

THE CHLORINATION OF MIDLOTHIAN COAL TO
PRODUCE A LIQUID ADSORBENT ACTIVE CARBON

by

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A Thesis Submitted To The Graduate Committee
In Partial Fulfillment of the Requirements For

The Degree Of
MASTER OF SCIENCE
in
CHEMICAL ENGINEERING

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Blacksburg, Virginia

1947

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I. INTRODUCTION

Methods for the preparation of active carbons from many kinds of carbonaceous material have been described in the literature. Many processes of activation for many different raw materials are used to obtain active carbons for specific purposes. In general, all of these processes involve a low temperature carbonization of the raw material followed by a slow, controlled oxidation of the carbonized product. A high temperature of carbonization (above 600°C.) results in a product which is not active and cannot be activated.

Any selection of a process or raw material must be based on a knowledge of the ultimate use of the product as well as on economic considerations. Certain physical properties are desirable for certain uses in addition to the general property of being adsorbent to foreign molecules. A gas adsorbent carbon should be dense with a rather small pore size; while liquid adsorbent carbons should be less dense, not friable, easily filterable from solutions, and have a larger pore size than the gas adsorbent type of carbon.

In view of the low yield obtained in any process of activation, a cheap and plentiful raw material would be advantageous. Coal is such a raw material and active carbons have been prepared and used to a limited extent from coals. It has been reported that an initial chlorination of a geologically young coal before

its carbonization results in a high yield of a good active carbon. The existence of large deposits of such a coal in the Piedmont section of Virginia and North Carolina which has not been exploited to any great extent, because it is not suitable as a fuel, seems to warrant a further investigation of this chlorination process with an idea of its possible economic use in the preparation of an active carbon.

The purpose of this investigation is the preparation of a liquid adsorbent active carbon from a high volatile Midlothian coal by a process of chlorination followed by carbonization and steam activation.

II. LITERATURE REVIEW

History. ⁽²⁰⁾ The ability of activated charcoal to remove color from solutions was known as early as the fifteenth century. This property was apparently forgotten, until in 1785 Lowitz used it in the production of tartaric acid crystals, although Scheele and Fontana reported the adsorption of gases by charcoal in 1777. The use of charcoal in the clarification of sugar solutions was first reported in 1794 by Lippman and later by Guillon in 1805. In 1811, Figuier demonstrated that bonechar was superior, in decolorizing properties, to charcoal and this material was put into use in the sugar industry by Derosne in 1812. Originally the char was discarded after use, but soon after its introduction Dumont and Schatten suggested that it could be regenerated and reused. In 1854, Shenstone invented a respirator filled with an active carbon to be worn in hospitals for protection against cholera and other contagious diseases. Early in the nineteenth century Graham, Weppon, Lazowski, Percy, and Rose reported the precipitation of metallic materials on charcoal from solutions. During the first World War the utilization of active carbon in gas masks was begun on a large scale. Since 1918 the unique properties of active carbon have made the material an important industrial with a wide field of application.

Uses of Active Carbon. Activated carbons are widely used commercially and these uses are generally divided into two classes: gas adsorbent types and liquid adsorbent types. Gregory ⁽⁷⁾ has

listed some of the uses of active carbon as follows: solvent recovery, natural gasoline recovery from natural gas, benzene recovery from manufactured gases, removal of odors and harmful gases from air, decolorizing of solutions, catalysts, gas-mask-cannister filling, production of high vacuums, medical remedies, and as a germicide. Many specific uses may be found under the general headings above. Chaney⁽⁴⁾ has pointed out five fields of use for gas adsorbent chars: recovery of gases and solvent vapors in dilute concentrations, purification of gases, catalysis of gas and vapor phase reactions, storage of compressed gases, and evacuation of vessels. A partial list of uses for liquid adsorbent carbons includes the following: clarification of solutions, purification of organic and inorganic acids, purification of organic liquids, decolorization of waxes, glues, and gelatines, removal of objectionable odors and colors from edible oils and fats, decolorization and purification of petroleum oils, water purification, recovery of rare metals from dilute solutions, recovery of alkaloids from solutions, and uses in pharmaceutical preparations.

The Nature of Activated Carbon. Gregory⁽⁷⁾ has defined active carbon as a more or less pure form of carbon characterized by a high adsorptive capacity for foreign molecules. This adsorptive power is due to the chemical nature of the carbon atom with its attendant free valences 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 attribute to its adsorptive power. Activated charcoals cover a wide range of adsorptive power for various foreign molecules, depending primarily upon the size of the capillaries and the size and chemical properties of the molecules to be adsorbed. Adsorption has been defined by Glasstone⁽⁶⁾ as the higher concentration of any particular material on the surface of a liquid or solid phase than is present in the bulk of the solution.

Kandillarow⁽¹⁵⁾ has stated that the increased activity of active carbon is due to a higher energy potential. This energy potential is decreased by a decrease in the active surface available at very high temperatures, the graphitic arrangement of carbon atoms in a crystal lattice at high temperatures, and by saturation of the active carbon atoms by the adsorbed molecules. The adsorptive properties of active carbon are believed⁽¹⁹⁾ to be due to the same fundamental form of carbon regardless of the source. The active form of carbon represents an unorganized or less complex configuration of free carbon which is gained by a low temperature (below 600°C.) carbonization; while carbon set free at higher temperatures assumes a stable arrangement due to the greater energy conditions existing at the moment of deposition and this form is inactive as an adsorbent.

The adsorptive power of active carbon was early⁽⁹⁾ attributed

to its large surface area alone but this theory was proved inadequate. Later when differences were found in the activity of separate carbons all amorphous carbons were credited with activity which was more or less masked by adsorbed hydrocarbons produced by thermal cracking during the carbonization of the carbonaceous raw material. It is now believed⁽⁹⁾ that active carbon surfaces are a mosaic of active patches and the specific attractive power of these active patches depends upon the conditions of activation. Ray⁽²⁵⁾ has stated that the adsorptive power of an active carbon is a function of the active surface available. This active surface is partly in the capillaries throughout the carbon.

It has been pointed out by Chaney and his co-workers⁽⁴⁾ that the direct product of low temperature carbonization is not active and to develop the properties of active carbon, the carbonization product must be subjected to special processes. The development of these properties in any carbon is termed "activation". It is thought⁽¹⁹⁾ to be impossible to develop any two of the special properties such as decolorizing effect, gas adsorption, or catalytic effect in the same char at the same time. This difference in active carbons seems to be one of structure rather than a difference in the active complex itself.

Hassler⁽¹⁰⁾ has stated that active carbon is not a chemical entity such as sodium chloride, but that the term applies to a whole class of substances. In industrial use, a major division

is made between carbons classed as gas adsorbent and carbons classed as liquid adsorbent. This classification is based on differences in physical properties though it is true that some good gas adsorbent chars are of no use whatsoever as liquid adsorbent carbons. These differences have been attributed to smaller pore and capillary size in the gas adsorbent type. However, other factors such as the influence of a solvent, electric charge on the particle being adsorbed, and the pH of the solution are involved. For example, Chaney⁽⁴⁾ has pointed out that the decolorizing power of a carbon for sugar solutions is increased when the solution is made acid.

According to Chaney⁽⁴⁾ the selection of an active carbon for decolorizing and taste removing is usually based on desirable physical properties. The carbon must be a porous material traversed by relatively large pores due to the large size of the particles to be adsorbed. Such a char will be of low relative density. The carbon should possess a definite structure so that it will not powder or "slime" thus making it difficult to filter from solutions. The viscosity of the solvent is important in that the rate of adsorption is a function of the diffusion velocity, therefore, for viscous solutions the carbon should be finely divided to increase the rate of adsorption, possibly at the sacrifice of high adsorptive capacity. Special properties are sometimes desirable such as a carbon free from acid soluble

ash for use in the purification of acids.

Raw Materials. Hassler⁽¹¹⁾ has reported that activated carbons can be prepared from any carbonaceous material, although considerable difference will be found in the ability of various raw materials to respond to activation. Chaney⁽⁴⁾ has demonstrated that the carbon formed by thermal decomposition of carbonaceous materials may exist in two forms, one active, and the other inactive and incapable of activation. The temperature of the carbonization seems to be the controlling factor, those carbons being deposited below 500° to 600°C. being of the active type while those deposited at higher temperatures are of the other type.

Hassler⁽¹¹⁾ has stated that in selecting a raw material some consideration must be given to the ultimate use of the product. This selection is based on the desired or necessary physical properties of the product. Thus, a dense raw material, such as coconut shells, is used to prepare gas adsorbent carbons; while a less dense material is used in the preparation of liquid adsorbent carbons.

Preparation of Active Carbons. In general⁽²⁵⁾ the preparation of active carbons is done in two steps, i.e. the carbonaceous material is subjected to a thermal decomposition (carbonization) followed by some type of activation process. These two steps may be done simultaneously⁽¹³⁾ or they may be done in two separate steps⁽²⁾, with the latter method that most generally used.

Chaney⁽⁴⁾ has designated the two types of carbon deposited at

different temperatures as alpha carbon (active) and beta carbon (inactive). The apparent inactivity of carbons deposited at low carbonization temperatures is explained by the fact that the hydrocarbons evolved during the carbonization period are adsorbed on the active carbon, thus saturating the active centers. This mixture of the alpha carbon and the adsorbed hydrocarbons before activation has been termed "primary carbon".

The activation process consists of a treatment of the primary carbon by heat, oxidizing agents, dehydrating agents, or solvents. This treatment serves to remove the adsorbed hydrocarbons from the active surface, to rupture the carbon-to-carbon linkages to produce free valences, and to increase the porosity of the product.

The most widely used method of activation involves the use of gaseous oxidizing agents. Chaney⁽⁴⁾ has termed this process as "differential" and "limited" oxidation. The principle of such selective chemical attack depends upon the slightly greater susceptibility to oxidation of the hydrocarbons in the adsorption complex than of the active carbon itself. By adjustment of the temperature and concentration of the oxidizing agent the adsorbed hydrocarbons may be removed from the surface of the active carbon effectively and the formation of inactive carbon may be reduced to minimum.

The use of steam as an oxidizing agent results in an endothermic reaction with its resulting ease of control. Mantell⁽²¹⁾ has stated that the best condition for steam activation is a steam

temperature of 900°C. The use of carbon dioxide or air as oxidizing agents results in an exothermic reaction which, due to difficulty of control, results in a large loss of primary carbon and in a lesser surface area. Chlorine⁽²⁾ acts as a mild oxidizing agent removing the adsorption complex but not rupturing the carbon-to-carbon bonds.

Several investigators^(17,1,15) have pointed out that the addition of chemical additives before carbonization may promote the activity of the resulting carbon. The actions of these additives have been divided into three groups:

1. Those that act as dehydrating agents causing the decomposition products to be evolved as water. Included in this group are zinc chloride, magnesium chloride, sulfuric acid, and phosphoric acid. Aleksecvskii⁽¹⁾ has stated, however, that zinc chloride acts as a catalyst for the pyrolysis of the deactivating substances, thus decomposing them into more readily volatile substances.
2. Those that provide a cellular framework for the deposition of primary carbon, protecting it from the cracked products of pyrolysis, and when dissolved out leaves a porous mass of active carbon. Bonechar owes its effectiveness to this type of substance and resulting structure. Among these

materials are calcium and sodium carbonates, sulfates, and silicates.

3. Those that have a chemical action on the products of decomposition, rendering them soluble or allowing them to escape freely. Potassium and sodium hydroxides are of this type.

In some cases^(4,16) solvents have been used to remove the adsorption complex from the primary carbon. Chaney⁽⁴⁾ has stated that this method is not used commercially due to the expense, and also to the fact that the porosity and density of the final product cannot be controlled. The problem of elimination of the solvent is also serious.

Evaluation of the Active Product. Many testing methods⁽²²⁾ have been developed in an attempt to obtain a standard method by which any carbon may be evaluated. However, the so-called standard methods of evaluation are of little practical value. Haessler⁽¹²⁾ has pointed out that the most effective method of testing, is by testing the actual carbon under conditions identical or parallel to the contemplated use.

The amount of adsorption⁽²³⁾ by an active carbon varies with the extent of the surface area. The change produced by grinding the char is small due to the tremendous surface area already available. Chaney⁽⁴⁾ has pointed out that the apparent density of the char is an indication of the available surface area.

Hassler⁽¹²⁾ has stated that many factors are involved in evaluating a char. The adsorption will vary with the pH of the char, the adsorption of the solvent itself, the viscosity, temperature, and concentration of the solution. Hassler⁽¹²⁾ has recommended that the iodine adsorption test be used to indicate the color and odor removing properties of a char, and the potassium permanganate adsorption test be used to indicate its colloid removing ability.

Chlorination of Coal. Only a small amount of work⁽³⁾ has been done on the chlorination of coal with the aim of preparing valuable products from the process. Most of the literature on this subject deals with the value of the halogens as an analytical tool for the study of coal.

Weiler⁽²⁷⁾ subjected coal to a drastic chlorination process, using chlorine and antimony pentachloride for six days at 200°C. and for four days at 400°C. The products obtained as volatile products were carbon tetrachloride, hexachloroethane, hexachlorobenzene, and other highly chlorinated hydrocarbon derivatives. Under this treatment only five per cent of the carbon originally present in the coal was evolved as volatile products. McCulloch and Eccles⁽¹⁸⁾ have reported that the chlorination of coal increased the amount of material extractable with such solvents as chloroform from one to three per cent to as high as 31 per cent. The amount of material extractable varied with the type of coal

being treated. Generally speaking, geologically old coals, such as anthracite, are not suitable for chlorination.

McCulloch⁽¹⁸⁾ has reported that the chlorination is achieved either by the action of chlorine gas on finely powdered coal or by placing the coal in suspension in a liquid medium, either aqueous or otherwise, and the chlorine gas diffused through such a medium, or the chlorine produced by a suitable reaction in the medium. The chlorination is carried out at a temperature of about 15°C. Boyk⁽³⁾ chlorinated 4-20 mesh coal at higher temperatures (25-230°C.) in a nickel vessel with gaseous chlorine, and Ochi⁽²⁴⁾ has reported chlorinating coal by treating one part of powdered coal with four parts of saturated chlorine water solution at 25°C.

McCulloch⁽¹⁸⁾ has reported that a highly adsorbent carbon was obtained by carbonizing the solvent extracted residue of the chlorinated coal. Boyk⁽³⁾ has stated that an excellent gas adsorbent carbon was obtained by carbonizing the chlorinated coal at 500°C. for one hour followed by a steam activation of the carbonized product. The steam carbonization was carried out at a temperature of 800°C. for a period of one hour. Ochi⁽²⁴⁾ has stated that a carbonization of the treated product using a carbonization temperature of 600°C. resulted in an active char with no further treatment. Hargraves⁽⁸⁾ has reported an active product from bituminous coal by a process of chlorination, carbonization, and steam activation of the resulting product.

III. EXPERIMENTAL

Purpose of the Investigation.

The purpose of this investigation is to prepare a liquid adsorbent type of active carbon from Midlothian coal by a process of chlorination followed by a low temperature carbonization of the chlorinated product and steam activation of the carbonized product.

Plan of Investigation.

The plan to be followed in this investigation is as listed below:

1. Review of the Literature. A review of the literature will be made for pertinent information on active carbon in general and for any specific information on active carbon from chlorinated coal.
2. Type of Coal to be Used. The type coal to be used in this investigation is a low temperature, high volatile coal found in the abandoned strip mine about $3\frac{1}{2}$ miles northeast of Midlothian, Virginia.
3. Plan of Procedure. The plan of procedure to be followed is as follows:
 - a. Crushing, Grinding, and Sizing of the Coal Samples. The coal will be crushed, ground, and screened to the following three sizes, i.e. passing through the 100, passing the

80 but retained on the 100, passing the 70 but retained on the 80 mesh screens of the U.S. Std. screen series.

- b. Proximate Analysis of the Coal Samples. A standard proximate analysis of the coal will be determined as indicated by Snell and Biffen⁽²⁶⁾.
- c. Chlorination of the Coal Samples. The screened samples of coal will be chlorinated by passing a stream of gaseous chlorine through a suspension of coal in water. Coal samples of each screen size will be chlorinated for varying times of 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours to determine the effect of different times of chlorination.
- d. Washing and Drying of the Chlorinated Coal Samples. Following chlorination, the coal samples will be filtered out of the suspension, washed with water, and oven dried at 90°C . for a period of two hours.
- e. Proximate Analyses of the Chlorinated Coal Samples. A standard proximate analysis of the chlorinated coal samples will be determined by the method outlined by Snell and

Biffen⁽²⁶⁾ to determine the effect of the chlorination of the coal.

f. Carbonization of the Chlorinated Coal Samples.

The chlorinated coal samples will be carbonized at a temperature of 500°C. for a period of 1 hour. An unchlorinated coal sample of each size will be subjected to an identical treatment to furnish a blank for comparison.

g. Steam Activation of the Carbonized Product.

Each sample of carbonized product will be steam activated at a temperature of 800°C. for a period of 1 hour.

h. Evaluation of the Activated Product. The

activated product will be evaluated and compared using the iodine and potassium permanganate adsorption tests as outlined by Hassler⁽¹³⁾.

Materials

The following materials were used in the chlorination of the coal samples:

Coal. Low temperature, high volatile bituminous coal found in an abandoned strip mine about 3½ miles northeast of Midlothian, Virginia. Used as the raw material in the preparation of the active char.

Chlorine, Liquid. One hundred pound cylinder, manufactured by the Matheson Co., East Rutherford, N. J. Used to chlorinate the coal samples.

The following materials were used in the evaluation of the activated product:

Thiosulfate, Sodium. Crystals, A.C.S. Standard grade. Lot No. 122845, manufactured by the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in determining per cent iodine and permanganate adsorbed by the char.

Iodine. Crystals, resublimed, A.C.S. Standard grade. Lot No. 52743, manufactured by the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in the determination of the per cent iodine adsorbed by the char.

Permanganate, Potassium. Granular, A.C.S. Standard grade, analyzed. Lot No. 52145, manufactured by the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in the determination of the per cent permanganate adsorbed by the char.

Iodide, Potassium. Crystals, A.C.S. Standard grade, analyzed. Lot No. 40666, manufactured by the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in the determination of the per cent permanganate adsorbed by the char.

Acid, Hydrochloric. C.P. grade, analyzed. Lot No. 32546-C, manufactured by the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in the determination of the per cent permanganate adsorbed by the char.

Dichromate, Potassium. Crystals, A.C.S. Standard grade. Lot No. 92542, manufactured by the J. T. Baker Chemical Co., Phillipsburg, N. J. Used to determine the normality of the sodium thiosulfate solution used.

Starch, Arrowroot. Powder, Lot No. 21, manufactured by the General Chemical Co., Philadelphia, Pa. Used as an indicator for the iodometric determinations made.

Acid, Sulfuric. C.P. grade, analyzed. Lot No. E-207018, manufactured by the General Chemical Co., New York, N. Y. Used in the determination of the per cent permanganate adsorbed by the char.

Paper, Filter. Whatman No. 30, 11 cm., ash content per circle 0.00032 gr. Manufactured by W. and R. Blaston Ltd., England.

Apparatus

The following apparatus used in crushing, grinding, and sizing of the coal samples is located in the Unit Operations Laboratory of the Department of Chemical Engineering, the Virginia Polytechnic Institute, Blacksburg, Virginia:

Crusher, Jaw. Blake type, 6 inch corrugated jaws. Manufactured by the Universal Crusher Co., Cedar Rapids, Iowa. Used for the initial crushing of the coal. Jaw setting $1/32$ of an inch.

Mill, Attrition. Size 13, Shop No. 237. Manufactured by the Robinson Manufacturing Co., Muncy, Pennsylvania. Used for final size reduction of the coal. Plate setting one-half turn from contact.

Riddle, Gyrotory. Combs gyrotory type. Manufactured by the Great Western Manufacturing Co., Leavenworth, Kansas. Used in the screening of the coal samples.

Screens. U.S. Standard, 8 inch, sizes 70, 80, and 100 mesh. Manufactured by the Precision Scientific Co., Chicago, Illinois. Used to separate the coal into various particle sizes.

The following apparatus was used in the determination of the proximate analyses of the chlorinated and unchlorinated coal samples:

Balance, Analytical. Chainomatic, dampened, max. wt. 201.1 gr., accuracy 0.0001 gr. Serial No. A-2238, manufactured by Seederer-Kohlbusch Inc., Jersey City, N. J. Used for weight determinations.

Oven, Drying. Serial No. 100-2761, catalog No. 1250 temperature range 35° to 180°C. 110 v., 60 cycles, 600 watts, 5.5 amps., 1 phase, Type A. Manufactured by the Precision Scientific Co., Chicago, Illinois. Used to determine the moisture content of the coal samples.

Furnace, Muffle. Serial No. 1400, type 9921, 1.35 kw., 220 v., 6.13 amps., working temperature 1750°F., max. temperature 1850°F. Manufactured by the Cooley Electric Manufacturing Co., Indianapolis, Indiana. Used in the determination of the ash and volatile matter content of the coal.

Miscellaneous. Porcelain crucibles, 30 cc., 6 required. Dessicators, 10 cm. I.D., 2 required. Used in the ash and volatile matter determinations of the coal samples.

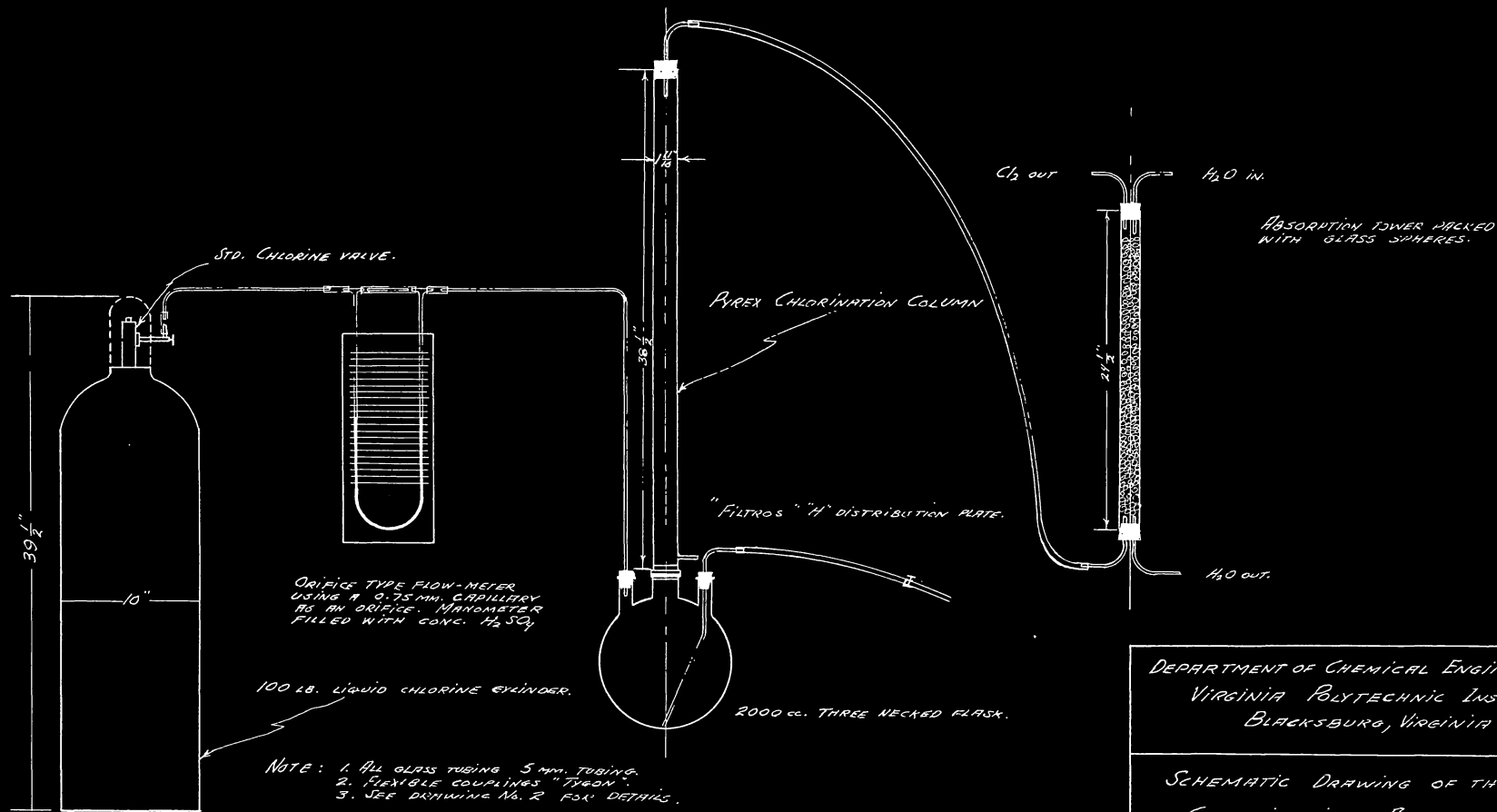
The apparatus used in chlorinating the coal samples was constructed as shown in Drawings No. 1, and 2, pages 22 and 23. The materials used in the construction of this apparatus were obtained from the Department of Chemical Engineering, the Virginia Polytechnic Institute, Blacksburg, Virginia and are listed as follows:

Column, Chlorination. Glass tubing, pyrex, 1-11/16 inches I.D., 39 $\frac{1}{2}$ inches in length. Used in chlorinating the coal samples.

Plate, Diffusion. Porous silica plate, Filtros type "H". Two inch diameter. Manufactured by Filtros Inc., East Rochester, N. Y. Used as a porous diffusion plate to distribute the chlorine into the chlorination column.

Tank, Distribution. Two liter, 3-necked flask, pyrex. Used as the base of the chlorination column and to feed chlorine into the distribution plate.

Flow-meter. Orifice type meter using a 0.75 mm. glass capillary tube as the orifice. U tube manometer constructed of 5 mm. glass tubing filled with concentrated H₂SO₄. Used to measure the chlorine flow into the chlorination apparatus.



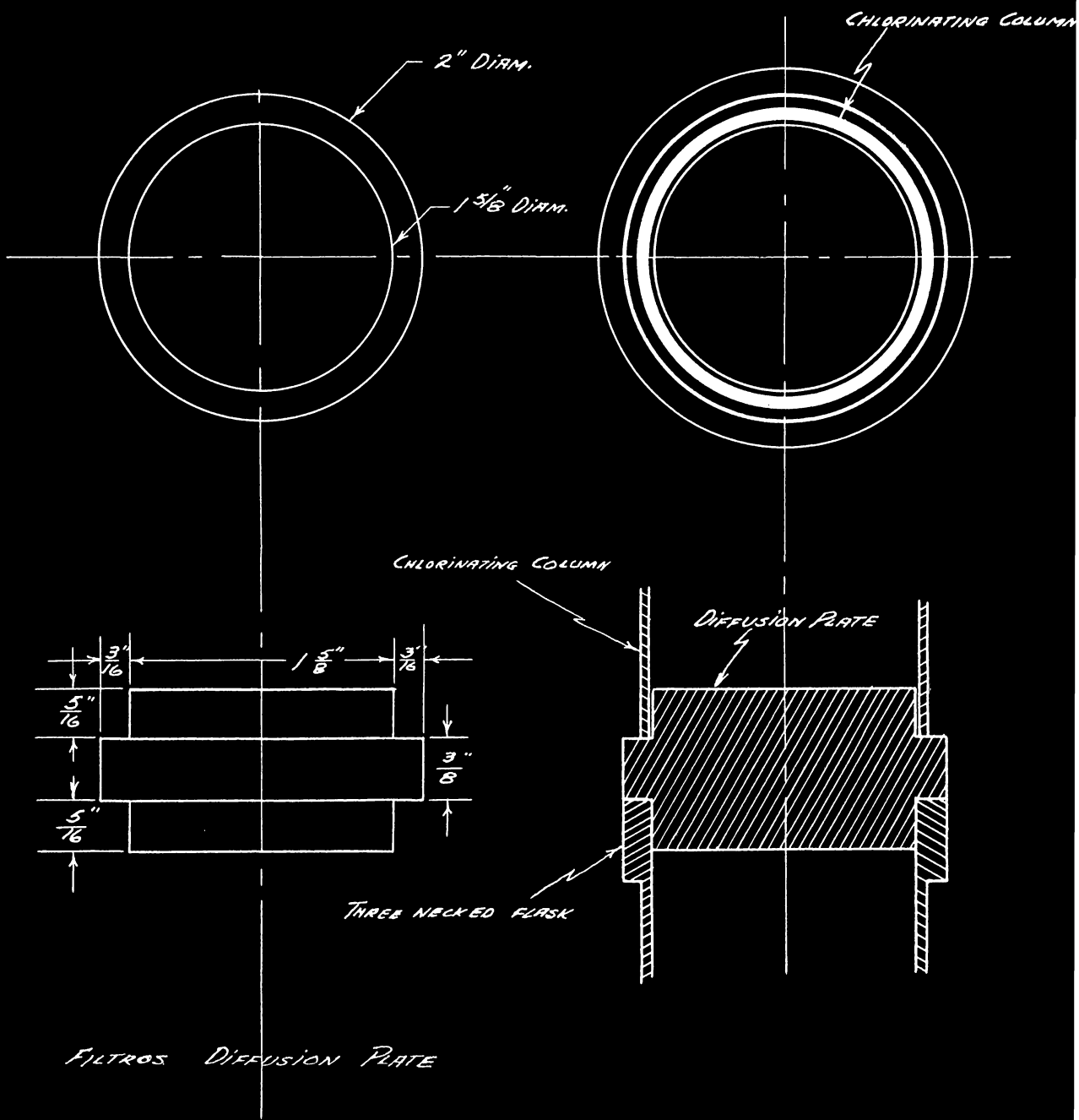
NOTE: 1. ALL GLASS TUBING 5 MM. TUBING.
 2. FLEXIBLE COUPLINGS "TYGON".
 3. SEE DRAWING No. 2 FOR DETAILS.

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 VIRGINIA POLYTECHNIC INSTITUTE
 BLACKSBURG, VIRGINIA

SCHEMATIC DRAWING OF THE
 CHLORINATION APPARATUS.

DRAWN BY: WNDT.
 CHECKED BY: JWB 8/15/47
 APPROVED BY: JWB 8/15/47

DATE: 8-13-47
 SCALE: NONE
 DRAWING No.: 1



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 BLACKSBURG, VIRGINIA

DETAILS OF DIFFUSION PLATE

DRAWN BY: ZWMT.	DATE: 8-12-47
CHECKED BY: JWB.	SCALE: 1"=1"
APPROVED BY: JWB.	DRAWING No. 2

Tower, Adsorption. Glass tubing, pyrex, 1 inch I.D., 24 $\frac{1}{2}$ inches in length. Packed with $\frac{1}{4}$ inch glass spheres. Used as an adsorption tower to adsorb the excess chlorine from the chlorination apparatus.

Scales, Three Beamed. Laboratory scales, 3 beamed, accuracy 0.2 gr. Manufactured by Fisher Scientific Co., Pittsburgh, Pennsylvania. Used in weight determinations of the sample to be treated and the treated samples.

Miscellaneous. Distribution plate sealed in the chlorination column and the distribution tank with "Varno" cement, self sealing rubber tape, and painted with D.C. 804 silicone resin. All glass tubing used was 5 mm. soft glass tubing. All flexible couplings made with 6 mm. I.D. "Tygon" tubing.

The apparatus used in carbonization and steam activation of the chlorinated product was designed and build by Mr. S. M. Gano⁽⁵⁾ for the activation of peanut hulls, and is shown in Drawing No. 3, page 26. Modifications made as listed below:

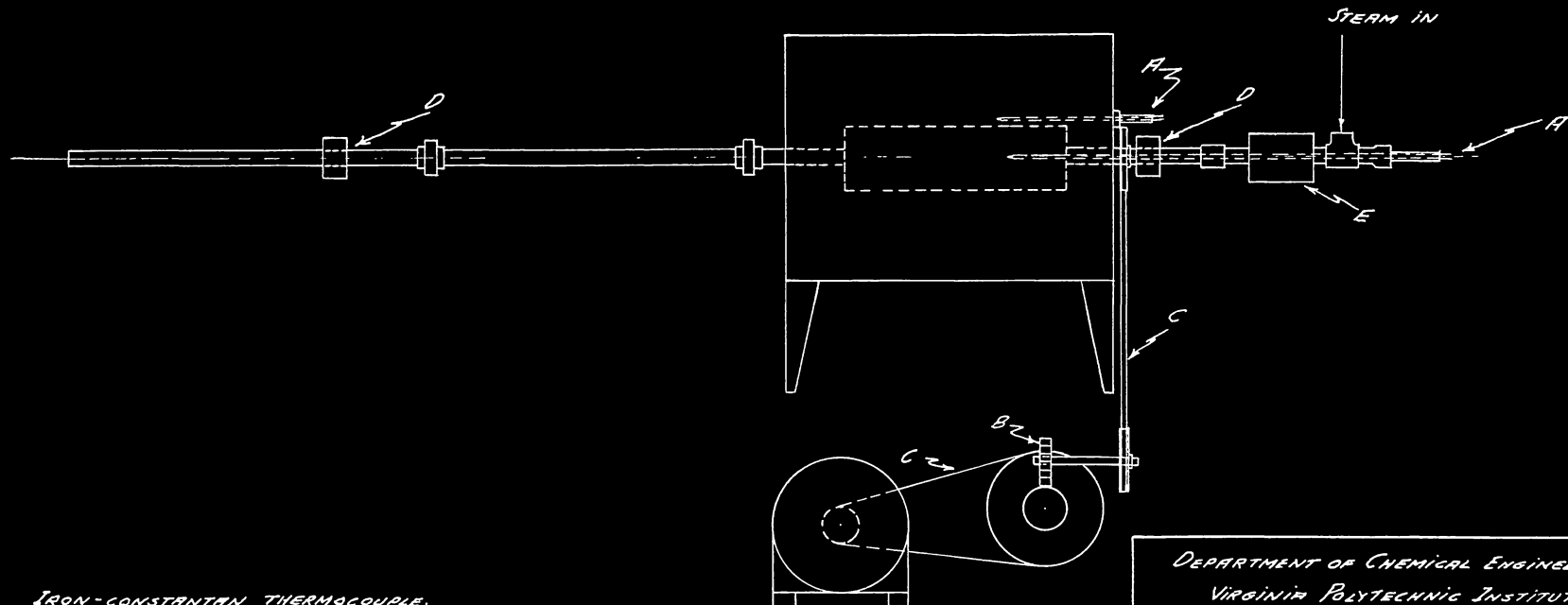
Steam Generator. One liter side arm flask, pyrex glass. Used as a vessel in which to generate steam for the steam activation of the products of carbonization.

Hot Plate. Round, "Autemp" heater, 115 v. Manufactured by the Fisher Scientific Co., Pittsburgh, Pennsylvania. Used to heat the steam generator to produce the steam for steam activation.

Thermocouples. Iron-constantan, porcelain insulating spacers used. Iron wire: #20 B. & S. gauge, Spool No. 88566-55. Constantan wire: #20 B. & S. gauge, Spool No. 89937-14. Manufactured by the Leeds & Northrup Co., Philadelphia, Pennsylvania. Used to manufacture the thermocouples used in measuring the temperature of the carbonization and steam activation apparatus.

Millivoltmeter. No. 321643, calibrated dial temperature readings in degrees Fahrenheit from 0° to 2000° for a copper-constantan thermocouple. Manufactured by the Fisher Scientific Co., Pittsburgh, Pennsylvania. Used as an indicator of the temperature of the kiln.

Potentiometer. Model No. F11-1. Serial No. 89571, compensating type. Manufactured by the Leeds & Northrup Co., Philadelphia, Pennsylvania. Used in the calibration of the thermocouples used.



- A- IRON-CONSTANTAN THERMOCOUPLE.
 B- WORM REDUCTION GEAR. NOMINAL RATIO 40:1.
 C- BELT DRIVE.
 D- PILLOW BLOCKS.
 E- ROTARY JOINT.

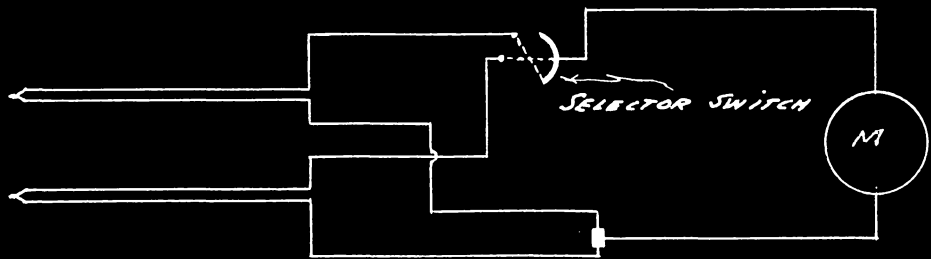
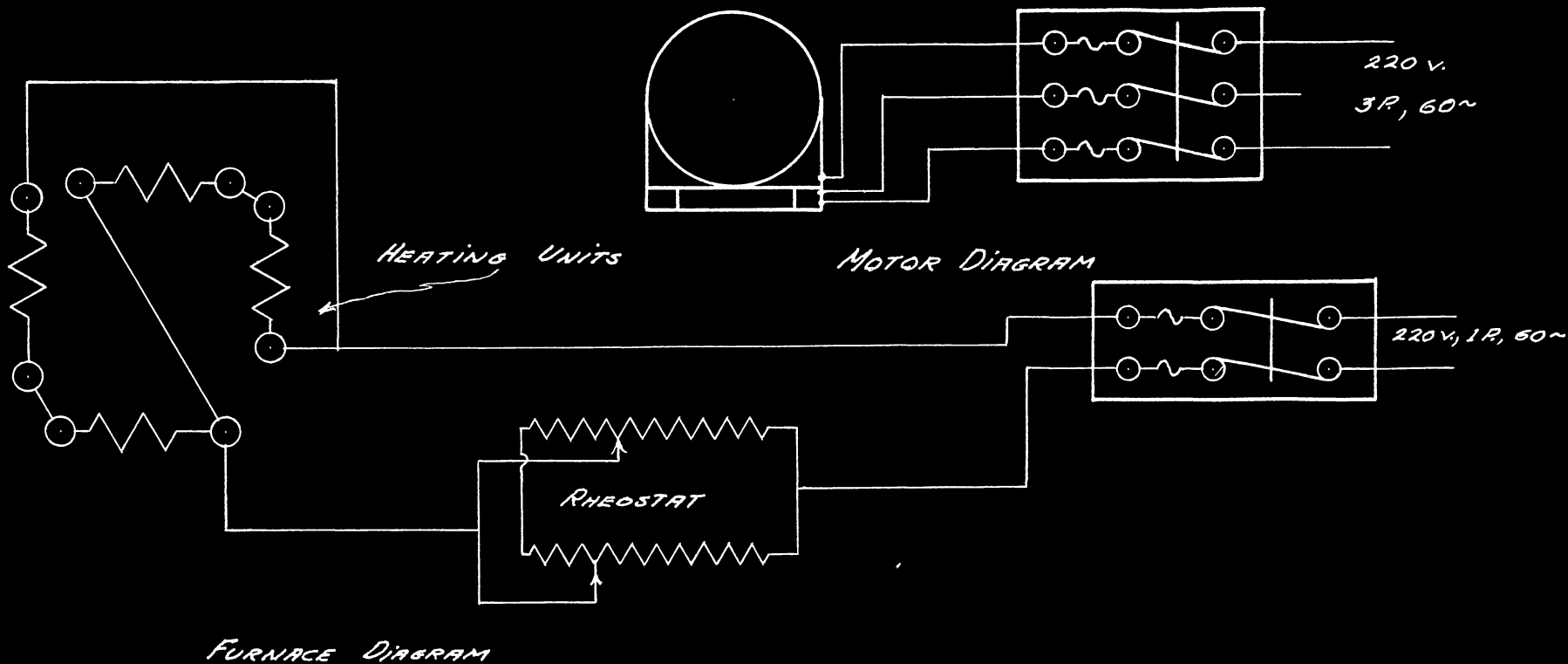
NOTE: 1. ALL PIPE AND FITTINGS USED, STD. 1" PIPE.
 2. KILN BODY OF 4" 16-B STAINLESS STEEL PIPE.
 3. BELT DRIVE FROM MOTOR. NOMINAL RATIO 4:1.
 4. ENTIRE APPARATUS MOUNTED ON A STAND.

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DIAGRAM OF STEAM
 ACTIVATION APPARATUS.

DRAWN BY: TUDOR.
 CHECKED BY: W.K.G.
 APPROVED BY: J.W.B. - 8/26/47

DATE: 8-25-47
 SCALE: $\frac{3}{8}'' = 1''$
 DRAWING NO: 3



Thermocouple Diagram.

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SCHEMATIC WIRING DIAGRAMS

DRAWN BY: W. H. W. DATE: 8-26-47
 CHECKED BY: A. B. SCALE: NONE
 APPROVED BY: J. W. B. 8/27/47 DRAWING NO: 4

The below listed apparatus was used in the evaluation of the activated product.

<u>Article</u>	<u>Size</u>	<u>No. Required</u>
Erlenmeyer Flasks	250 cc.	4
Beakers	150 cc.	4
Burette	50 cc.	1
Gravity Funnels	6 cm.	2
Volumetric Flask	1000 cc.	1
Gooch Crucibles	20 cc.	2
Suction Flasks	500 cc.	2

Method of Procedure

The following procedures were followed in preparing the coal samples for chlorination:

1. Crushing, Grinding, and Sizing of the Coal Samples.

- a. Fifty pounds of the Midlothian coal as received, were placed in the jaw crusher with the jaws set at a setting of $1/32$ of an inch.
- b. The reduced coal after one pass through the jaw crusher was then given one pass through the attrition mill with the plates set at 0.036 inches from contact.
- c. The coal after one pass through both the jaw crusher and the attrition mill, with the exception of 5 pounds used for determining the

proximate analysis of the coal as received, was subjected to a screening to obtain the coal of the desired particle sizes. The screens used were 70, 80, and 100 mesh U.S. Standard screens. The coal sample was placed on the 70 mesh screen and the nest placed in the gyratory riddle. After 3 hours of agitation in the riddle the screens were removed and the following coal sizes were kept as raw material, -100; -80, +100; and -70, +80 mesh. The materials remaining on the 70 mesh screen were not used in the investigation.

2. Proximate Analysis of the Coal as Received.

- a. A representative sample of the coal as received was obtained by successive quarterings of a 5 pound sample selected at random from the crushed and ground, but unsized, coal. The quarterings were continued until a final sample weight of approximately 50 grs. was obtained.
- b. Duplicate analyses were made for each determination using approximately 1 gr. samples according to the method as stated by Snell and Biffen⁽²⁶⁾. The duplicate runs were made to serve as a check. If the analyses as determined did not agree within 0.5% the analysis was repeated. If the analysis checked within

0.5% the values were arithmetically averaged and reported as the determined value.

3. Chlorination of the Coal Samples.

- a. One hundred gram samples (± 0.5 gr.) of each coal size were used in the chlorination tests. Each sample was weighed out on the laboratory scales and placed in suspension in tap water. Tap water was used because it contained no substance known to effect the reaction. The temperature of this suspension was observed and recorded.
- b. The suspension of coal in water was then poured into the top of the chlorination column. Care was taken to insure that all of the suspension went into the column. A thermometer was suspended into the mixture, the top of the chlorination column sealed, the time recorded, and the chlorine turned into the system. The chlorine flow was adjusted by means of the chlorine valve and the flow-meter to a value of about 12 liters per hour. This 12 liters per hour of chlorine flow represented an excess of chlorine which served to agitate the suspension, thus keeping the coal in suspension. The chlorine was allowed to flow for varying periods of 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours for each size of coal.

In each case the temperature of the reaction mixture was observed and recorded every 15 minutes.

- c. Upon completion of the predetermined time of chlorine flow the reaction mixture was removed from the column through the side arm. The mixture was then filtered to remove the coal, using a Buchner funnel and a suction flask. The filtered chlorinated coal was washed with tap water to remove HCl, and dried in the drying oven at a temperature of 90°C. for a period of 2 hours. The washed, filtered, and dried coal samples were then weighed (± 0.5 gr.) on the laboratory scales and placed in sample bottles.
- d. Standard proximate analyses were then determined⁽²⁶⁾ on the coal to determine the effect of the chlorine treatment on the coal.

4. Carbonization and Steam Activation of the Chlorinated and Unchlorinated Coal Samples.

- a. The thermocouples were installed as shown on Drawings No. 3 & 4, pages 26 and 27. The thermocouples were then calibrated with the millivoltmeter and potentiometer. Simultaneous readings were taken from the millivoltmeter and the potentiometer and recorded. From the values in millivolts observed with the potentiometer,

true temperatures were obtained from the Leeds & Northrup tables⁽²⁸⁾ and plotted against the temperature readings of the millivoltmeter.

- b. One hundred grams of each size range of the chlorinated and unchlorinated coal samples were used in the carbonization and steam activation processes. Each sample was weighed (± 0.5 gr.) on the laboratory scales. The weight was recorded and the weighed sample placed in the kiln. The kiln was then assembled (see Drawing No. 3, page 26) and secured into position in the furnace, after which bricks were placed into position to serve as an insulating door to the furnace. One liter of distilled water was added to the steam generating flask. The steam generating flask was then placed in position over a hot plate to furnish steam for activation.
- c. Electric power was then switched into the rotating mechanism and the heating units of the kiln and furnace respectively. The hot plate was then switched on "low" to allow the water in the steam generator to heat almost to the boiling point.
- d. The temperature of the furnace was allowed to heat to 500°C , the time noted and recorded. The rheostat controlling the power to the heating units

was then adjusted so as to maintain the temperature at 500°C. Since it required about 5 minutes to heat the water in the steam generator from the preheat temperature to the boiling point, the hot plate was adjusted to the "high" position after the furnace temperature had been maintained at 500°C for 55 minutes. Thus, at the end of 1 hour steam was available for treatment of the carbonized charge. At the end of the 1 hour period at 500°C the furnace rheostat was adjusted to raise the furnace temperature up to 800°C. and at the same time steam was admitted into the system. The time was noted when the furnace had reached 800°C. and the rheostat adjusted to maintain this temperature. At the expiration of 1 hour, the power was turned off of the heating units, the bricks at the furnace entrance removed, and the furnace allowed to cool to room temperature (25°C.). The steam flow was maintained until the kiln had cooled below red heat (approx. 500°C.).

- e. After cooling the kiln was removed from the furnace, disassembled, the activated product removed, weighed on the laboratory scales (± 0.5 gr.) the weight recorded, and the samples placed in sample

bottles. The amount of water remaining in the steam generating flask was measured and the difference in weight recorded as the steam used.

- f. The kiln body was washed with distilled water, dried, and the cycle repeated on another coal sample.

5. Evaluation of the Activated Product.

- a. A standard iodine adsorption test was made on each sample of the activated char, as outlined by Mantell⁽¹³⁾.

- b. A standard potassium permanganate adsorption test as outlined by Mantell⁽¹³⁾ was made on each sample of activated carbon.

- c. A filtration test was made on each sample.

This test is not a standard test but carried out as follows: three-tenths of a gram of the activated product was placed in a 150 ml. beaker and thoroughly wetted with 50 ml. of water. The mixture was stirred for 1 minute. After stirring the mixture was filtered through qualitative filter paper. The time necessary for complete filtration was observed and recorded. The time of filtration was used as a comparison to compare the filtration characteristics of the active chars produced.

Data and Results

The data obtained in the preparation of active carbon from Midlothian coal, the evaluation of the product, and the comparison of the product is given in the form of tables, grouped as follows:

- a. The data used to compare the change in weight and the variation in the proximate analyses of the treated and untreated samples is given in:

TABLE I - DATA AND RESULTS OF PROXIMATE ANALYSES OF MIDLOTHIAN COAL BEFORE AND AFTER CHLORINE TREATMENT. Page 38.

- b. The data used to evaluate and to compare the active product for adsorptive ability is given in:

TABLE II - DATA AND RESULTS FOR IODINE AND PERMANGANATE ADSORPTION TESTS ON STEAM ACTIVATED MIDLOTHIAN COAL BEFORE AND AFTER TREATMENT WITH CHLORINE.

Page 39.

The results obtained in the investigation of the chlorination of Midlothian coal to obtain a liquid adsorbent char are shown in the following graphs:

Figure 1. - Plot of Total Time of Chlorination Versus Per cent Volatile Matter in Coal Samples. Page 41.

Figure 2. - Plot of Total Time of Chlorination Versus Per Cent Ash in Coal Samples. Page 42.

Figure 3. - Plot of Total Time of Chlorination Versus Change in Weight of Chlorinated Coal Samples. Page 43.

Figure 4. - Plot of Total Time of Chlorination Versus Per Cent by Weight I_2 adsorbed by Steam Activated Midlothian Coal. Page 44.

Figure 5. - Plot of Total Time of Chlorination Versus Per Cent by Weight $KMnO_4$ Adsorbed by Steam Activated Midlothian Coal. Page 45.

Figure 6. - Plot of Total Time of Chlorination Versus Time of Filtration of Steam Activated Midlothian Coal. Page 46.

Figure 7. - Plot of True Temperature
Versus Millivoltmeter Read-
ings. Page 47.

Figure 8. - Plot of Total Time of Chlor-
ination Versus Percentage
Fixed Carbon in Coal Samples.
Page 48.

Figure 9. - Plot of Reaction Temperature
Versus Time of Chlorination
Run No. 7. Page 49.

TABLE I
DATA AND RESULTS
OF PROXIMATE ANALYSES OF MIDLOTHIAN
COAL BEFORE AND AFTER CHLORINE TREATMENT

Run #	Coal Size (U.S. Std. mesh)	Cl ₂ Time (hrs.)	Wt. Change (grs.)	Vol. Matter. (%)	Fixed Carbon (%)	Ash (%)
---	----	--	---	34.75	55.33	9.92
1	-100	1	+1.85	37.55	56.25	6.20
2	-100	1½	+5.49	37.41	57.43	5.16
3	-100	2	+7.16	39.01	55.47	5.52
4	-100	2½	+14.22	42.80	52.74	4.46
5	-100	3	+31.05	44.45	51.66	3.89
6	-100	3½	+32.17	46.43	49.66	3.91
7	-100	4	+42.62	48.72	47.67	3.61
8	-80,+100	1	-2.82	38.80	54.56	6.64
9	-80,+100	1½	+5.55	39.85	55.21	4.94
10	-80,+100	2	+12.22	40.94	54.60	4.46
11	-80,+100	2½	+17.53	41.57	54.55	3.88
12	-80,+100	3	+18.07	41.83	54.43	3.74
13	-80,+100	3½	+26.20	44.83	51.50	3.67
14	-80,+100	4	+34.48	47.06	50.27	2.67
15	-70,+80	1	-0.91	35.50	55.78	8.72
16	-70,+80	1½	+3.09	37.05	55.56	7.39
17	-70,+80	2	+3.89	37.40	55.29	7.31
18	-70,+80	2½	+5.75	38.17	55.97	5.86
19	-70,+80	3	+8.27	38.05	56.29	5.66
20	-70,+80	3½	+12.73	39.73	56.40	4.45
21	-70,+80	4	+17.96	40.50	50.27	4.17

Note: All weights and percentages calculated on the dry basis.

TABLE II

DATA AND RESULTS

FOR IODINE AND PERMANGANATE ADSORPTION TESTS ON STEAM ACTIVATED MIDLOTHIAN COAL BEFORE AND AFTER Cl_2 TREATMENT

Coal Size (U.S.Std. mesh)	Cl_2 Flow Time (hrs.)	I_2 Removed (% by weight)	$KMnO_4$ Removed (% by weight)
-100	0	14.9	25.2
-100	1	17.3	29.9
-100	1½	36.7	35.3
-100	2	30.2	46.8
-100	2½	53.7	49.4
-100	3	81.0	63.2
-100	3½	86.2	67.3
-100	4	89.9	69.0
-80,+100	0	13.2	28.5
-80,+100	1	16.7	24.5
-80,+100	1½	29.6	25.0
-80,+100	2	32.4	29.5
-80,+100	2½	41.0	38.4
-80,+100	3	54.0	48.2
-80,+100	3½	59.1	52.1
-80,+100	4	64.3	55.3
-70,+80	0	13.7	12.8
-70,+80	1	16.5	18.1
-70,+80	1½	20.4	22.1
-70,+80	2	30.1	28.2
-70,+80	2½	49.8	41.4
-70,+80	3	56.1	49.7
-70,+80	3½	73.6	50.0
-70,+80	4	74.4	50.9

TABLE III

DATA AND RESULTS

FOR PER CENT YIELD AND EASE OF FILTRATION OF STEAM
ACTIVATED MIDLOTHIAN COAL BEFORE AND AFTER CHLORINATION

Coal Size (U.S.Std. mesh)	Cl ₂ Flow (hrs.)	Steam Used (grs.)	Yield (%)	Filtration Time (secs.)
-100	0	310	60.9	50
-100	1	370	61.7	66
-100	1½	390	51.5	75
-100	2	340	51.2	77
-100	2½	380	52.0	80
-100	3	310	48.0	80
-100	3½	340	44.0	77
-100	4	340	50.5	81
-80,+100	0	350	56.8	33
-80,+100	1	370	59.3	38
-80,+100	1½	330	61.3	46
-80,+100	2	380	63.3	38
-80,+100	2½	370	65.0	45
-80,+100	3	310	61.4	39
-80,+100	3½	370	57.6	44
-80,+100	4	380	58.2	42
-70,+80	0	390	55.4	26
-70,+80	1	340	59.7	29
-70,+80	1½	310	61.5	30
-70,+80	2	320	62.8	31
-70,+80	2½	390	53.0	30
-70,+80	3	360	52.7	29
-70,+80	3½	390	45.0	33
-70,+80	4	380	49.2	31

FIGURE 1

PLOT OF
TOTAL TIME OF CHLORINATION
VS
PERCENT VOLATILE MATTER IN COAL SAMPLES

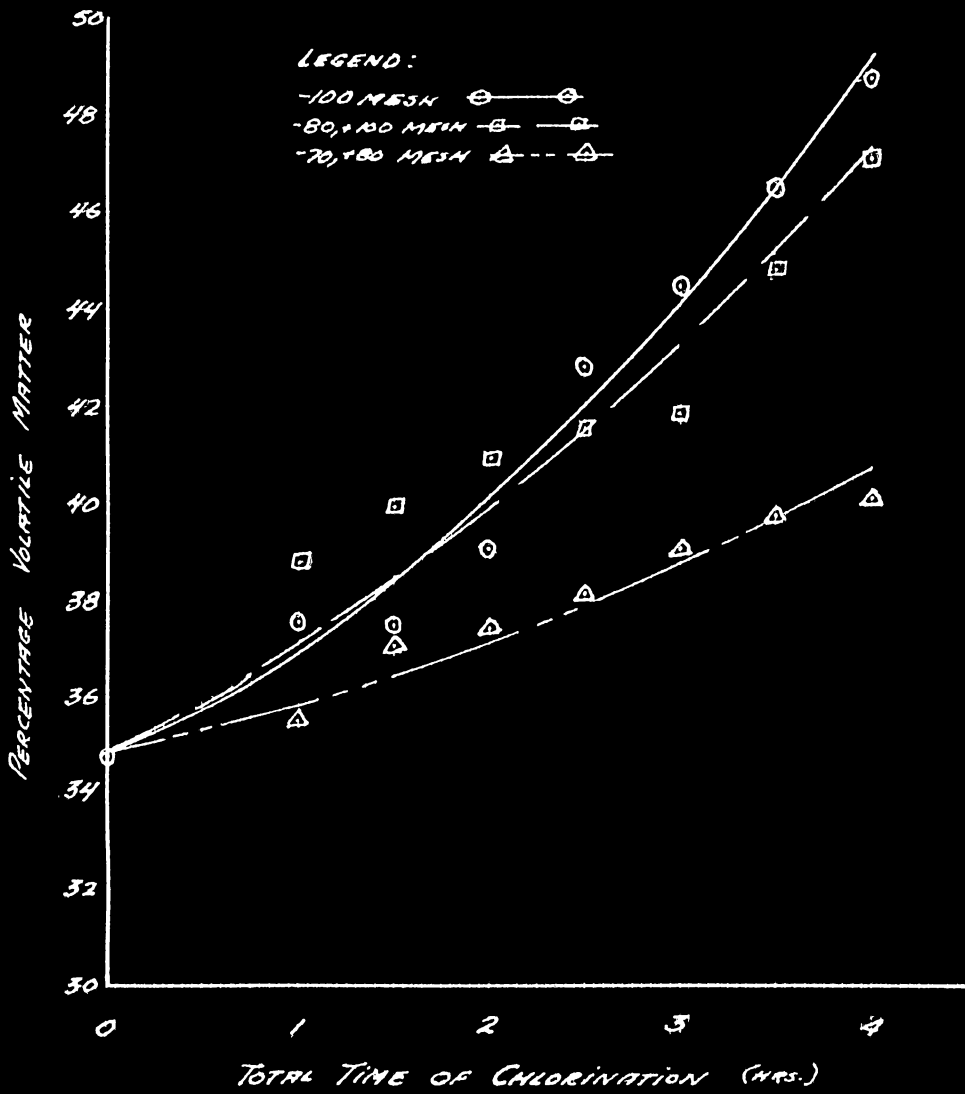


FIGURE 2

PLOT OF
TOTAL TIME OF CHLORINATION
VS
PERCENT ASH IN COAL SAMPLES

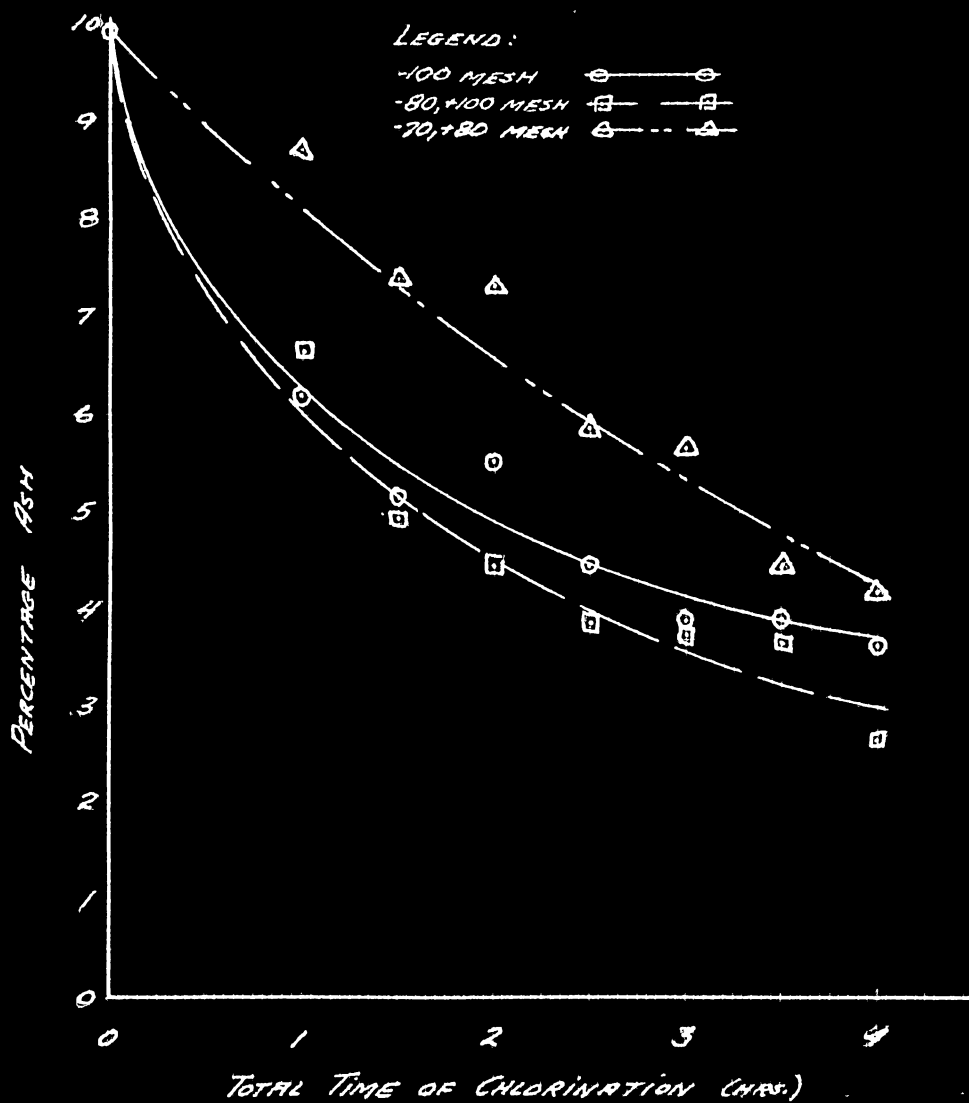
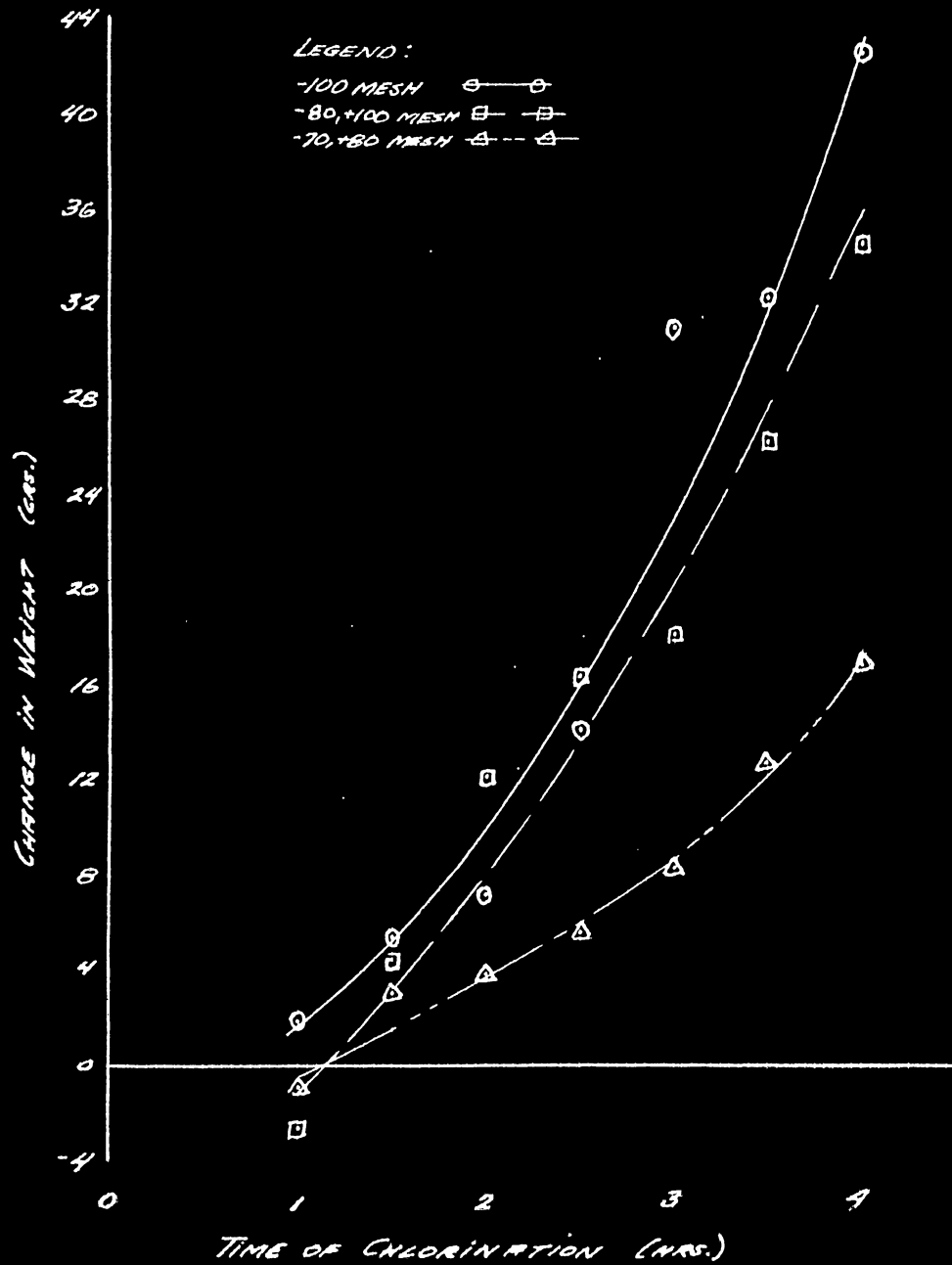


FIGURE 3

PLOT OF
TOTAL TIME OF CHLORINATION
VS
CHANGE IN WEIGHT OF CHLORINATED COAL SAMPLES



44

FIGURE 4

Plot of
TOTAL TIME OF CHLORINATION
VS
PERCENT BY WEIGHT I_2 ADSORBED
BY
STEAM ACTIVATED MICHLOTHIAN COAL

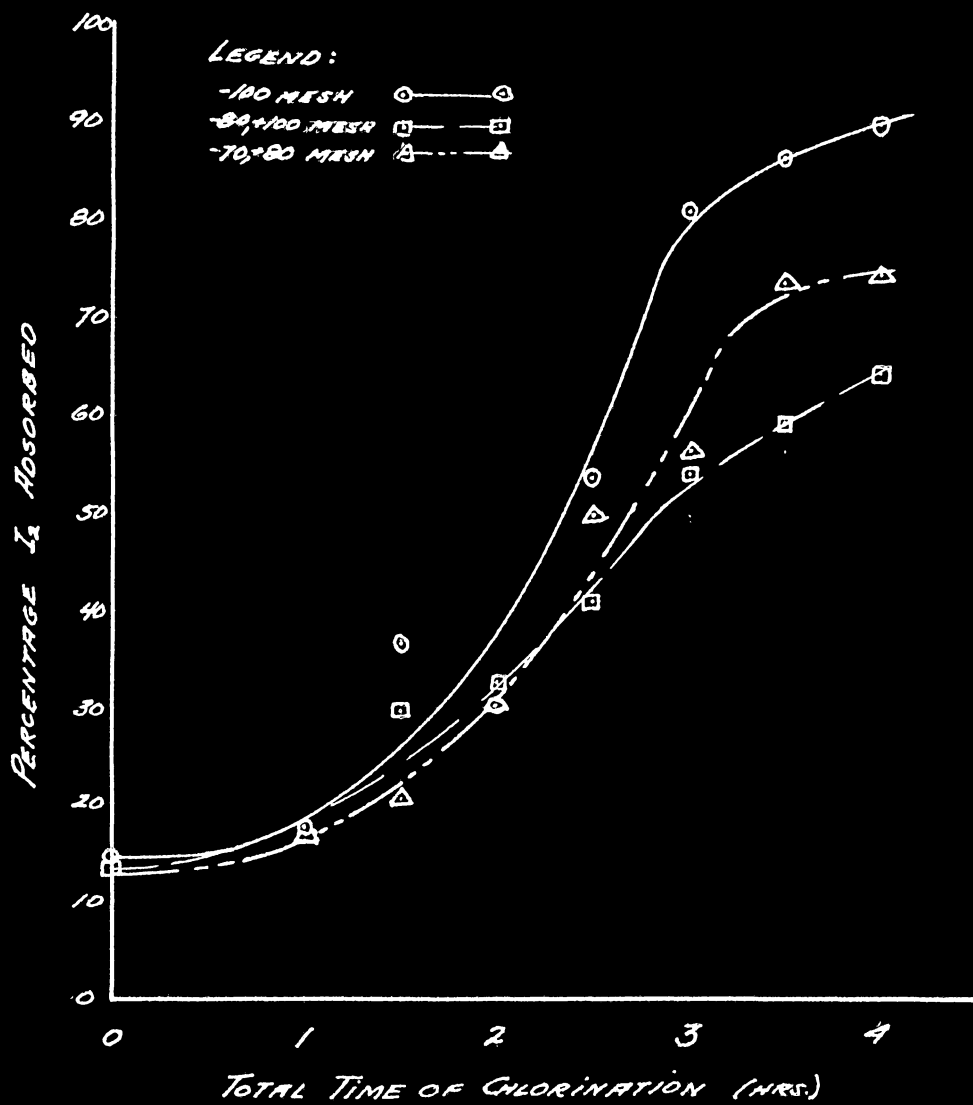


FIGURE 5

PLOT OF
TOTAL TIME OF CHLORINATION
VS
PERCENT BY WGT. $KMnO_4$ ADSORBED
FOR
STEAM ACTIVATED MIDLOTHIAN COAL

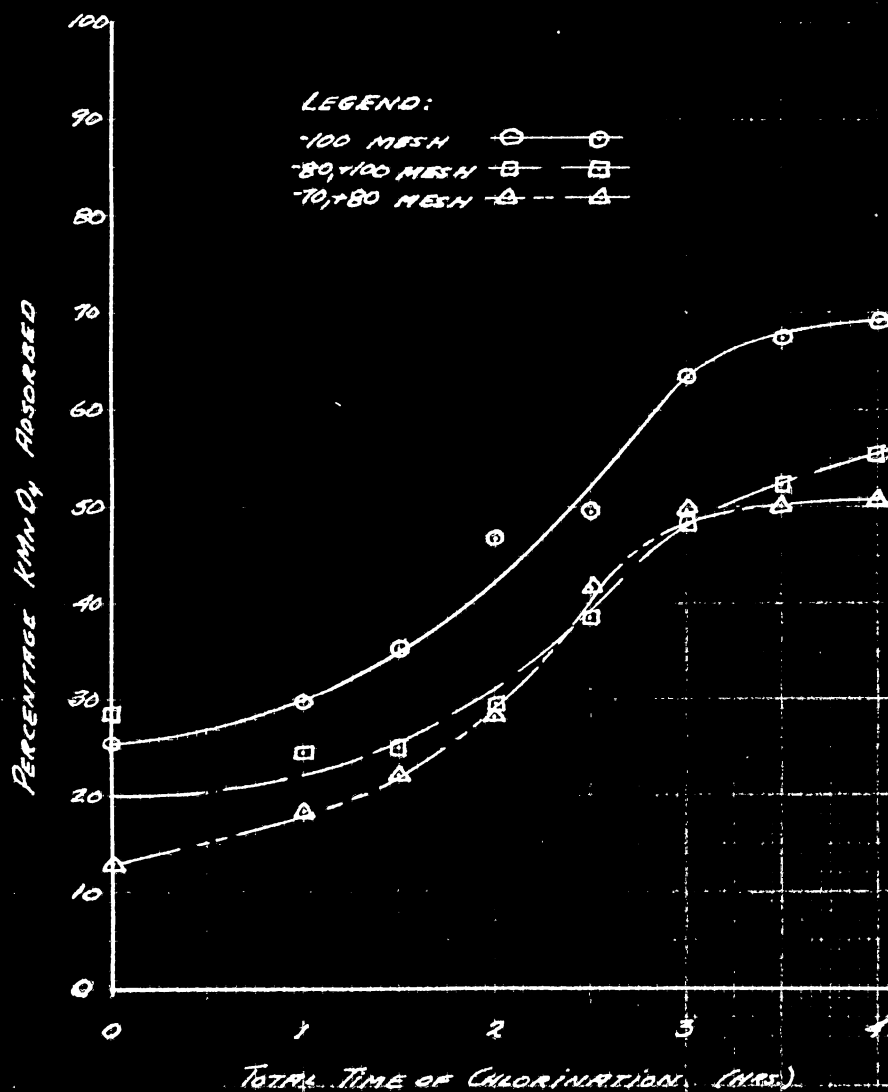
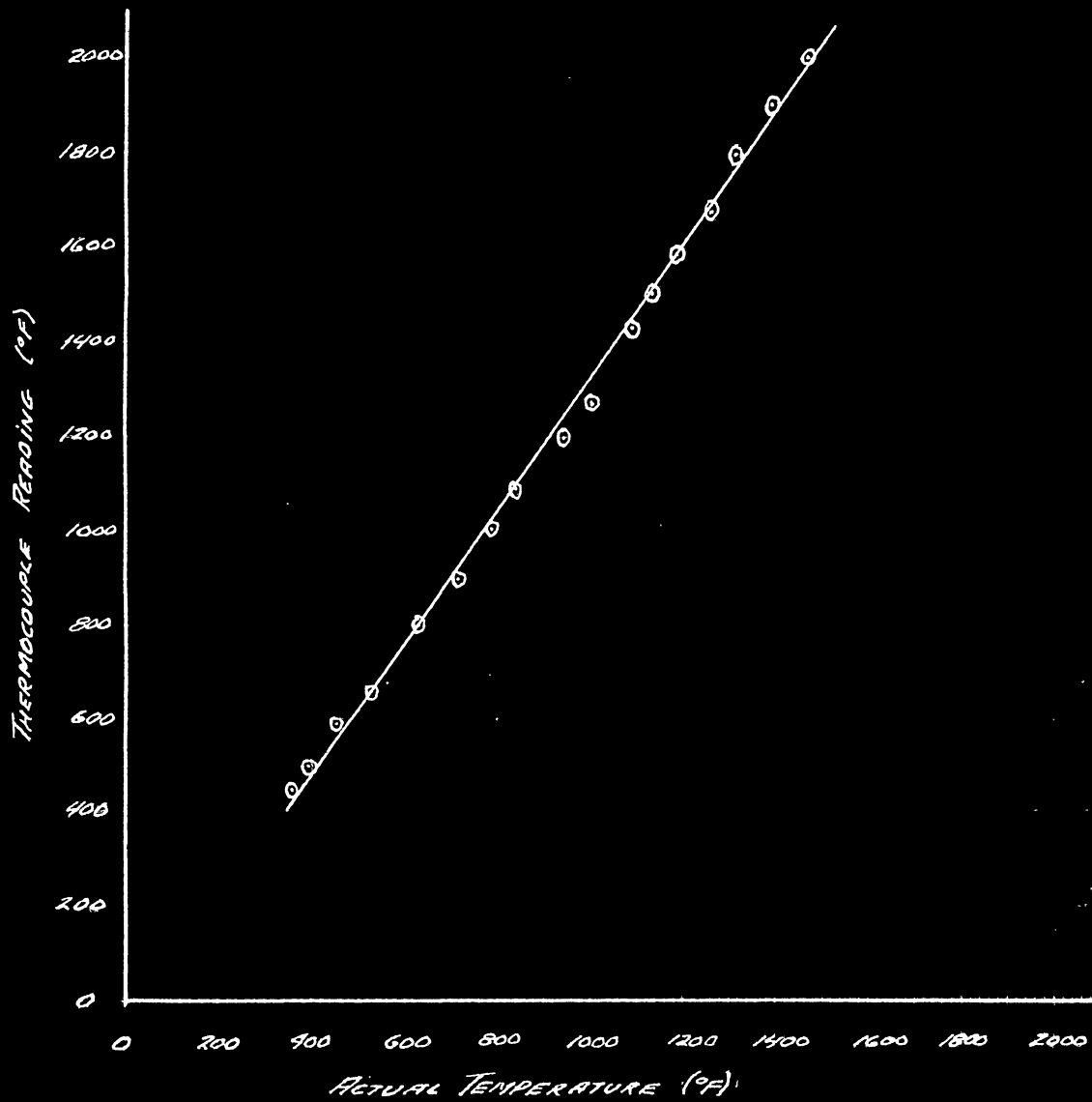


FIGURE 6

CALIBRATION CURVE
FOR
IRON-CONSTANTAN THERMOCOUPLE
USING
FISHER SCIENTIFIC Co. MILLIVOLTMETER
SERIAL No. 321634



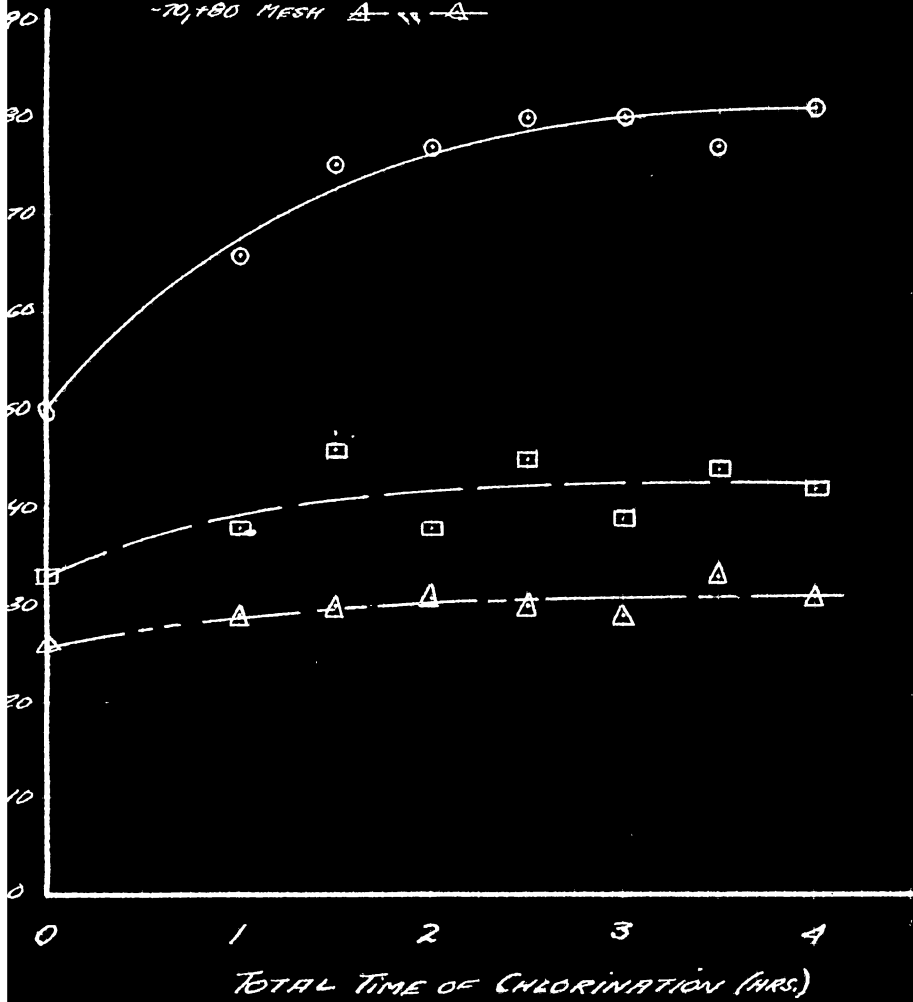
9/6/47
JWB 9/8/47

FIGURE 7

Plot of
TOTAL TIME OF CHLORINATION
VS
TIME OF FILTRATION

LEGEND:

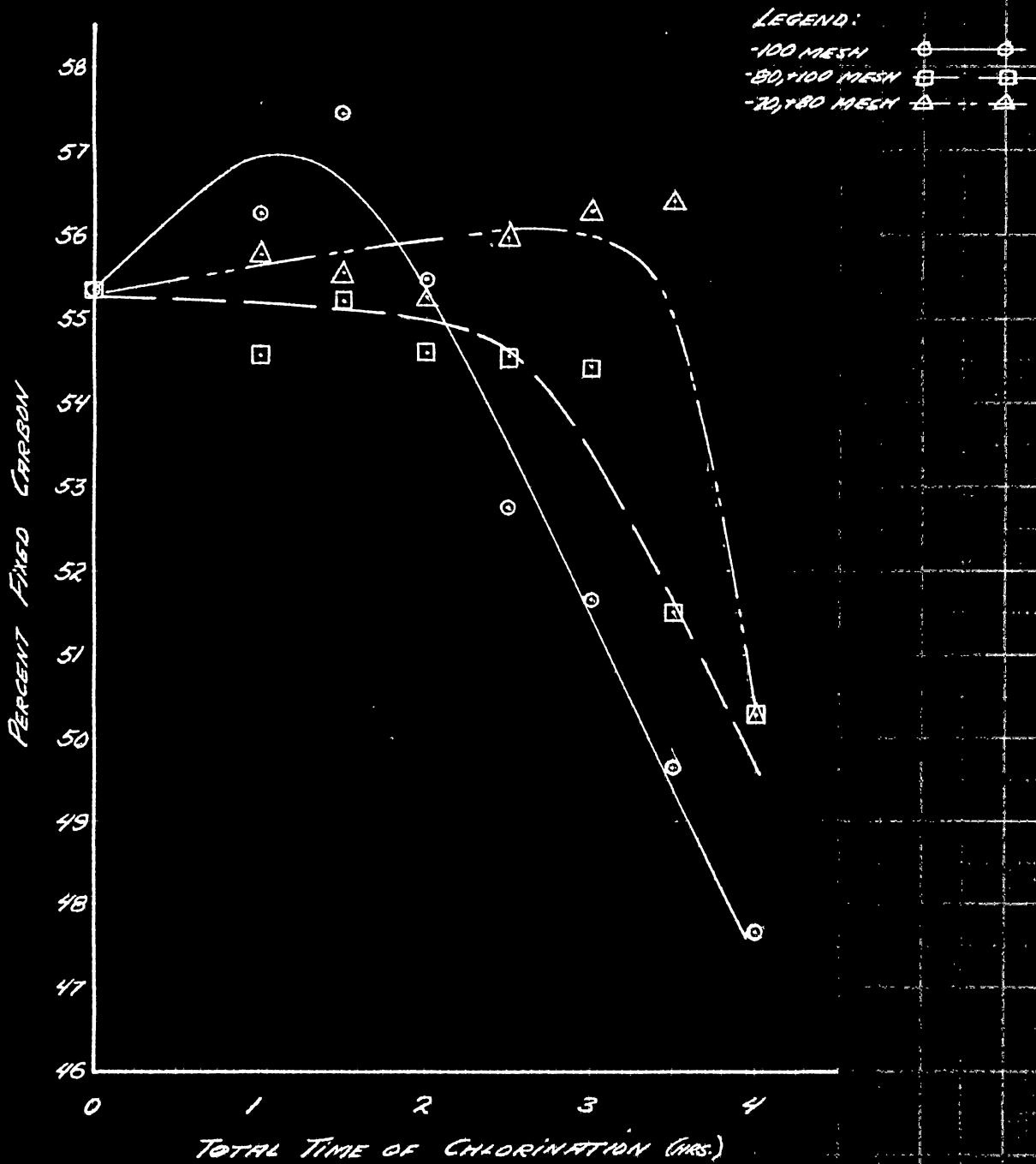
- 100 MESH ○—○
- 80,100 MESH □—□
- 70,100 MESH △—△



Woods 9/18/41
7-10-918/41

FIGURE 8

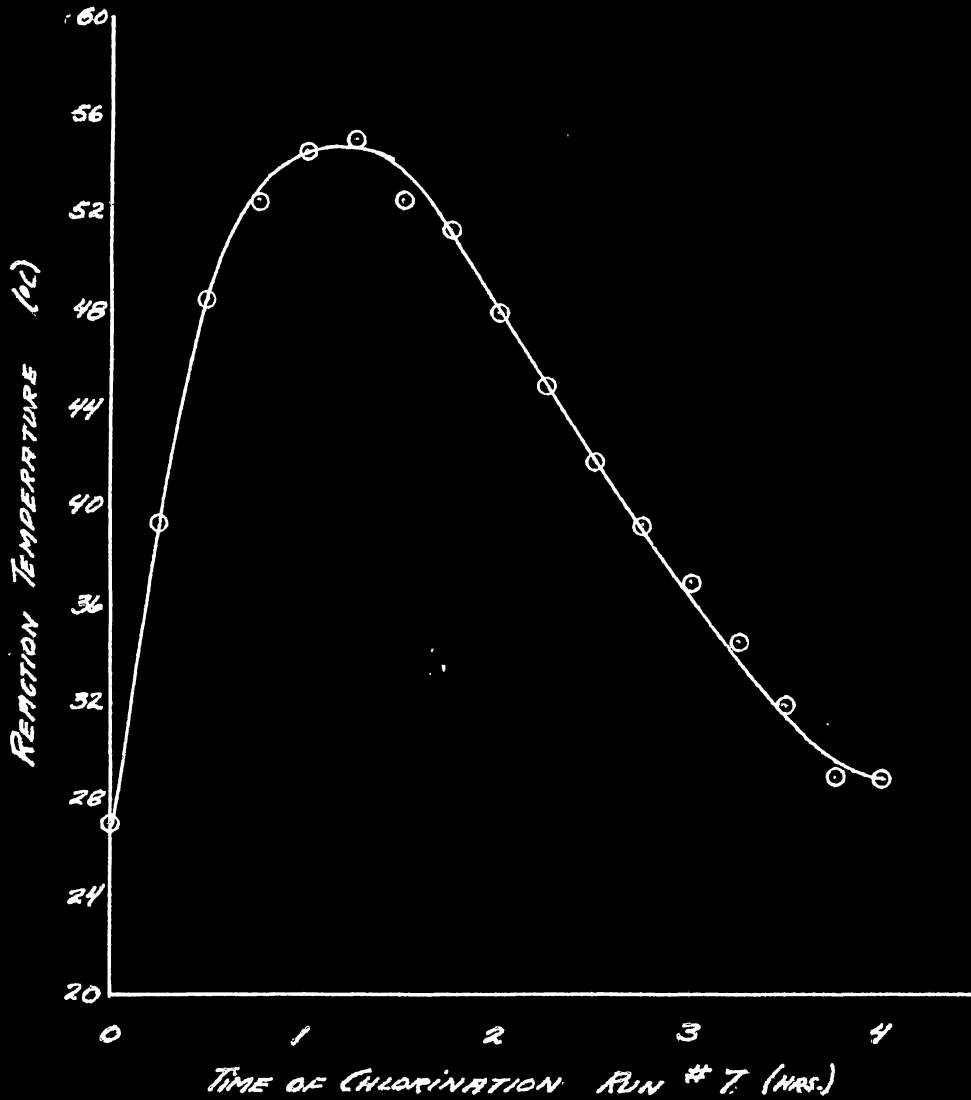
PLOT OF
TOTAL TIME OF CHLORINATION
VS
PERCENT FIXED CARBON IN COAL SAMPLES



MAST 9/9/47
ZWB 9/10/47

FIGURE 9

PLOT OF
REACTION TEMPERATURE
VS
TIME OF CHLORINATION RUN No. 7



NOTE: THIS CURVE IS TYPICAL OF THE TEMPERATURE CURVES OBTAINED. TEMPERATURE OBSERVATIONS ON OTHER RUNS AGREES WITHIN $\pm 2.0^{\circ}\text{C}$

WJW 9/10/47
JOB 9/10/47

IV. DISCUSSION.

A. Discussion of Results

1. It was originally thought that the rate of the reaction between the coal and chlorine would be dependent upon the surface area of the coal particles. On this basis it was decided to vary the size of the particles to be used. Preliminary tests indicated that coal, of particle sizes below 200 mesh U. S. Standard screens, was very difficult to suspend in water. This was assumed to be due to the surface tension of the water and the hydrocarbon nature of the coal surface. To overcome this difficulty a solution of the commercial detergent "Dreft" was used to lower the surface tension of the water, thus making it possible to suspend the coal in the water. Several chlorination tests were made using this solution, but analyses determined on the products showed no correlation and no apparent changes in weight of the chlorinated products were noted. It is believed that the detergent coated the coal particles thus preventing contact between the coal and the chlorine. The use of the detergent was discontinued. Thus the lower limit of particle size was 100 mesh and this was used as the least particle size. Preliminary tests indicated that coal particles larger than that which passed through the 70 mesh screen would not stay in suspension. Therefore, the limits in size of the coal particles

which could be used were the 70 mesh and the 100 mesh screens. On this basis the coal particle sizes used in this investigation were -100; -80, 100; and -70, 80 mesh U. S. Standard screen series.

2. Chlorination of the Coal Samples, Effect of Particle Size.

A review of the literature (3,18) indicated that a reaction would take place between the coal in suspension and chlorine. It was thought that the rate and thus the extent of this reaction would depend on the surface area of the coal particles. In the search of the literature information was found⁽³⁾ to the contrary, indicating that the reaction was somewhat independent of the surface area. However, using the change in weight of the coal samples on chlorination, 43.8% for -100 mesh coal chlorinated for 4 hours, 35.5% for -80, 100 mesh coal chlorinated for 4 hours, and 18.6% for -70 80 mesh coal chlorinated for 4 hours, as an indication of the extent of the reaction, the results of this investigation (Figure 3, page 43), indicate that the particle size and thus the surface area per unit volume is the controlling factor. The initial decrease in weight, -2.82 grs. for -80, 100 mesh and -0.91 grs. for -70, 80 mesh coals, indicates that some of the ash is leached out of the coal. It is thought that the materials being leached out were the mineral constituents (iron, aluminum, etc.) of the ash, which were going into solution as

soluble chlorides. The fact that the -100 mesh coal did not show a decrease in weight is thought to be due to the fact that the reaction took place sufficiently fast for the gain in weight on chlorination to off-set the decrease in weight due to leaching out of the ash.

The variations in the proximate analyses of the chlorinated and unchlorinated coal samples, as shown in Figures 1 and 2, pages 41 and 42, bears out the original assumption that the rate of the reaction is a function of the surface area of the coal particles. The percentage volatile matter increased parabolically with increasing times of chlorination, with the -100 mesh coal increasing from 34.75% at 0 chlorination to 48.72 at 4 hours of chlorination, the -80, 100 mesh coal increasing from 34.75 to 47.06%, and the -70, 80 mesh coal increasing from 34.75 to 40.50% over the same range of chlorination time. The parabolic decrease in the ash content of the coal samples with increasing chlorination time indicates the leaching out of the ash. The -100 mesh coal decreased in ash content from 9.92% to 5.61%, the -80, 100 mesh coal changed from 9.92% to 2.67%, and the -70, 80 mesh coal decreased from 9.92% to 4.17% over the same chlorination time range of four hours. The fact that the -70, 80 mesh coal shows the largest decrease in ash content (9.92% - 2.67%) is contrary to that which was expected. This dis-

crepancy might be explained by the fact that no definite procedure was followed in sampling and possibly the samples used in these determinations were not truly representative. The curves of the -100, and the -80, 100 mesh samples show a tendency to level off at an ash content of about 3.5% where apparently all of the constituents of the ash forming soluble chlorides have been leached out, probably leaving silica predominant.

The variations in the percentage fixed carbon (Figure 8, page 48) are explained by the fact that the value for fixed carbon is determined by difference analyses and the volatile matter analyses.

The variations in the temperature of the reaction mixture (Figure 9, page 49) upon chlorination of the suspension of coal in water can be explained by the assumption that the mineral constituents of the ash are leached out as soluble chlorides formed by a reaction between the chlorine in solution and the metals in the ash. The reactions forming metallic chlorides are exothermic and the heats of solution of metallic chlorides are positive, thus both the formation of the chlorides and the solution of the chlorides liberate heat to the system. The rapid rate of temperature rise occurs over the same period of chlorination that the sharp decrease in ash content takes place, therefore, it is assumed

that this temperature increase is due to the formation and solution of metallic chlorides formed from the ash. After a chlorination time of $1\frac{1}{2}$ hours is reached the temperature begins to decrease. This more gradual decrease is due primarily to natural cooling. The maximum temperature reached was about 56°C . The reaction mixture cooled until a temperature of about 29°C . was reached which was about 5°C . above room temperature (24°C .).

3. Carbonization and Steam Activation of the Treated and Untreated Samples. No attempt was made to vary the conditions of the carbonization and the steam activation of the coal samples. The temperatures and cyclic durations were chosen from the literature⁽³⁾ and were as follows: carbonization at 500°C . for 1 hour and steam activation at 800°C . for 1 hour. Identical tests, as those made on chlorinated samples, were made on unchlorinated samples of each coal size (-100; -80, 100; and -70, 80 mesh) to serve as reference tests. These unchlorinated samples upon carbonization and steam activation formed a hard porous coke, whereas in no case, following identical treatment, did the chlorinated coal samples cake. The explanation of this observed fact is not known. The literature indicates⁽³⁾ that the rate of steaming is not a critical factor so long as the steam flow rate is not sufficiently large to carry the material being activated from

the activation chamber. Therefore, no attempt was made to hold the steam flow constant (varied between 310 and 390 cc. used). No attempt was made to analyze the condensate from this treatment, however, most of the condensate was obviously water with a strong odor of phenol.

4. Evaluation and Comparison of the Activated Product. A search of the literature revealed several methods⁽¹²⁾ for testing the adsorption activity of active chars. It was pointed out that these methods are not conclusive and that any evaluation should be carried out under conditions parallel to the intended use of the char. However, to gain some idea of the relative merits of the chars prepared, the iodine and potassium permanganate adsorption tests were used.

a. Iodine Adsorption Tests. The results of the iodine adsorption tests indicated that the activity of the chars increased with the time of chlorination. The resulting curves (Figure 4, page 44) show a tendency to flatten out at a chlorination time of 3 hours, at approximately 85% adsorbed by the -100 mesh coal, 65% adsorbed by the -80, 100 mesh coal, and 75% adsorbed by the -70, 80 mesh samples. This shows that chlorination treatment beyond three hours is not effective in increasing the total ad-

sorption activity for iodine. Between chlorination times of 0 hours and 2 hours the difference in activity between the different particle sizes does not exceed 6%. However, after 2 hours of chlorination time the difference in activity of the different particle sizes is marked. The -100 mesh size increases to a maximum adsorption of 89.9% at 4 hours of chlorination, the -80, 100 mesh sample to a maximum of 64.3% at 4 hours, and the -70, 80 mesh sample to a maximum of 74.4% at the 4 hour chlorination time. The fact that the -70, 80 mesh sample shows a larger adsorption than does the -80, 100 mesh sample indicates that the adsorption of the non-polar iodine from solutions is not strictly a function of the surface area.

- b. Potassium Permanganate Adsorption Tests. The results of the permanganate adsorption tests show a similarity to those obtained with the iodine tests. The resulting curves (Figure 5, page 45) show a tendency to flatten out at a chlorination time of about 3 hours. A more marked difference was evident in the adsorption

activity of the three particle sizes in the 0 to 2 hour chlorination range with a maximum difference of about 12% between the -100 mesh size and the -70, 80 mesh size. The adsorption activity of the carbons increases to a maximum of 69% for the -100 mesh sample, 55.3% for the -80, 100 mesh sample, and 50.9% for the -70, 80 mesh sample at a chlorination time of 4 hours. The lower maximum adsorption of the permanganate solution than of the iodine solution indicates that the forces causing the adsorption are probably non-polar in nature.

The general increase in activity with increase in chlorination time is marked for all particle sizes investigated indicating that the chlorine treatment has a very definite effect on the adsorption activity of the char produced. This might be explained in accordance with the theory of Alekseevskii⁽¹⁾ as to the action of zinc chloride in promoting the activity of carbons. In this case, the chlorine acts as a catalyst for the pyrolysis of the deactivating substances. In light of the modern theory of the structure of coal⁽¹⁷⁾, the reaction might be assumed to take place in such a way that the bonds between the basic polycyclic carbon structure of coal and the side

chain hydrocarbons are broken, thus enabling the deactivating hydrocarbons to be more easily volatilized and driven off.

5. Filtration Characteristics of the Activated Product. The preparation of a liquid adsorbent char was the purpose of this investigation, and with the importance of the filtering characteristics of a liquid adsorbent char in mind, it was thought desirable to obtain some idea of the relative ease of filtration from solutions of the carbons prepared. The method used in testing the filtration characteristics of the carbons prepared does not constitute any standard test.

As was expected the -100 mesh coal samples, though more adsorbent, were appreciably more difficult to filter from the solution, with the difficulty of filtration becoming less as the initial particle size became greater. The greater difference in filtration time between the -100 mesh and the -80, 100 mesh particle sizes and between the -80, 100 mesh and -70, 80 mesh particle sizes is explained by the fact that not much difference in actual physical dimensions exists between the -70, 80 mesh and the -80, 100 mesh particles. The increase in filtration time with increasing time of chlorination from 50 sec. to the constant value of about 78 secs. for the -100 mesh, from 33 secs. to

the constant value of about 42 secs. for the -80, 100 mesh, from 26 secs. to the constant value of about 31 secs. for the -70, 80 mesh coal samples is difficult to explain and no explanation is offered. It can be stated that the filtration time for unchlorinated coal is no indication of the actual time due to the fact that the carbon used here was obtained by crushing the coke obtained by activating the unchlorinated coal samples.

B. Limitations

1. Chlorination of the Coal Samples. The limitations under which the chlorination of the coal samples was carried out are as follows:
 - a. The range of particle sizes of the coal was limited to sizes less than 70 mesh, and for particle sizes less than 100 mesh the coal was not separated into constituent size groups.
 - b. The temperature range of the reaction mixture was limited to the change caused by the reaction itself.
 - c. No investigation was made of the chlorination reaction for times of chlorination of less than 1 hour or greater than 4 hours.
 - d. The reaction was carried out at night under electric lighting to eliminate variable light intensity and its effect upon the reaction.
 - e. No investigation was made of other suspension mediums other than tap water.
 - f. No attempt was made to analyze the chlorinated coal for organic chlorides to determine how the reaction had taken place.

2. Carbonization and Steam Activation of the Coal Samples. The limitations under which the carbonization and steam activation of the coal samples took place were as follows:

- a. The temperature and duration of the carbonization cycle was 500°C. and 1 hour.
- b. The steam activation cycle was limited to a temperature of 800°C. and a time of 1 hour.

3. Evaluation and Comparison of the Activated Product. The limitations of the tests used in the evaluation and comparison of the activated product were as follows:

- a. The iodine and potassium permanganate adsorption tests used were not conclusive as pointed out by Hassler⁽¹³⁾.
- b. The filtration test did not constitute a standard test and the results may not be construed as quantitative.

C. Recommendations

1. Chlorination of the Coal Samples. It is recommended that further investigations be made of the chlorination of this type coal. The following specific investigations are recommended:

- a. An investigation of the effect of light in the ultraviolet range, should be made in view of the photosensitivity of chlorination reactions.
- b. An investigation of the effect of different suspension mediums such as, carbon tetrachloride, chloroform, and benzene on the reaction and on the active product formed.
- c. An investigation of the direct chlorination of powdered coal without the use of a suspension medium should be made with the object of lessening chlorine consumption.
- d. An investigation of chemical products other than active carbon should be made to determine other possibly valuable by-products of this reaction and also to gain insight as to how the reaction proceeds.
- e. Further investigation using a wider range of particle sizes, i.e. mesh sizes greater than 70 mesh, and sized samples of less than 100

mesh (-150, 200; -200, 300) should be made.

- f. An investigation of the effect of chlorination catalysts such as iron, ferric salts, and sodium hydroxide on this reaction should be made to possibly increase yield.

2. Carbonization and Steam Activation of the Coal Samples. It is recommended that further investigations be made of the carbonization and steam activation processes as follows:

- a. An investigation to determine the influence of variations of cyclic durations and temperatures for the carbonization and steam activation cycles.
- b. An investigation of the possibility of preparing a gas adsorbent char by a similar process.
- c. An investigation of the constituents of the condensate formed during the steam activation of the carbonized product.
- d. An investigation of the effect of the rate of cooling on the activity of the product.

V. CONCLUSIONS

A. Reaction Between Chlorine and Midlothian Coal.

On the basis of the proximate analyses of Midlothian coal before and after treatment with chlorine for 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours, on coal particle sizes of -100; -80, 100; and -70, 80 mesh U. S. Standard screens and the change in weight of the treated coal samples the following conclusions were drawn:

1. The ash content of the coal decreased from 9.92% to 3.61% for -100 mesh, from 9.92% to 2.67% for -80, 100 mesh, and from 9.92% to 4.17% for -70, 80 mesh coal sizes on being chlorinated for 4 hours.
2. The volatile matter content of the coal increased from 34.75% to 48.72% for -100 mesh coal, from 34.75% to 47.06% for -80, 100 mesh, and from 34.75% to 40.50% for -70, 80 mesh particle sizes after being chlorinated for 4 hours.
3. The fixed carbon determination of the coal decreased from 55.33% to 47.67% for the -100 mesh, from 55.33% to 50.27% for the -80, 100 mesh, and from 55.33% to 50.27% for -70, 80 mesh particle sizes, upon chlorination for 4 hours.
4. The percentage change in weight varied with the particle size showing a maximum change of 43.8% for the -100 mesh, 35.5% for -80, 100, and 18.6% for the -70, 80 mesh particle sizes after chlorination for 4 hours.

B. Influence of Chlorination on the Caking

Properties of Midlothian Coal.

On the basis of a visual examination of the product of carbonization at 500°C. for 1 hour, and steam activation at 800°C. for 1 hour of Midlothian coal samples of -100; -80; 100; and -70, 80 mesh U. S. Standard screen particle sizes, and chlorinated in an aqueous suspension for times of 0, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours, the following conclusion was drawn:

1. The initial chlorination of coal prevents caking.

The products using unchlorinated coal as a raw material were in the form of hard porous coke, whereas those products made from chlorinated coal as a raw material in no case caked.

C. Adsorptive Properties of the Steam Activated Product.

On the basis of the adsorptive tests using iodine in a 0.01 N solution and potassium permanganate in a 0.5 N solution as adsorbates and Midlothian coal of mesh sizes (U. S. Standard screen) -100; -80, 100; and -70, 80, treated with chlorine for 0, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours, carbonized at 500°C. for 1 hour, and steam activated at 800°C. for 1 hour as the adsorbents, the following conclusions were reached:

1. The amount of iodine adsorbed increased with the time of chlorination for each particle size. Iodine adsorbed increased from 14.95% to 89.9% for -100 mesh, from 13.28% to 64.3% for -80, 100 mesh, and from 13.75% to 74.4% for the -70, 80 mesh particle sizes, from unchlorinated to 4 hours of chlorination.
2. The amount of permanganate adsorbed increased with the time of chlorination and decreased with increasing particle size. Permanganate adsorbed increased from 25.25% to 69.0% for -100 mesh, from 28.55% to 55.3% for -80, 100 mesh, and from 12.80% to 50.9% for -70, 80 mesh particle sizes, for times of chlorination from unchlorinated to 4 hours of chlorination.

D. Filtration Characteristics of the Active Product.

On the basis of filtration tests made on samples of Midlothian coal of mesh sizes of -100; -80, 100; and -70, 80, chlorinated for times of 0, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours, carbonized at 500°C . for 1 hour, and steam activated at 800°C . for 1 hour, the following conclusions were reached.

1. The ease of filtration varied inversely with the initial particle size. The average filtration time for the -100 mesh coal was 78 sec., the average time of filtration for the -80, 100 mesh sample was 42 sec., and the average time of filtration for the -70, 80 mesh samples was 31 secs.

VI. SUMMARY.

Little work has been done on the chlorination of coal with the idea of preparing valuable products from the reaction. Several investigators have reported the preparation of active carbons from coal by chlorination. The investigation was undertaken to determine the possibility of preparing a liquid adsorbent active char from Midlothian coal, unsuitable as a fuel, thus preparing a useful product from a waste material.

A low temperature, high volatile coal, found near Midlothian, Virginia, was ground, screened to various sizes (-100; -80, 100; and -70, 80 mesh U. S. Standard screens), and chlorinated in an aqueous suspension for periods of 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, and 4 hours. A maximum increase in weight of 43.8% for -100 mesh, 35.5% for -80, 100 mesh and 18.6% for -70, 80 mesh coals was obtained after 4 hours of chlorination. Proximate analyses before and after chlorination indicated that the rate of reaction varied with the initial particle size. A decrease in ash content was assumed to be due to leaching out mineral constituents as soluble chlorides.

Following chlorination the coal samples were filtered, washed, dried, carbonized at 500°C. for 1 hour, followed by steam activation at 800°C. for 1 hour. Unchlorinated samples subjected to an identical treatment, formed a hard porous coke, whereas the chlorinated samples after treatment were found in the form of grayish particles of about the original size. Iodine and potassi-

um permanganate adsorption tests on the chars produced indicated an increase in activity with increasing chlorination time, leveling off at a chlorination time of about 3 hours for each sample. (I₂ max. adsorption 89.9% for -100, 64.3% for -80, 100, and 74.4% for -70, 80 mesh initial particle size. KMnO₄ max. adsorption 69.0% for -100, 55.3% for -80, 100, and 50.9% for -70, 80 mesh sizes, all after 4 hours chlorination). Adsorption activity varied inversely with initial particle size.

Filtration tests of the carbon produced showed increasing difficulty in filtration with decreasing initial particle size. (Average time of filtration was 78 secs. for -100, 42 secs. for -80, 100, and 31 secs. for -70, 80 mesh particle sizes.)

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VIII. ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. R. A. Fisher of the Department of Chemical Engineering, the Virginia Polytechnic Institute for his guidance and aid throughout this investigation.

The author wishes to express his gratitude to Dr. F. C. Vilbrandt, Head of the Department of Chemical Engineering, the Virginia Polytechnic Institute for his many valuable suggestions and criticisms.

Gratitude is expressed to Prof. F. W. Bull, Department of Chemical Engineering, the Virginia Polytechnic Institute for his encouragement throughout the thesis and his many valuable suggestions.

Appreciation is also expressed to Mr. H. A. Scott for his suggestion as to this subject, to Mr. O. A. Holstein for his assistance in the construction of equipment, and to Mr. F. G. Masuelli for his valuable criticisms of the written material.