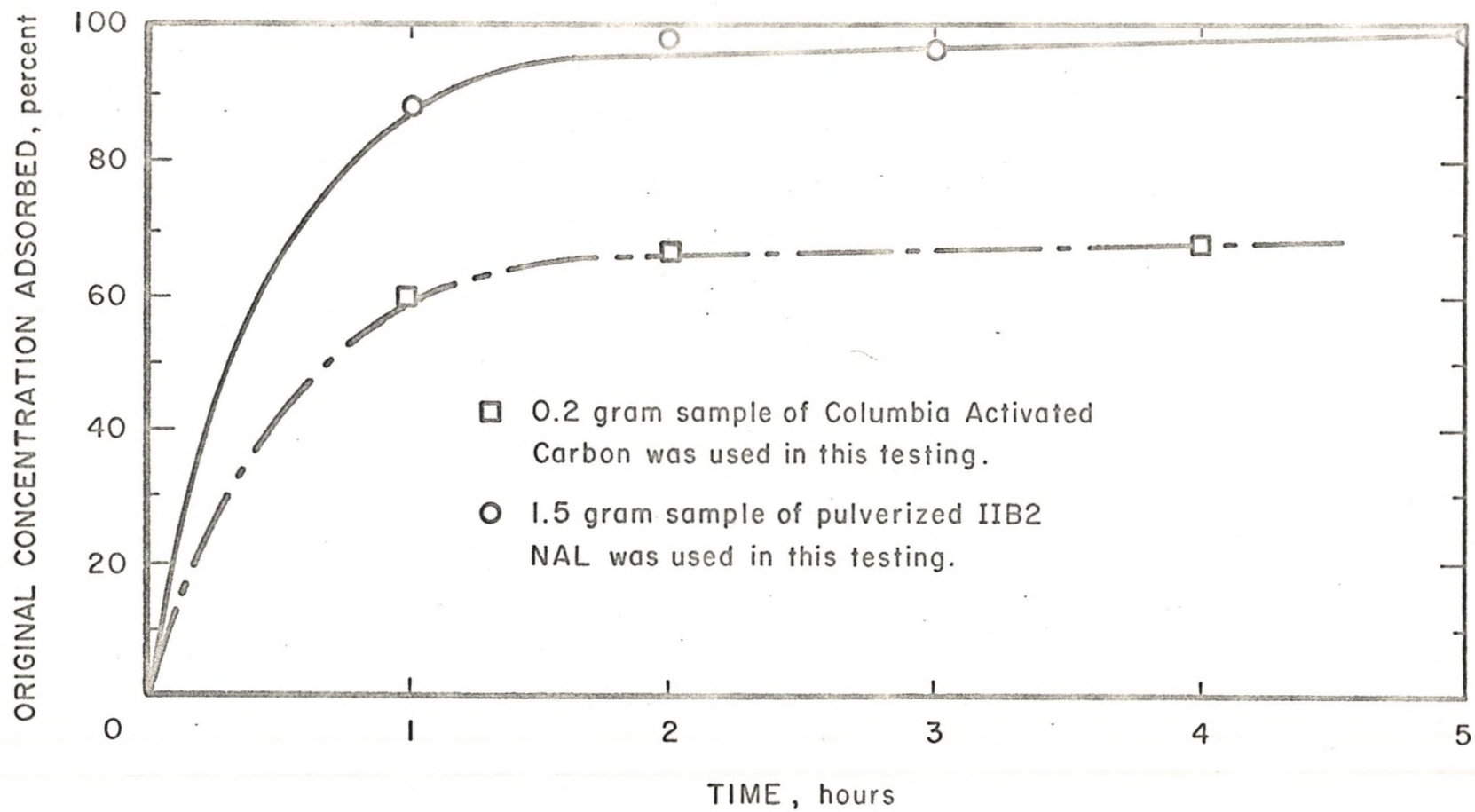
FIG 5. Plot of Methylene Blue Adsorption of Columbia A.C. and sample IIB2 versus time.

The y-axis is labeled "ORIGINAL CONCENTRATION ADSORBED, percent" with values 20, 40, 60, 80, 100.

The x-axis is labeled "TIME, hours" with values 0, 1, 2, 3, 4, 5.

Legend:
□ 0.2 gram sample of Columbia Activated Carbon was used in this testing.

O 1.5 gram sample of pulverized IIB2 NAL was used in this testing.
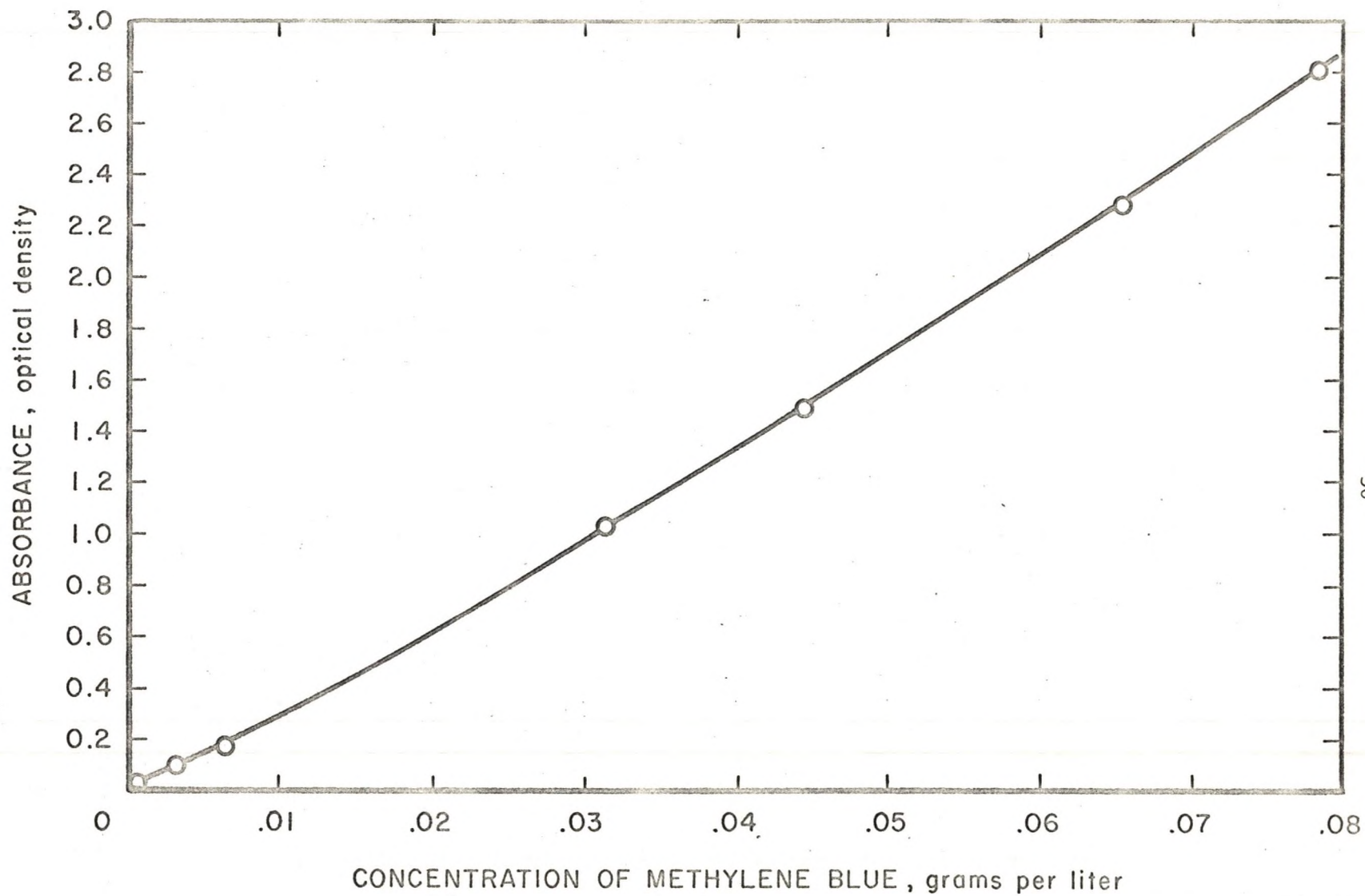
FIG 6. 550 millimicrons absorbance versus concentration.
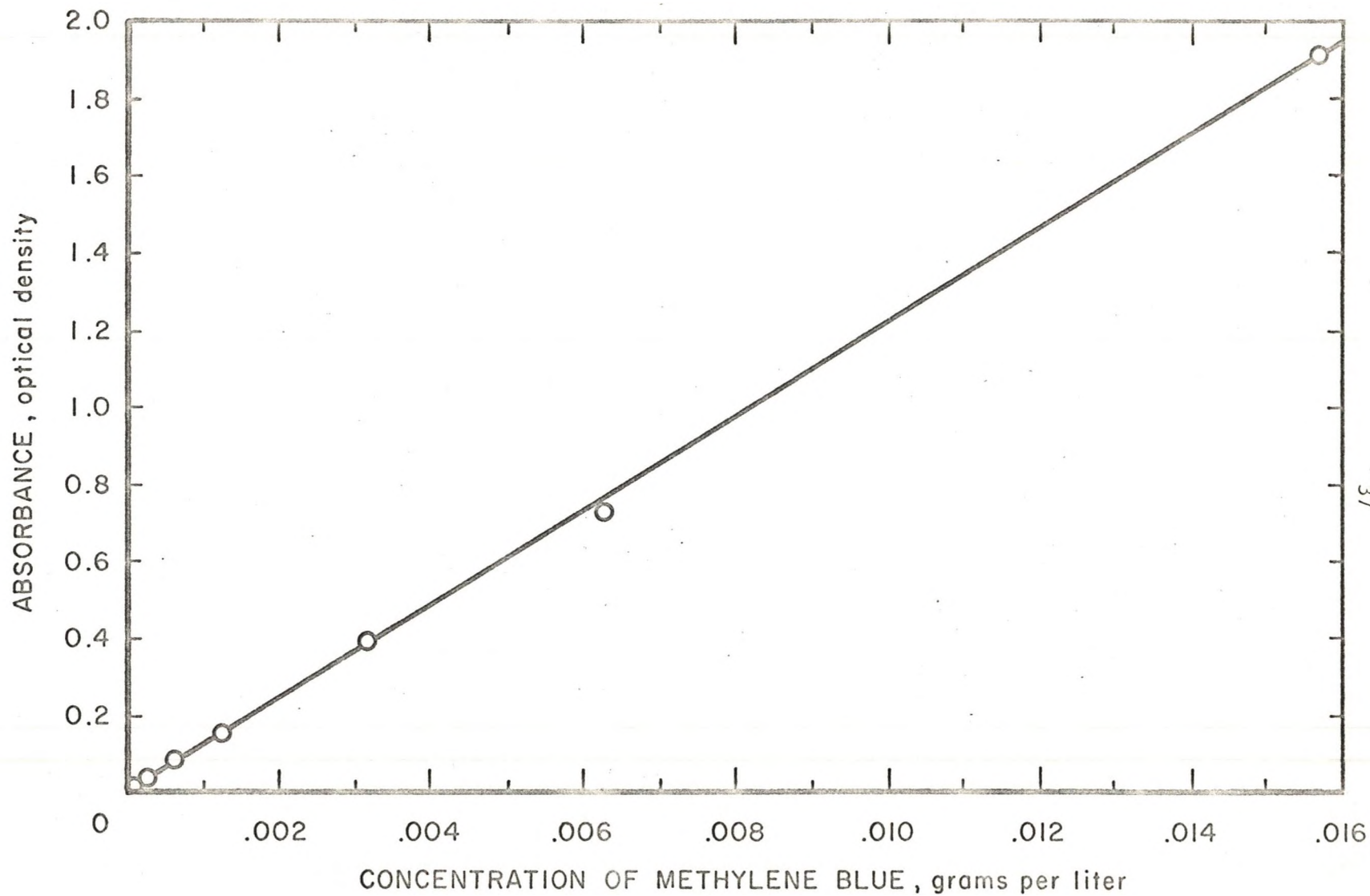
FIG 7. 600 millimicrons absorbance versus concentration.

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3. Every fifteen minutes 200 ml. of methylene blue and 1/3 gram of filter aid were added to one of the beakers and it was placed on the stirrer.

4. After one hour had elapsed the pH was taken. The contents of the beaker were then filtered and then the filtrate was analyzed with a Beckman spectrophotometer.

See appendix B for further notes on the methylene blue test.

Acid Leaching Procedure

Many carbons produced today are acid leached after the activation process to remove soluble inorganic constituents from the carbon. Acid leaching is also used to adjust the pH of the carbon so that it will be suitable for certain applications. It is felt that acid leaching would be necessary for active carbons produced from leonardite since it has a high content of sulphur, which would be objectionable in many applications. Also, it is necessary to remove any of the chemical additives from the final carbon structure, since these additives would most likely affect the carbon's adsorptive power.

The acid leaching process consisted of adding concentrated hydrochloric acid and water to the activated carbon granules. Water was added in a sufficient amount to cover the granules and enough acid was added to make the mixture definitely acidic. The mixture was allowed to sit until the evolution of gases stopped. In most cases this was at least 24 to 36 hours. In the rest of this work the symbols or initials AL will stand for acid leached, and the initials NAL will stand for not acid leached.

CHAPTER VII

RESULTS

A preliminary experiment was performed to determine the optimal activation conditions for 6 to 16 mesh raw leonardite char. The optimal conditions were then used in the subsequent activation of the modified leonardite granules. The author realizes that the optimal conditions as determined for raw leonardite char are most likely not the optimal conditions for the activation of the other leonardite granules, but it would be an impossibility to optimize the activation conditions for each differently modified leonardite in the time available.

In this optimizing experiment the activation temperature and the steam rate were varied. The effect of residence time in the activating furnace was not investigated. The results of this experiment indicated that the temperature has a more pronounced effect on the adsorptive power of the carbon than the steam rate. Different optimal conditions existed depending on which test was used to determine the adsorptive power. This is a wholly reasonable situation, however, since it is known that the optimum activation conditions depend to a certain degree on the type of adsorbent. Hassler (20) states that some adsorptive powers, such as for iodine and phenol, develop equally well over a wide range of temperatures, whereas others, such as the decolorization of molasses, may develop within a narrow range of temperatures.

A statistical analysis was used to determine if there was a significant difference in the temperature and steam treatments during activation. The analysis of variance tables are given in Appendix C. A graphical representation of the data for the methylene blue test and for the heat of wetting test are given in figures 8, 9, 10 and 11.

The results of the methylene blue test are given in per cent relative efficiency. The relative efficiency is based on the carbon which was most efficient in removing the methylene blue from the solution. This carbon was the one activated at 950° C with a 296 gram per hour steam rate. The relative efficiency of a carbon is the number of grams of that carbon which are required to reduce the concentration of methylene blue to some standard equilibrium concentration divided by the number of grams of the base carbon which are required to do the same decolorization. In this case it was the number of grams required to reduce the methylene blue concentration from its original concentration of 0.5618 grams per liter to the equilibrium value of 0.300 grams per liter. The complete isotherms for the carbons produced under these nine different conditions were not determined. One gram samples of the carbons were used in this test. The values obtained for the amount the concentration was reduced per gram of carbon (x/m in Freundlich's equation) at the equilibrium concentration were extrapolated a short distance on log-log paper to the 0.300 gram per liter equilibrium concentration. A complete isotherm for one of the nine carbons was determined and the assumption was made that the isotherms of the eight other carbons produced from this common raw material would have essentially the same slope as the one determined. Since the extrapolation distance was short this should be a valid assumption.

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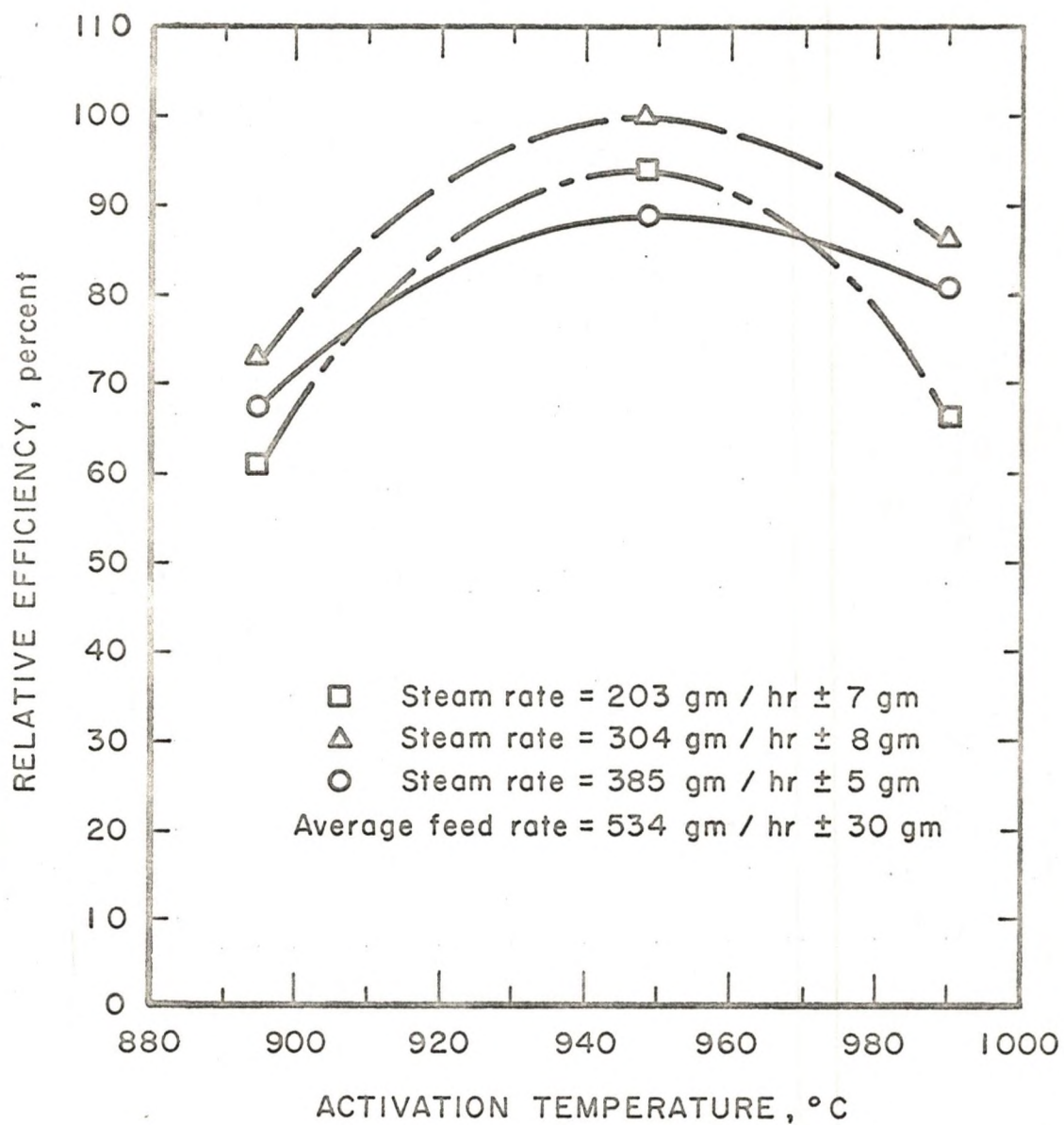
FIG 8. Relative efficiency of methylene blue adsorption of acti-
vated leonardite versus activation temperature for various
steam rates.
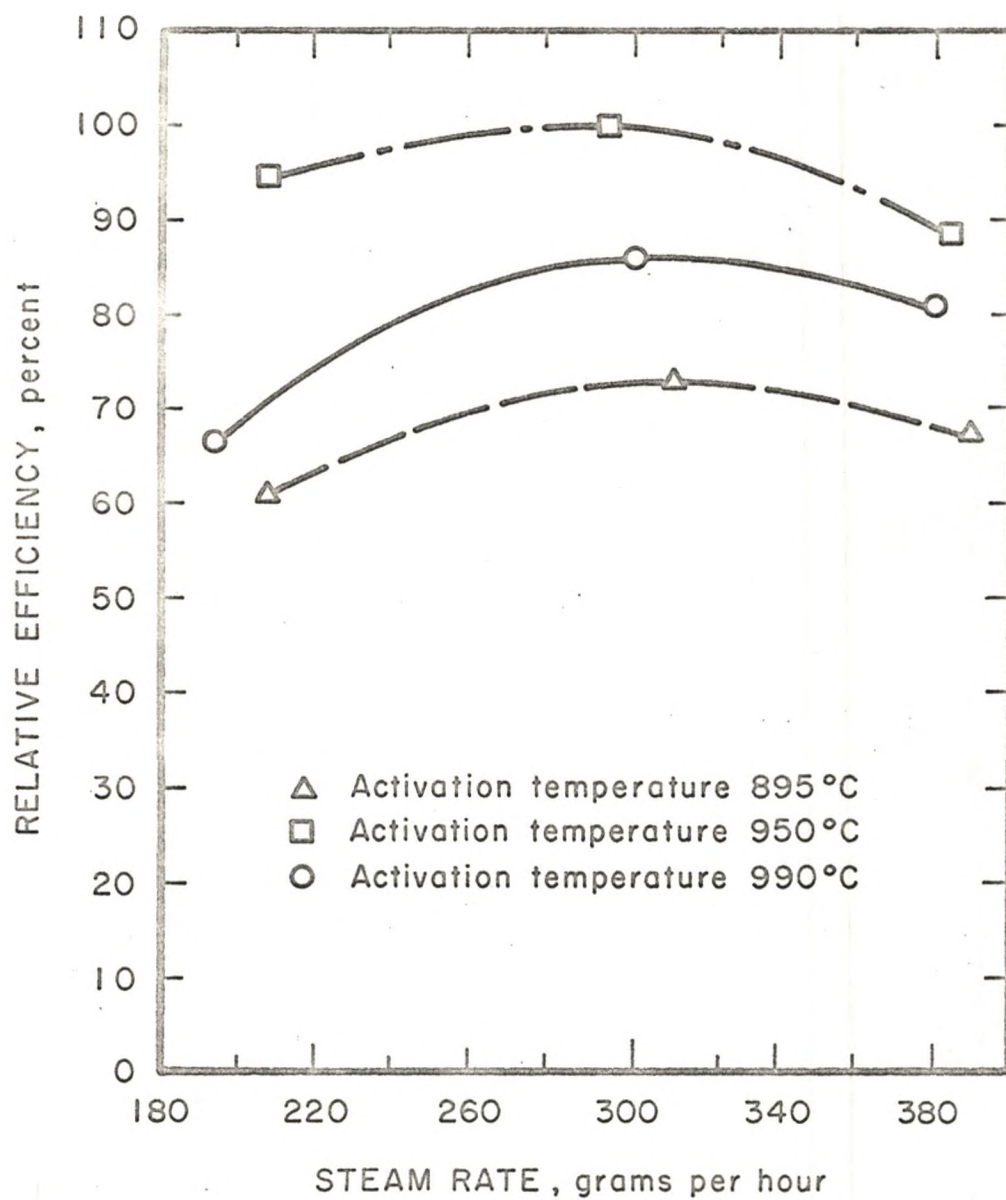
FIG 9. Relative efficiency of activated leonardite for methy-
lene blue adsorption versus steam rate for various
activation temperatures.
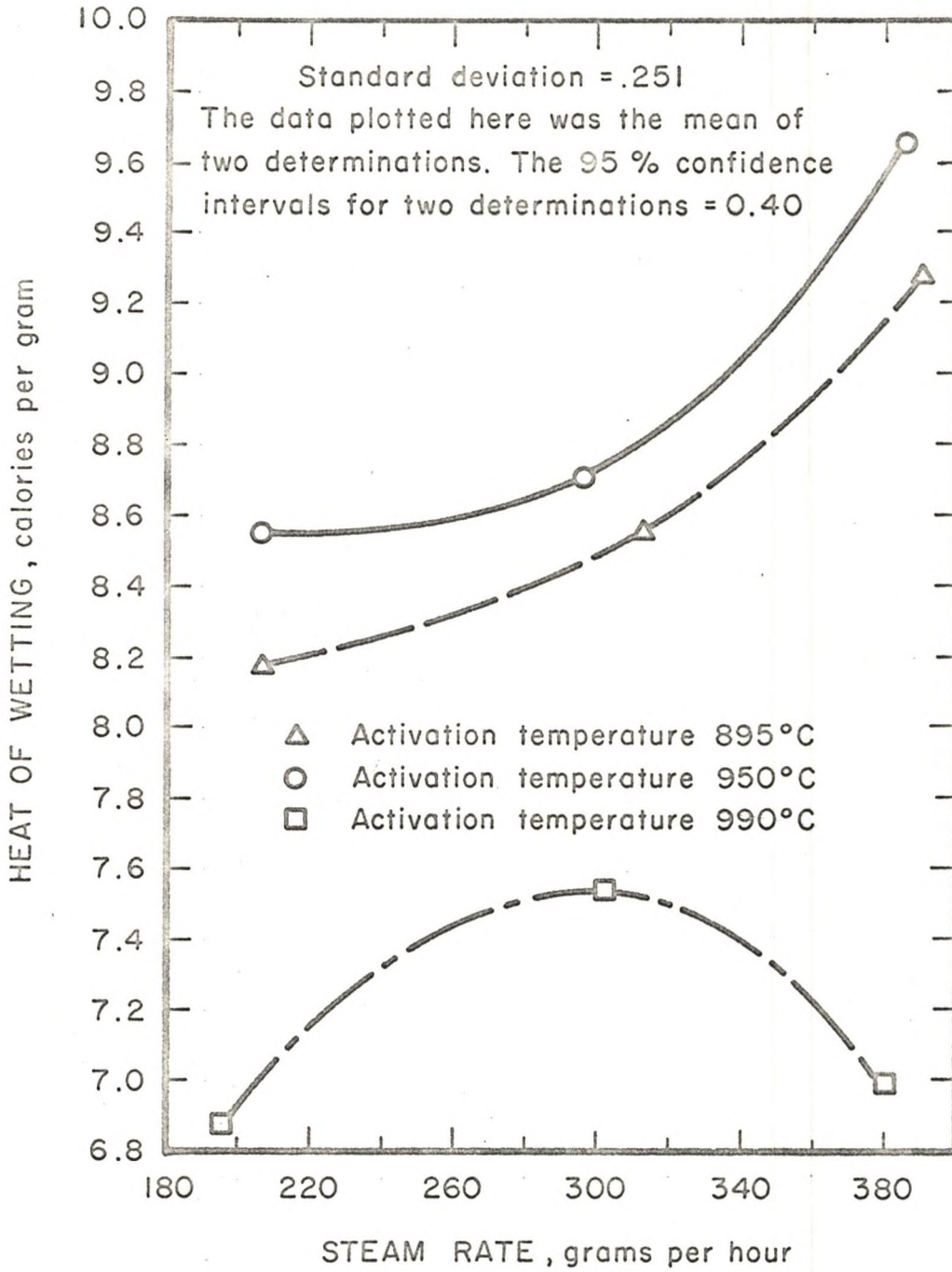
FIG 10. Optimal activation conditions from heat of wetting NAL.
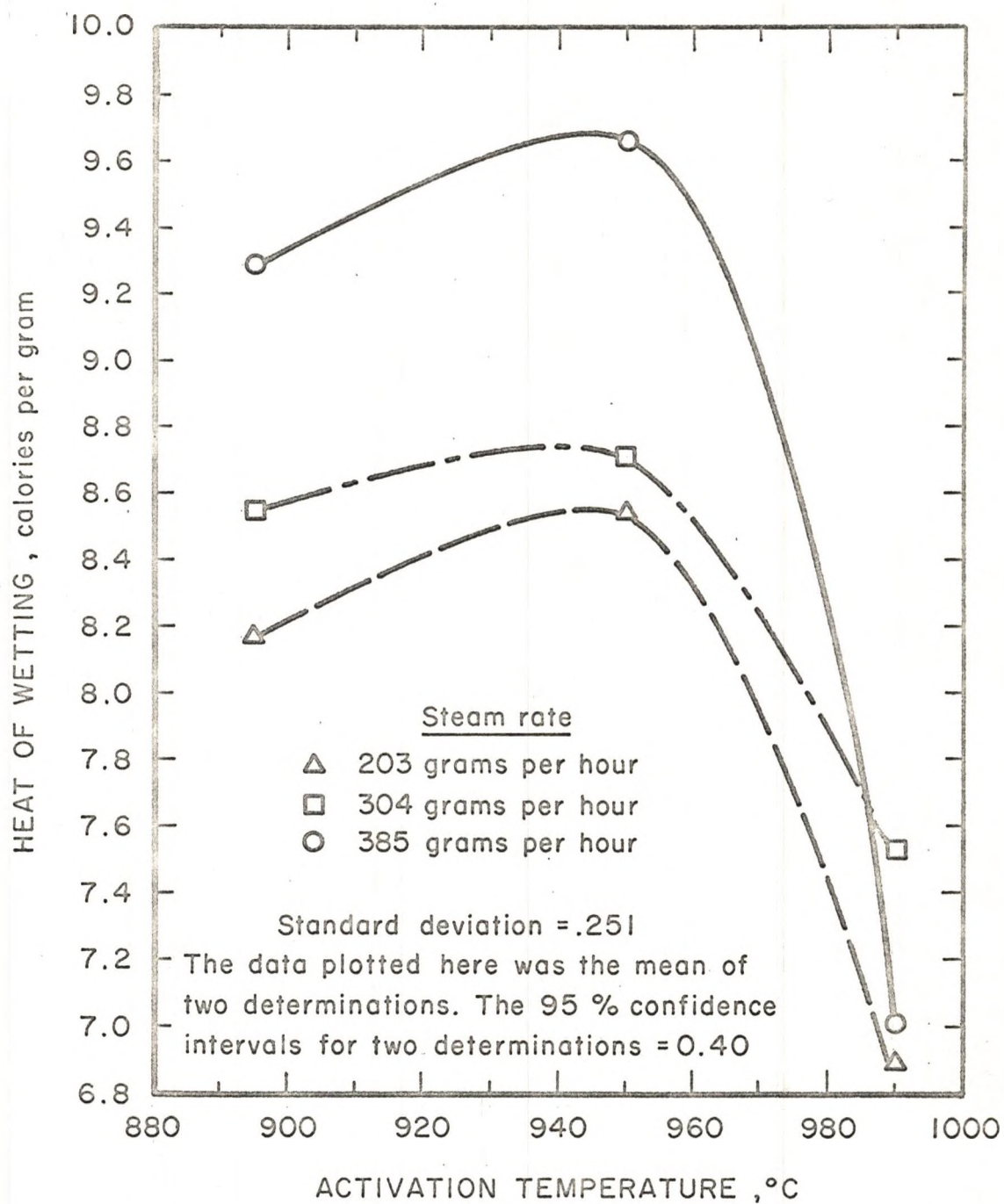
FIG 11. Optimal activation conditions from heat of wetting NAL.

The methylene blue test results indicate that for a carbon feed rate of approximately 534 grams per hour the optimal activation conditions are:

Temperature . . . . . 950° C

Steam rate . . . . . 300 grams per hour

Interaction between the two variables could not be determined in this test since replicates of the data were not taken. The lengthy procedure required for the test limited the number of determinations which could be made. The analysis of variance indicated that for the methylene blue test the temperature effect was significant at the 0.02 level, while the steam effect was significant at the 0.20 level. The standard deviation was 5.1 per cent for this test (Note the results of the test are in per cent).

The results for the optimal activation conditions from the service time test were to a certain degree similar to those of the heat of wetting test, but the residual or error variance of the service time test was so large that no significant difference could be determined for the different values of temperature or steam rate. Replicates for the service time test could not be made because there was not enough of the carbon samples left.

Duplicate determinations were made for the heat of wetting test on the samples that were not acid leached. Since there were duplicates for this test the interaction effect between the two variables was tested and found significant. If the interaction of two variables is significant, it indicates that the effects of the factors are different at different levels of each other and that the individual results should be compared

rather than the means for the different levels of the variables, to find the optimum effect (48). It seems reasonable that an interaction between the two variables does exist since as the temperature changes the rate of reaction will change. When the rate of reaction changes it will cause the effect of the steam to vary at the different levels of temperature.

By using Tukey's (49) method for comparing several means (see Appendix C) it was possible to determine which means were significantly different from the others. The results were that the carbon activated at a temperature of 950 degrees C with a steam rate of 385 grams per hour was significantly better than all the other carbons produced except the carbon activated at 895 degrees C with a 390 gram per hour steam rate. If the optimum conditions do exist in the range of variables investigated, the heat of wetting test indicates that it would be at a temperature between 895° C and 950° C and at a steam rate of 385 grams per hour. Since the optimum is occurring along the edge of the grid studied it would be wise to do more testing before drawing a conclusion from the heat of wetting test. The standard deviation for the heat of wetting test was 0.251 calories per gram. The 95 per cent confidence interval was 0.57 cal. per gram for one determination and 0.40 cal. per gram for two determinations. In view of these two tests the activation conditions used as optimal conditions were those as determined from the methylene blue test.

The tables in Appendix D give the activation data and the test results for the various carbons produced. Freundlich isotherms exhibiting methylene blue decolorization power are shown in figures 12 and 13. Isotherms are a very compact way of expressing the adsorptive
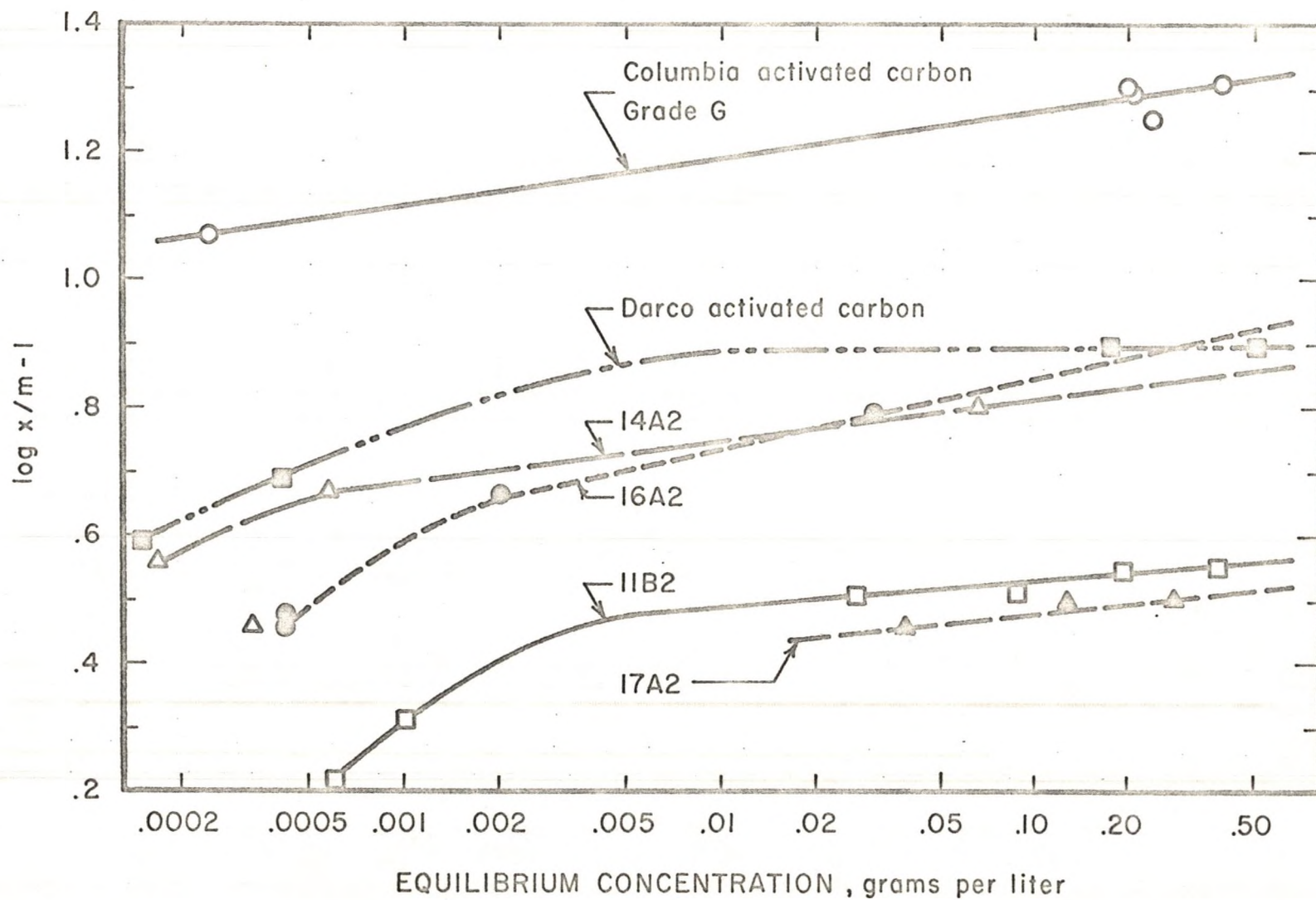
FIG 12. Methylene blue decolorization isotherms.
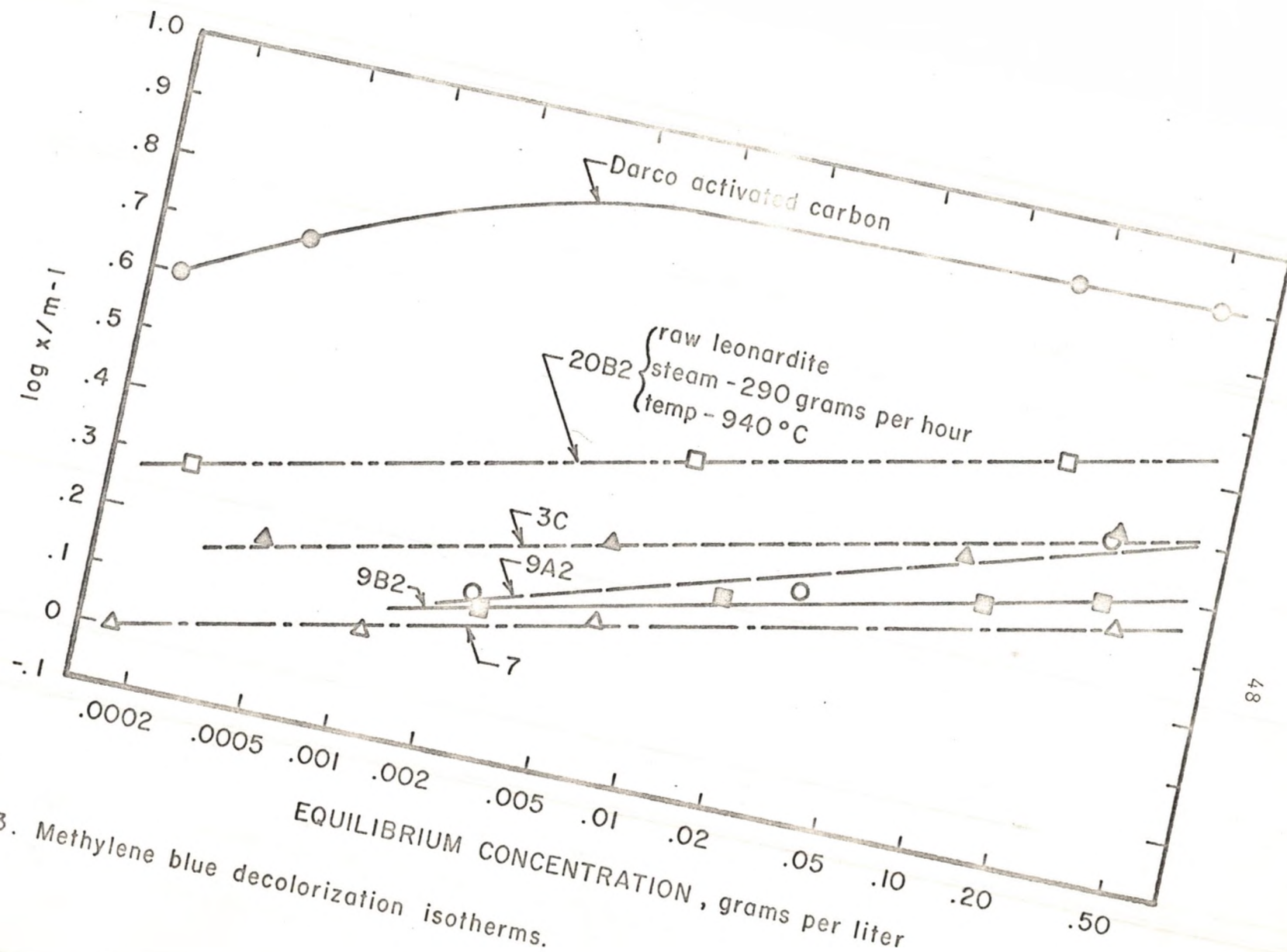
FIG 13. Methylene blue decolorization isotherms.

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characteristics of a carbon in a specified system. When an isotherm is
at a high level and only has a slight slope, this means that the adsorp-
tion is large throughout the entire range of concentrations studied. If
the isotherm is at a low level with a slight slope it indicates that the
carbon adsorbs proportionately less of the impurity throughout the range
studied. Similarly, carbons which have steep slopes will adsorb well
in the region where they are at a high level, and will be poor adsorbers
where they are at a low level. Thus the performance of two carbons for
the same application can be conveniently compared by examination of the
isotherms obtained under similar conditions. The relative efficiency in
per cent of two carbons for decolorizing to some given concentration is
simply the ratio of the x/m values for the respective carbons times 100.
By studying the isotherms for the various carbons we can see that
Columbia activated carbon grade G is superior to all the rest of the
carbons. For decolorizing a 0.59 gram per liter solution of methylene
blue to 0.20 gram per liter Darco would be approximately 69 per cent
as efficient as Columbia grade G. The best carbons prepared from
leonardite for methylene blue decolorization were the pelletized car-
bons. Their sample code numbers range from 12 to 17. It is apparent
from the isotherms that carbons 14 and 16 are almost equivalent to
Darco in decolorizing power. (Note that all samples used in the
methylene blue test were acid leached.) Carbon number 14 had zinc
chloride as an additive and carbon number 16 was 18 per cent leonard-
ite and 20 per cent pitch.

The various carbons were also compared by means of the heat
of wetting test. Under similar conditions the following results were
obtained as shown in Table 4.

TABLE 4

RESULTS FOR ACTIVATED CARBONS PREPARED FROM COLLOIDAL SUSPENSIONS

Alkali Used	Lb. Additive per lb. Leonardite		Heat of Wetting in calories per gram	Description of Granule
NaOH	0.02	$Ca(OH)_2$	4.28	Medium hardness. Somewhat easy to powder.
NaOH	0.026	$Ca(OH)_2$	4.15	Medium hardness. Somewhat easy to powder.
NH_3	0.10	H_3PO_4	7.14	Hard. Not easily powdered.
NH_3	0.015	$CaCO_3$	6.58	Fairly hard. Does not powder.
NH_3 *	0.02	$Ca(OH)_2$	10.09	Soft. Powdery when crushed.
None	5/16 mesh leon.		8.70	Fairly hard but has a tendency to powder.

*This material was activated at a slower feed rate.

The results indicate that raw leonardite when carbonized and activated gives equal if not better adsorptive power to those carbons prepared using a colloidal suspension and additives. Of course, when raw leonardite char is activated very little can be done to improve the physical characteristics of the granules. The heat of wetting of Columbia activated carbon grade G was 24.33 calories per gram, which is considerable higher than any of the activated carbons made from leonardite. The heat of wetting of Darco was 11.64 calories per gram.

For the pelletized carbons the following results were obtained as shown in Table 5.

TABLE 5

RESULTS FOR ACTIVATED CARBONS PREPARED BY PELLETIZING LEONARDITE

Lb. additive per lb. leonardite	Heating of Wetting in Calories per gram		Per Cent Ash	
	NAL	AL	NAL	AL
none	9.27	12.62	48.18	26.04
0.0027 H_3PO_4	10.70	9.57	42.80	28.77
0.0028 $ZnCl_2$	10.90	14.29	45.47	20.59
0.10 Pitch	9.73		40.36	
0.20 Pitch	9.94	10.44	38.15	20.24
0.10 Pitch Wetting Agent	8.90		36.87	23.33

The pelletized carbons showed marked improvement in adsorptive properties over carbons prepared by the previous methods. It is interesting to note that in both experiments when H_3PO_4 was the additive a lower heat of wetting was obtained for the acid leached samples. In both cases, pelletized and colloidal precipitation, the acid leaching reduced the per cent ash by 11 and 14 per cent respectively. Apparently some of the active sites for adsorption were either destroyed during the acid leaching or filled as the result of acid leaching. Even though the adsorptive power of the pelletized leonardite was greater, they had a serious drawback due to the weakness of the pellets. When the pellets were crushed they broke down into a fine powder.

The results indicate that zinc chloride enhances the adsorptive power of the activated carbon, especially if the carbon is acid leached after the activation step. It is also evident that phosphoric acid did not improve the adsorptive properties, and that using pitch as an additive did not improve the pellet strength.

CHAPTER VIII

RECOMMENDATIONS FOR FUTURE EXPERIMENTATION

One of the major difficulties in producing an active carbon by the methods attempted in this work was in obtaining granules with sufficient strength and abrasion resistance. Fieldner, Hall, and Galloway (42) did extensive work on the production of activated carbon from various coals, and in their work they obtained satisfactory granules with lignite and pitch mixtures which were briquetted. It would be interesting to know if satisfactory results would be obtained if this method of preparation was applied to leonardite.

In their work they mention that for coals containing large quantities of volatile matter a preliminary carbonization step before briquetting usually gives more satisfactory granules after carbonization and crushing. Chemical additives such as zinc chloride or calcium hydroxide could be added before briquetting to possible increase the adsorptive properties of the granules, since these additives increased the adsorptive properties of the granules produced in this work. Fieldner, Hall and Galloway (43) report that the amount of pitch required for briquetting varies from 25 to 40 per cent depending on the nature and fineness of the raw material. They also state that it is desirable to use pitch which is free from sulphur, low in melting point, and low in free ash content. Jacque C. Morrel has several patents concerning the

production of structural activated carbons using pitch binders and com-
pression molding (U. S. Patents 2,008,146; 2,008,147; and 2,008,144).

Part of the difficulty in this work of producing a carbon with
good structural strength is undoubtably due to the high content of vola-
tile matter in the leonardite. On a moisture free basis the proximate
analysis of the leonardite used in this study was as follows:

> volatile matter . . 44.31%
>
> fixed carbon . . . 42.38%
>
> ash 13.41%

Evidently, after carbonization, where a greater portion of the 44.31
per cent of the volatile matter is removed, the integrity of the carbon
structure is partially destroyed resulting in poor structural strength.
Of course, it would not be possible to partially carbonize the leonardite
and then hope to prepare a colloidal suspension from it since its chemi-
cal nature would have been altered. Therefore, in future work involving
the activation of leonardite a briquetting or molding technique on
partially carbonized leonardite using suitable binders is recommended.

Also, in future work involving activation of leonardite (or any
other material) with a rotary kiln the effect of residence time in the
kiln should be investigated. It is possible that residence time in the
kiln has considerable influence on the adsorptive properties of the final
product. In this work the activating agent, steam, was passed counter-
currently to the carbon. Since the two principal reactions which occur
in the process of activation with steam occur almost instantly (21), it
is possible that the steam is consumed almost exclusively at the end of
the reactor where it enters. Of course, the diffusion rate of the steam

into the granule is not known and it should be considered too. If the
rate of diffusion is negligible, then much of the length of the reactor
is not being utilized. Hassler (22) states that some direct-fired kilns
have been designed to permit the introduction of oxidizing gases at
several points to maintain a better activation environment throughout
the length of the reactor.

CHAPTER IX

SUMMARY

The purpose of this research was to determine the feasibility of producing granular activated carbon from leonardite by modifying the structure, carbonizing and activating. Two methods were used to modify the leonardite structure hopefully to increase the carbon activity and to obtain desirable structural characteristics. The two methods used were:

(1) Colloidal preparation. A colloidal suspension of leonardite was prepared using sodium hydroxide or ammonium hydroxide. Three chemical additives, calcium hydroxide, calcium carbonate, and phosphoric acid were added to the colloidal suspension to precipitate the suspension into hard dense granules and/or to aid in the activation of the granules.

(2) Pelletized granules. Powdered leonardite was pelletized in a rotary drum using a five per cent solution of sodium hydroxide. Chemicals were again added to increase the granule strength and to aid in the activation. The additives used were pitch, phosphoric acid, and zinc chloride.

After the granules had dried they were carbonized at 560° C for approximately one hour. The carbonized granules were then activated in

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a rotary tube furnace using steam as an activating agent. A preliminary
experiment was performed at a constant feed rate using leonardite char
to determine the optimal steam rate and temperature for activation. The
results of this test indicated that for a feed rate of 534 grams per hour
the optimal activation conditions for methylene blue adsorption were:

Temperature . . . . . . 950° C

Steam Rate . . . . . . 300 grams per hour

This test revealed that the temperature effect on activation was consid-
erably greater than the effect of the steam rate. The optimal activa-
tion conditions as determined from the heat of wetting test was incon-
clusive, but it did indicate that there was an interaction between the
temperature and the steam rate, that a temperature between 895 and 950
degrees C was desirable, and that the steam rate should be at least 380
grams per hour. Further work would be required to determine the optimal
activation conditions from this test. The optimal activation conditions
determined from the methylene blue test were used in the activation of
the prepared granules.

The results of the methylene blue test and the heat of wetting
test indicated that raw leonardite char when activated has more adsorp-
tive capacity than those carbons prepared using colloidal suspensions
and additives. These tests also indicated that generally the pelletized
carbons had greater adsorptive capacity than the activated leonardite
char. Two of the pelletized carbons were approximately equivalent to
Darco grade S-51 for methylene blue adsorption. One of these had a zinc
chloride additive, while the other was twenty per cent pitch. The
pelletized carbon with zinc chloride additive had a heat of wetting of

14.29 calories per gram (acid leached), compared to the heat of wetting value of 24.33 calories per gram for Columbia grade G. The heat of wetting of Darco grade S-51 was 11.64 calories per gram.

The abrasion resistance of the pelletized carbons was poor. The abrasion resistance of the colloidally prepared carbons was somewhat better than this although they were not nearly as hard as Columbia grade G. The abrasion resistance of the activated leonardite char was approximately equivalent to that of the colloidally prepared carbons.

Heat of Wetting Test

Correction for Initial Carbon Temperature

The correction on the initial benzene temperature to account for the heat gained or lost due to a different carbon temperature was made by making a simple heat balance. When the carbon is at a higher temperature than the benzene the calculation is made as follows for a temperature of the benzene of approximately 26° C:

Heat lost by carbon = Heat gained by the system

$$(T_d - x)(.17)m = x(21.774)$$

or

$$x = (.17m\ T_d)/(21.774 + .17m)$$

where,

T_d = Difference between carbon temperature and initial benzene temperature.

x = Correction to be added to the initial benzene temperature.

m = Weight of carbon.

For a lower carbon temperature than the initial benzene temperature the correction is:

$$x = (.17m\ T_d)/(21.774 - .17m).$$

Further Information on the Methylene Blue Test

The structural formula for methylene blue is: (31)

$(CH_3)_2 N$ ... S ... $N(CH_3)_2Cl$
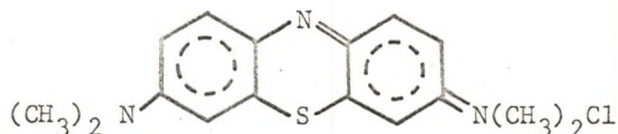
When methylene blue is dissolved in water it undergoes hydrolysis:

$$RCl + H_2O = ROH + HCl$$

In this state the solution contains equilibrium concentrations of hydro-chloric acid, chloride ions, hydrogen ions, methylene blue hydroxide, methylene blue chloride, and dye (R). Because of the many different chemical identities present it is difficult to determine quantitatively the amount adsorbed in each form. Hassler (23) states that small por-tions of carbon sufficient for partial decolorization of the solution cause an increase in the amount of free HCl. The interpretation of this is that at least a portion of the dye (R) is adsorbed as ROH. This up-sets the equilibrium and results in further hydrolysis of the dye which in turn frees more HCl. In most cases the chloride ion is adsorbed in-dependently of the dye color.

DETERMINATION OF OPTIMAL CONDITIONS

FOR ACTIVATION

Methylene Blue Test

Data:

		Temperature		
		895	950	990
Steam	203	61.09	94.41	66.90
Rate	304	73.05	100.00	86.31
	385	67.60	88.91	81.01

Analysis of Variance Table

Source	Sum of Squares	Degrees of Freedom	Mean Square	F calc.
Temp.	1124.5618	2	562.2809	21.5575
Steam	230.1824	2	115.0912	4.4125
Error	104.3312	4	26.0828	
Total	1459.0754	8		

Temp effect significant at .02 level.

Steam rate effect significant at .20 level.

95% Confidence interval = $\pm$ 2.776 $\sqrt{26.08}$ = $\pm$ 14.1.

$s = 5.1.$

DATA FOR OPTIMIZATION OF

ACTIVATION

		Service Time		Heat of Wetting			Methylene Blue (AL)		
Temp	Steam	NAL	AL	NAL	NAL	AL	Equil. Conc.		% Rel Efficiency
990	381	4.20	4.95	6.81	7.20	7.11	0.2712		81.01
990	196	4.72	3.82	6.62	7.15	6.38	0.3148		66.90
990	303	3.93	5.50	7.38	7.68	8.23	0.2566		86.31
950	296	6.25	6.10	8.70	8.73	8.36	0.2132		100.00
950	385	7.60	5.99	9.31	10.01	8.71	0.2492		88.91
950	207	5.57	4.99	8.50	8.59	7.47	0.2306		94.41
895	207	5.35	5.03	8.09	8.26	7.40	0.3445		61.09
895	391	4.95	6.10	9.17	9.39	8.63	0.3233		67.60
895	313	6.45	5.70	8.46	8.65	8.29	0.2928		73.05

HEAT OF WETTING TEST (DUPLICATES) NAL

Analysis of Variance

Source	Sum of Squares	Degrees of Freedom	Mean Square	F calc.	F crit.
Temp.	11.5881	2	5.7941		
Steam	1.8255	2	0.9127		
RxC	1.3493	4	0.3373	5.347*	F.05 (4,9) = 4.72
Subtotal	14.7629	8			
Error	0.5677	9	0.0630		
Total	15.3306	17			

* There is interaction between the steam effect and the temperature effect. Must compare means of each different condition individually.

<u>Tukey's Method</u>   for comparison of several means.

$$\overline{s}\ (\overline{x})^2 = \ s\ (x)^2/k$$

$$\overline{s}\ (\overline{x}) = .1775$$

$$\overline{s}\ (x) = .251$$

$$\frac{WSD*}{\overline{s}\ (\overline{x})} = \ 3.34$$

$$WSD = .59285$$

Temp. °C	Steam gm/hour	Ave. Heat of Wetting calories per gram
950	385	9.66
895	390	9.29
950	296	8.715
895	313	8.555
950	207	8.545
895	207	8.175
990	302	7.53
990	380	7.005
990	196	6.885

*WSD stands for Tukey's "Wholly Significant Difference."

TABLE 6   FORMULATION OF EACH PREPARED CARBON, ACTIVATION CONDITIONS, BULK DENSITY,
AND PER CENT ASH

Sample	Main Contents	Steam Rate ml/hr	Feed Rate gm/hr	Activation Temperature	Bulk Density		Per Cent Ash	
					NAL* gm/ml	AL* gm/ml	NAL	AL
3B	10 lb. Leon., 22.5 lb. H_2O 0.8 lb. NaOH, 0.2 lb. $Ca(OH)_2$	388	540	960	.570	.548	46.34	34.88
3C	10 lb. Leon., 22.5 lb. H_2O 0.8 lb. NaOH, 0.2 lb. $Ca(OH)_2$	297	540	960	.580	.522	45.95	29.70
3F	10 lb. Leon., 22.5 lb. H_2O 0.8 lb. NaOH, 0.2 lb. $Ca(OH)_2$	200	500	960	.612	.569	40.45	27.77
4A	10 lb. Leon., 23.5 lb. H_2O 1.25 lb. NH_3(28%), 0.2 lb. $Ca(OH)_2$	274	292	960	.336		46.73	
4B	10 # leon. 23.5 lb. H_2O 1.25 lb. NH_3(28%), 0.2 lb. $Ca(OH)_2$	272	296	960	.350	.297	41.99	31.72
5	10 lb. leon., 20.5 lb.H_2O 1.9 lb. NH_3(28%), 0.2 lb. $Ca(OH)_2$	Not activated because of the poor quality of the granules.						
6	15 lb. leon., 32.5 lb.H_2O 1.2 lb.NaOH, 0.4 lb.$Ca(OH)_2$	182	514	950	.583	.410	43.98	28.33
7	15 lb. leon., 34 lb. H_2O 0.6 lb.$CaCO_3$, 1.2 lb.NaOH	182	461	950	.638	.551	45.10	26.31
9A	15 lb. leon., 33 lb. H_2O 2.7 lb. NH_3(28%), 0.2 lb. $CaCO_3$	195	454	950	.560	.505	20.04	19.71
9B	15 lb. leon., 33 lb. H_2O 2.7 lb.NH_3(28%), 0.2 lb. $CaCO_3$	340	454	875	.554	.573	30.81	19.81
11A	10 lb. leon., 27 lb. H_2O 1.9 lb.NH_3(28%), .15 lb $CaCO_3$	290	534	945	.544	.490	29.90	31.78

TABLE 6--Continued

Sample	Main Contents	Steam Rate ml/hr	Feed Rate gm/hr	Activation Temperature	Bulk Density		Per Cent Ash	
					NAL* gm/ml	AL* gm/ml	NAL	AL
11B2	10 lb. leon., 27 lb. H_2O 1.9 lb. NH_3(28%), 0.15 lb. $CaCO_3$	348	454	945	.549	.460	34.24	32.21
12A1	Leonardite pelletized with 5% NaOH	313	471	950	.394	.337	48.18	26.04
13A2	Leonardite with 0.27% H_3PO_4 additive, pelletized with 5% NaOH	310	553	950	.446	.418	42.80	28.77
14A2	Leonardite with 0.28% $ZnCl_2$ additive, pelletized with 5% NaOH	308	562	950	.439	.393	45.47	20.59
15A2	900 gm. leon.,100gm pitch pelletized with 5% NaOH	306	512	950	.383	----	40.36	----
16A2	800 gm.leon.,200 gm pitch pelletized with 5% NaOH	308	440	950	.361	.321	38.15	20.24
17A2	900 gm.leon., 100 gm pitch pelletized with H_2O and wetting agent	304	422	950	.348	----	36.87	23.33
23A2	10 lb. leon., 24.9 lb. H_2O 1.9 lb NH_3(28%), 1.2 lb H_3PO_4 (85%)	316	551	950	.608	.542	34.71	23.72
22D2	Leonardite	296	514	950	.537	.495	30.55	20.18
Col.AC Grade B	Coconut shells				.480		3.43	
Darco Grade S-51	Lignite (Texas) Powdered				.401		14.48	

*NAL denotes not acid leached, and AL denotes acid leached.

TABLE 7   RESULTS OF THE HEAT OF WETTING TEST
                AND THE SERVICE TIME TEST
                FOR THE PREPARED CARBONS

Sample	Heating of Wetting in calories per gram		Service Time (NAL) Min.
	NAL	AL	
3B	3.39	5.42	1.45
3C	4.28	5.42	2.91
3F	4.59	4.66	3.05
4A	10.09		7.65
4B	9.54	11.66	7.01
5			
6	4.16	5.94	5.43
7	2.91	4.21	1.40
9A	5.87	6.85	4.71
9B	7.64	7.25	7.42
11A2	6.58	6.81	5.09
11B2	8.24	8.50	5.58
12A	9.27	12.62	9.33
13A	10.71	9.58	10.21
14A	10.90	14.30	9.29
15A	9.73		7.31
16A	9.94	10.44	6.07
17A	8.90		6.44
23A	7.14	6.10	3.72
22D	8.71	8.37	6.25
Col. A.C. Grade G	24.45		27.88
Darco Grade S-51*	11.64		

*powder

TABLE 8   DATA FOR METHYLENE BLUE
ADSORPTION ISOTHERMS

Sample Number	Test Number	Weight of carbon, m, in grams	pH of Solution	Final Conc. of Solution, C, gms./liter	Conc. of Blank, Co, gm./liter
11B2 A.L.	1	0.7814	4.15	0.387	0.6694
	2	2.0155	4.5	0.027	0.6694
	3	3.1531	4.6	0.001	0.6694
	4	3.9440	4.25	0.0006	0.6694
	5	1.1580	4.48	0.193	0.5986
	6	1.5522	4.10	0.087	0.5986
17A2 A.L.	1	1.0237	3.8	0.273	0.5986
	2	1.5014	3.8	0.128	0.5986
	3	2.0060	3.8	0.0377	0.5986
Pulverized Columbia Activated Carbon Grade-G	1	0.5000	4.6	0.00024	0.5986
	2	0.1020	5.0	0.3924	0.5986
	3	0.2040	5.3	0.2040	0.5986
	4	0.2002	5.1	0.2369	0.5986
	5	0.2002	5.2	0.1974	0.5986
20A2 A.L.	1	1.0085	3.7	0.2342	0.5986
	2	4.0060	3.6	0.00017	0.5986
	3	2.0350	3.6	0.0285	0.5986
	4	3.0060	3.6	0.00047	0.5986
20B2 A.L.	1	1.0010	3.8	0.1989	0.5986
	2	2.0150	3.6	0.0115	0.5986
	3	3.0020	3.6	0.00024	0.5986
3C A.L.	1	0.9767	7.0	0.3236	0.5986
	2	3.8755	7.2	0.00048	0.5986
	3	1.9495	7.6	0.1036	0.5986
	4	2.9070	7.9	0.00697	0.5986
7 A.L.	1	1.0037	4.3	0.3812	0.5986
	2	3.9970	4.2	0.0068	0.5986
	3	5.0059	4.2	0.00115	0.5986
	4	6.0039	4.2	0.00017	0.5986
9A2 A.L.	1	1.0250	4.0	0.3126	0.5986
	2	3.0270	3.5	0.03167	0.5986
	3	4.0375	3.6	0.00256	0.5986

TABLE 8--Continued

Sample Number	Test Number	Weight of carbon, m, in grams	pH of Solution	Final Conc. of Solution, C, gms./liter	Conc. of Blank, Co, gm./liter
	1	1.0070	3.6	0.3354	0.5630
9B2	2	2.0040	3.3	0.1354	0.5630
A.L.	3	3.0010	3.1	0.01784	0.5630
	4	4.0020	3.1	0.0028	0.5630
	1	0.9675	5.2	0.0644	0.6694
14A2	2	2.0810	5.8	0.00033	0.6694
A.L.	3	1.2764	5.4	0.00059	0.5986
	4	1.6409	5.5	0.000173	0.5986
	1	1.0228	4.15	0.0305	0.6694
16A2	2	1.2869	4.80	0.00197	0.5986
A.L.	3	1.7156	4.9	0.00042	0.5986
	4	2.0761	5.0	0.00042	0.6694
Darco	1	0.2294	4.0	0.497	0.6694
Grade	2	0.6332	3.8	0.170	0.6694
S-51	3	1.3519	4.1	0.00040	0.6694
	4	1.7006	3.95	0.00016	0.6694
3B A.L.,but	1	0.9970	9.2	0.283	0.5986
less acid was	2	4.0150	9.6	0.00073	0.5986
used than on	3	2.0120	9.4	0.0900	0.5986
the other	4	3.0375	9.4	0.00281	0.5986
samples.					
	1	1.0136	6.0	0.268	0.5986
3F	2	4.0052	6.8	0.00035	0.5986
A.L.	3	3.0035	6.25	0.00395	0.5986
12A1*	1	1.0977	4.8	0.0160	0.6694
A.L.	2	1.4450	5.2	0.00092	0.5986
	3	1.8837	5.3	0.00016	0.5986
13A2*A.L.	1	.9148	5.4	0.0619	0.6694

*Too large of carbon dosage was used in the rest of the tests for these carbons. This caused the final concentration to be too low to determine accurately.

TABLE 9   ACTIVATING CONDITIONS FOR LEONARDITE AND LIGNITE CHAR
AND THE RESULTS OF TESTING

Sample	Contents	Steam Rate	Feed Rate	Activation Temp.	Bulk Density NAL	Bulk Density AL	Per Cent Ash NAL	Per Cent Ash AL	Heat of Wetting NAL	Heat of Wetting AL	Service Time (NAL)
22A	Leonardite 5/16	381 ml/hr	564 gm/hr	990° C	.487	.479	32.99	25.22	7.00 cal/gm	7.11 cal/gm	4.20 min.
22B	Leonardite 5/16	196	564	990	.529	.490	31.81	24.26	6.89	6.38	4.72
22C	Leonardite 5/16	303	564	990	.490	.458	34.12	23.86	7.53	8.23	3.93
22D	Leonardite 5/16	296	514	950	.537	.495	30.55	20.18	8.71	8.37	6.25
22E	Leonardite 5/16	385	514	950	.432	.464	35.06	28.89	9.66	8.71	7.60
22F	Leonardite 5/16	207	514	950	.497	.466	35.74	29.35	8.55	7.47	5.57
22G	Leonardite 5/16	207	524	895	.570	.531	28.78	19.78	8.18	7.40	5.34
22H	Leonardite 5/16	391	524	895	.504	.505	30.34	26.62	9.29	8.63	4.95
22I	Leonardite 5/16	313	524	895	.540	.511	30.87	24.07	8.57	8.29	6.58
21A2	Lignite	449	396	950	.465	.436	29.57	17.34	9.00	9.14	6.51
21B2	Lignite	449	410	950	.511	.464	20.97	13.67	7.64	7.98	5.12
21C2	Lignite	540	410	950	.514	.439	23.87	13.38	7.76	7.57	4.52
20C2	Leonardite 8/16	297	552	950	.532	.488	37.21	21.83	8.45	8.84	7.57
20C4	Leonardite 8/16	179	552	950	.512	.477	33.41	23.57	7.93	8.60	6.04
20A2	Leonardite 5/12 mesh	287	480	875	.568		16.83				
20B2	Leonardite 5/12 mesh	290	542	940	.525		19.80				

TABLE 10 METHYLENE BLUE ADSORPTION DATA FOR DETERMINATION OF OPTIMAL ACTIVATION CONDITIONS FOR LEONARDITE GRANULES   The final concentration of the blank, Co, was 0.5618 gm/liter

Sample Number	pH of Solution	Final Concentration, C, gm/l.	$x=$ C_o-C	$m=$ Weight of Carbon	x/m	Log x/m $\log x/m$	Log x/m at Conc. = 0.30 gm/l.	Calculated $m=$ x/m at 0.30 gm/l.	Calculated $m=\dfrac{x_c *}{(x/m)}$ $_c$ **	Relative Efficiency Compared to 22D2
22A2	3.8	0.2712	0.2906	1.0262	0.2832	.452-1	0.459-1	0.288	0.9027	81.01%
22B2	4.1	0.3148	0.2470	1.0268	0.2406	.3815-1	0.379-1	0.2395	1.0931	66.90%
22C2	4.1	0.2566	0.3052	1.0054	0.3036	.482-1	0.490-1	0.309	0.8473	86.31%
22D2	4.0	0.2132	0.3486	1.0075	0.3460	.539-1	0.554-1	0.358	0.7313	100.00%
22E2	4.2	0.2492	0.3126	0.9987	0.3130	.4955-1	0.503-1	0.3183	0.8225	88.91%
22F2	4.0	0.2306	0.3312	1.0096	0.3281	.5165-1	0.529-1	0.338	0.7746	94.41%
22G2	4.6	0.3445	0.2172	0.9719	0.2235	.3488-1	0.340-1	0.2187	1.1971	61.09%
22H2	---	0.3174	0.2444	1.0140	0.2410	.388-1	0.384-1	0.2420	1.0818	67.60%
22I2	3.8	0.2928	0.2690	1.0332	0.2604	.416-1	0.417-1	0.2615	1.0011	73.05%

$*x_c = C_o-C = 0.5618 - 0.300 = 0.2618$ gm/liter.

$**(x/m)_c$ is the calculated x/m .
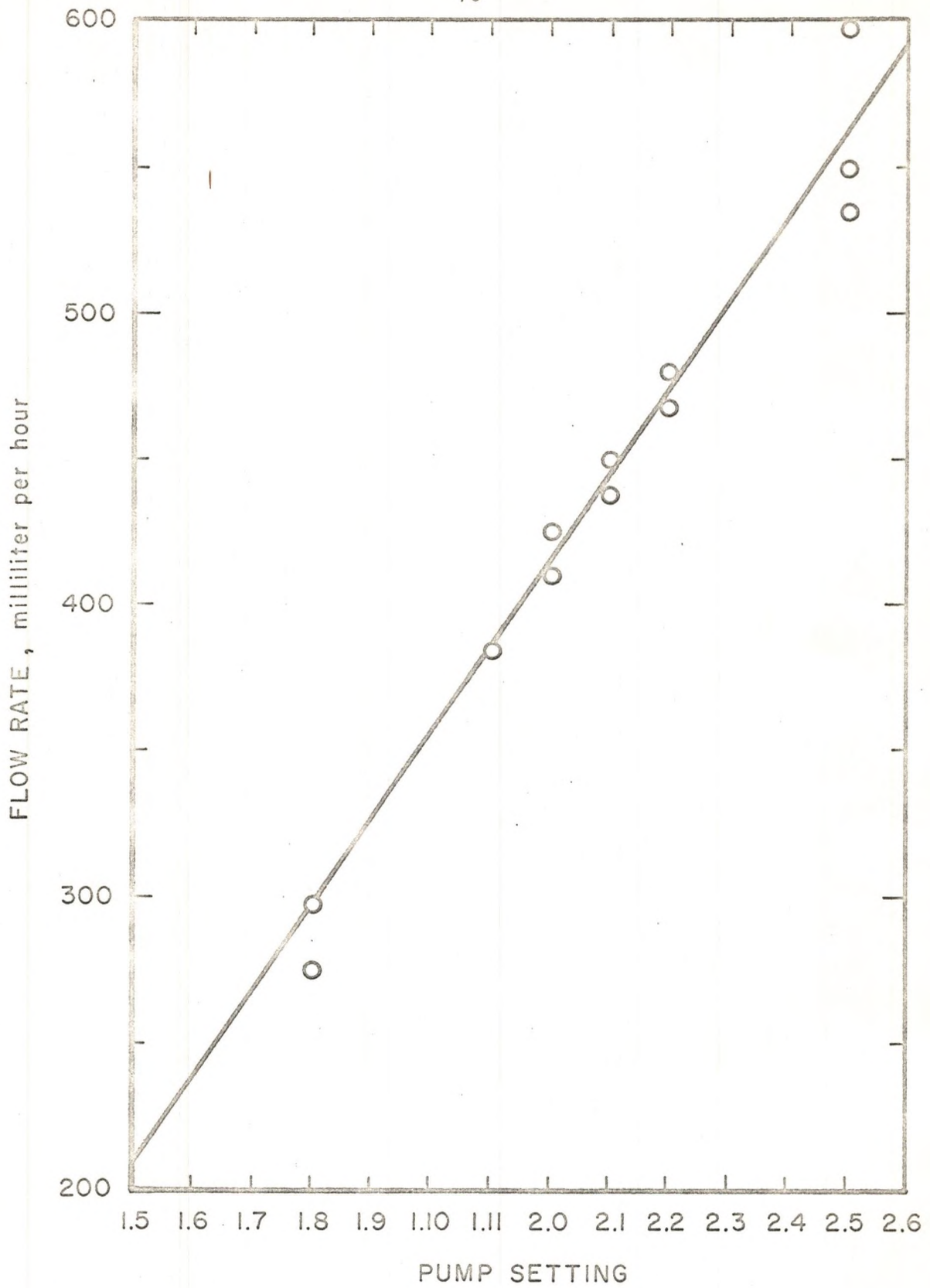
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APPENDIX E

FIG 14. Sigma pump calibration.

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