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AN ABSTRACT OF THE THESIS OF Uen-ping David Wang for the Master of
Science in Applied Science presented December 20, 1971

Title: Adsorption of Sulfur Dioxide on Douglas Fir Woodchips

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

Frank P. Terraglio, Chairman

Nan-Teh Hsu

Harry J. White

Rudolph S. Buddee

In recent years, people have raised their alertness to the hazard of air pollution. Sulfur dioxide is one of the most dangerous chemical compounds among those air pollutants. A study on removing sulfur dioxide from an air stream by adsorption using woodchips as the adsorbent is presented in this thesis.

The reason for using wood as an adsorbent is that wood is a porous material and possesses a large surface of cell cavities which can hold a great amount of moisture. As sulfur dioxide gas is passed through the wood bed, it would be either condensed in the cell space of the wood by intermolecular attraction, adsorption or dissolved in the moisture held in the wood.

This work was started with a review of literature. Then related

references were collected and a proposal written. Douglas fir was chosen for the experiment because it is the most common kind of wood in the Pacific Northwest. After the process and proper equipment was set up, woodchips were screened and dried to prepare for further experiments. It was decided to use three different concentrations of sulfur dioxide. For each of the concentrations of sulfur dioxide, five levels of moisture (0%, 11%, 20%, 50% and saturated) were assigned to the selected woodchips. Fifteen combinations or experiments were done for the research.

The results of the experiments show that dry wood (0% moisture content) had comparatively low characteristics in the adsorption of sulfur dioxide. For instance, at an influent SO_2 concentration of 1.12 ppm., about 6 grams of dry woodchips adsorbed 29.37 μg . of sulfur dioxide in comparison to 2090.5 μg . of SO_2 adsorbed in the same weight of woodchips but saturated with moisture. At an influent SO_2 concentration of 1.83 ppm., the adsorption of sulfur dioxide increased from 7.73 μg . for the dry wood to 745.15 μg . in the water saturated wood. For an influent SO_2 concentration of 4.60 ppm., dry wood adsorbed 15.26 μg . of SO_2 while the moisture saturated wood adsorbed 1446.2 μg . The amount of dry woodchips used in above mentioned experiments were all about 6 grams. These data show that the moisture saturated wood adsorbed about 90 times the amount of sulfur dioxide that the dry wood adsorbed. It is clear that the wood adsorptivity increased with increasing moisture content. It was also found that wood adsorptivity and retention time were affected by the different flowrate of carrier gas. The figures show that most of the data fit a Freundlich equation. Other equations were developed to calculate the adsorptivity and retention time by obtaining the influent and effluent concentration of sulfur dioxide through the adsorbent bed.

ADSORPTION OF SULFUR DIOXIDE

ON

DOUGLAS FIR WOODCHIPS

by

UEN-PING DAVID WANG

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in

APPLIED SCIENCE

Portland State University

1971

TO THE OFFICE OF GRADUATE STUDIES:

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This thesis is dedicated to my parents.

Hung-Jen Wang and I-Ann C. Wang

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CHAPTER I

INTRODUCTION

In the past century there has been a radical change in man's existence. Improvement in nutrition, agriculture, communication, hygiene, and medicine have extended man's life span tremendously. These improvements have also increased population density on the earth. This increasing population and longevity, together with a high standard of living and rapid industrial development now generate a pressure on the environment because of the accompanying increase in waste products of all sorts. The existence of such products in the atmosphere is the problem which is termed "Air Pollution".

Air is our most important resource. Of the four fundamental resources of land, fuel, water and air, air is the most limited in supply and cannot be replaced by other substances. Yet, air in the United States and the rest of the world is continually being polluted by different sources. It has been reported that the total estimable economic loss from air pollution in the United States is about \$12 billion per year. (15,28) In California alone, smog does about \$15 million of visible damage and \$132 million of non-visible total damage to the agricultural crops. (35) Before the sun is further dimmed, before more flowers wither and die, before more people suffocate in a rank and poisoned world, we must change our ways and learn to live within the laws of nature. We must learn the facts of life and prevent its being polluted from its sources.

Among many contaminants contributing to the pollution, sulfur dioxide is one of the most important. Major sources of sulfur dioxide released to the atmosphere are presented in Table I. (13,27) Table II (10) is for the State of Oregon in 1968. Damage by sulfur dioxide has been reported in many papers (14,18,23,30,37) and the reduction of sulfur dioxide in the atmosphere is desirable. The purpose of this thesis is to study the use of woodchips as an adsorbent to remove sulfur dioxide from a gas stream. Further developments might bring about the recovery of waste woodchips for additional industrial usage. In addition, operating costs in some industries could be reduced if satisfactory results could be found to recover sulfur dioxide and ways could be found to make use of woodchips.

TABLE I

**ATMOSPHERIC SULFUR DIOXIDE EMISSIONS IN 1963 AND
1966 BY SOURCES IN THE UNITED STATES**

Process	Sulfur Dioxide* in			
	1963		1966	
	Thousand tons	Percent of total emissions	Thousand tons	Percent of total emissions
Burning of coals:				
Power generation (211,189,000 tons 1963 data)	9,580	41.0	11,925	41.6
Other combustion (112,630,000 tons 1963 data)	4,449	19.0	4,700	16.6
Subtotal	14,029	60.0	16,625	58.2
Combustion of Petroleum Products:				
Residual oil	3,703	15.9	4,386	15.3
Other products	1,114	4.8	1,218	4.3
Subtotal	4,817	20.7	5,604	19.6
Refinery Operation	1,583	6.8	1,583	5.5
Smelting of Ores	1,735	7.4	3,500	12.2
Coke Processing	462	2.0	500	1.8
Sulfuric Acid Manufacturing	452	1.9	550	1.9
Coal Refuse Banks	183	0.8	100	0.4
Refuse Incineration	100	0.4	100	0.4
Pulp and Paper Production			75	0.3
Total emissions	23,360	100.0	28,637	100.0

*A small amount of this tonnage is converted to sulfuric acid mist before discharge to the atmosphere. The rest is eventually oxidized and/or washed out. Only under unusual meteorological conditions does accumulation occur.

TABLE II

SULFUR DIOXIDE EMISSIONS IN THE STATE OF OREGON IN 1968

	Sulfur dioxide	
	Thousand tons per year	Percent of annual total
Mobil Sources		
Motor vehicles	4.54	9.56
Aircraft	0.0	0.0
Ships	0.84	1.77
Subtotal	5.38	11.33
Fuel Burning		
Oil-Domestic	4.49	9.47
-Commercial	5.28	11.12
-Industrial	11.37	23.95
Gas-Domestic	0.00	0.00
-Commercial	0.00	0.00
-Industrial	0.01	0.01
Wood residual	0.0	0.0
Subtotal	21.15	44.57
Refuse Burning	0.0	0.0
Agricultural/Forestry		
Field burning	0.0	0.0
Slash burning	0.0	0.0
Subtotal	0.0	0.0
Wood products		
Pulp and Papers	18.89	41.92
Other industries		
Metal industry	1.00	2.11
Asphalt paving	0.0	0.0
Miscellaneous	0.04	0.08
Subtotal	1.04	2.19
Total Emissions	47.45	100.00

Note: Emissions listed as 0.0 indicates source not significant or not considered. Emissions listed as 0.00 indicates emissions computed but less than 0.005.

CHAPTER II

LITERATURE REVIEW

There has been a vast quantity of research literature in the past century reporting the elimination of sulfur dioxide from gas mixtures by using the processes of absorption and adsorption. Solutions of water (29), ammonium hydroxide (1), manganese oxyhydroxide (1), lime (1), zinc oxide (26), amines and many other chemicals have been used to absorb SO_2 by the process of absorption and solid materials such as charcoal (12), silica gel (24), molecule sieve, zeolite (21), anion resins (19), activated alumina, soils (31), and many other porous materials were also used as an adsorbent to selectively remove sulfur dioxide from flue gases. The motivation of using wood as an adsorbent was that the wood is one of the porous materials and it had been reported to react with the dilute sulfur dioxide solution readily.

1. One of the major constituent of cell walls in wood is lignin. The lignin content (5) of softwoods ranges from 25 to 35 percent; that of hardwoods is usually considerably lower, varying from 17 to 25 percent. Scientists found that at ordinary temperature the sulfonation of lignin in wood takes places quite readily. Brauns and MacLaurin (3) treated extracted sprucewood flour with 5% of sulfur dioxide solution at room temperature and found that sprucewood combined with sulfurous acid quite rapidly at first (see Fig. 1). In long-term experiments, lasting 16 months, western hemlock chips were treated with a 10% solution of sulfur dioxide at room temperature. The amount of sulfur taken up by the wood, the amount of wood

Fig. 1. The absorption of sulfur dioxide solution (5%) by sprucewood.

recovered, its lignin content, the amount of lignin dissolved, and the amount of sulfur in the lignin are shown in Fig. 2 and Fig. 3. It is found that the curve on the absorption of sulfur dioxide in both Fig. 2 and Fig. 3 was identical with that found in Fig. 1.

2. In analyzing the wood ash, it was found that the mineral matters ranged from about 0.5 to 5 percent, sometimes even higher depending on the different woods. The most abundant metallic oxide component of wood ash is calcium oxide (lime), which may comprise one-half to three-fourths of the total. (3) Lime when dissolved in water can readily react with sulfur dioxide to form calcium sulfite or sulfate and adhere on the surface of wood. The amount of the product, of course, is very low.

3. The sorption phenomena using wood as sorbent to hold the sulfur dioxide includes both the process of absorption and adsorption. This is because wood has large porous cell cavities and can hold a certain amount of moisture. The term "Absorption" is used to define any other condition in which liquid or gases are engulfed by another substance; solution, chemical reaction, diffusion, or capillary action may be involved. The term "Adsorption" is used to define the condition in which the gases, liquids or dissolved substances are condensed on the surfaces of solids through intermolecular attraction.

4. All woods can be considered as porous in the broad sense. That is, they possess air space. This void air space imposes limits on the amount of water it can absorb and is therefore the determining factor in the wood-liquid relationship. Also, the porosity of wood provides for good characteristics of physical adsorption.

5. Wood is a cellular material and can hold a large amount of moisture in its cell cavities. The amount of moisture that wood can contain in

Fig. 2. Sulfonation of spruce groundwood with 2, 5, and 10% SO_2 solutions: ²¹ —, (%) sulfur in lignin; — — —, (%) sulfur in wood; — · — · — · —, (%) yield of sulfonated wood.

Fig. 3. Sulfonation of hemlock protolignin with 10% SO_2 solution at room temperature: ²¹

a, lignin in wood (%) b, lignin dissolved (%)

c, sulfur in lignin (%) d, sulfur in wood (%)

e, yield of sulfonated wood (%)

this waterlogged condition varies according to the kind and to the piece, ranging from 40 percent of the oven-dry weight for the heaviest kinds of wood to nearly 2,000 percent for the lightest. (4)

6. Sulfur dioxide is quite soluble in water and its solubility has been reported by Sherwood (29) in 1925 (see Appendix I). We can, therefore, imagine that sulfur dioxide will be retained in the wood cell walls by dissolving it into water.

CHAPTER III

THE PROCESS OF SORPTION

1. The Absorption process

Absorption (11,32) is a unit operation in which a soluble component of gas mixture is dissolved in a liquid. This is one of the techniques for transferring material from one homogeneous phase to another and is based mostly on the equilibria between two phases. The apparatus used for contacting a liquid and a gas stream continuously may be constructed in several different ways: 1) a tower filled with an irregular solid packing material, 2) an empty tower into which the liquid is sprayed, or 3) a tower containing a number of bubble-cap or sieve plates. Ordinarily, the gas and liquid stream flow countercurrently through the equipment in order to obtain the greatest rate of absorption. Occasionally, gas absorption operations are carried out in spray columns, wet-wall columns, stirred vessels, or mechanically aided devices.

2. The adsorption process (8,24)

Intermolecular attraction between the solid and gaseous or liquid solutes may cause such solute molecules to be selectively retained in the pores or cavities, resulting in their being separated from the carrier gases. As indicated by Monnet (9) almost all sorbents can be considered to contain a significant fraction of micropores, ranging from 5 to 60 percent by volume. The adsorption processes can be classified in two ways: 1) chemisorption and 2) physisorption.

2.1 Chemisorption: At higher temperatures, adsorption may occur through a true reaction or chemical bonding. This is termed chemisorption. Chemisorption is the result of much stronger binding forces, comparable with those leading to the formation of chemical compounds. This adsorption may be regarded as the formation of a sort of surface compound and is seldom reversible. Fig. 4 is a typical chemisorption case, oxygen on charcoal at 100°C.

2.2 Physisorption: Physical adsorption is due to the operation of forces between the solid surface and the adsorbate molecules that are similar to the van der Waals forces between molecules. In contrast to chemisorption, physisorption generally is quite readily reversible, i.e., when the pressure is decreased, the adsorbed gas is desorbed along the same isotherm curve. The case of nitrogen on silica gel at -196°C, Fig. 4, is an example of physisorption. A comparison between chemisorption and physisorption is given in Table III.

Adsorption is usually analogous to a condensation of gas molecules. Its selective action is most pronounced in a monomolecular layer next to the solid surface, but at times selectivity may persist to a height of three or four molecules. Adsorption capacity of a solid for a solute tends to increase with the fluid-phase concentration of the solute. The effective rate of adsorption is determined by one more of several diffusional steps. Individual steps in the transport mechanism, any one of which may restrict the overall performance in a certain region of operating condition, are:

- (1) Diffusion in the solid phase (or, for an adsorbent, diffusion in the adsorbed surface layer).
- (2) Reaction at the phase boundaries.
- (3) Pore diffusion in the fluid phase within the particles.

Fig. 4. Two typical examples of adsorption isotherms

TABLE III

COMPARISON OF PHYSICAL ADSORPTION AND CHEMISORPTION

	Physical Adsorption	Chemisorption
Heat of adsorption	Small, same order as normal liquefaction	Large, many times greater than the heat of normal liquefaction
Rate of adsorption	Controlled by resistance to mass transfer Rapid rate at low temperatures	Controlled by resistance to surface reaction Negligible rate at low temperatures
Specificity	Low, entire surface available for physical adsorption	High, Chemisorption limited to active sites on the surface
Surface coverage	Complete and extendable to multilayers	Incomplete and limited to unimolecular layer
Adsorption above critical temperature	None	No restriction
Adsorption at low partial pressure	Small	Large
Adsorption at high partial pressure	Large, may extend to infinite amount	Slight increase
Activation energy	Low, nearly negligible	High, corresponding to a chemical reaction
Quantities adsorbed per unit mass	High	Low

(4) Mass transfer from the flowing phase to the external surfaces of the sorbent particles.

(5) Mixing between different parts of the contacting equipment.

3. Adsorption equilibria and isotherm

The amount of gas adsorbed by a solid under equilibrium conditions may be expressed either as percentage by weight or else as the mass or volume of gas (reduced to standard condition), both on the basis of unit mass of gas-free adsorbent. In general, adsorption isotherms, in which the volume of gas adsorbed is plotted against partial pressure at various parameters of constant temperature, are commonly used. The plot of adsorption isotherms can be simplified by plotting the volume or mass of gas adsorbed against the relative saturation of the gas instead of against partial pressure. This is shown in Fig. 5, where the relative saturation is defined by the following ratio:

$$x = p^* / P \quad [1]$$

where p^* = equilibrium partial pressure of vapor
 p = saturation vapor pressure

There are five general types of isotherms of adsorption (6) as shown in Fig. 5. In type I the adsorption isotherm is hyperbolic, approaching a constant asymptotic value at a relative saturation of unity. The explanation of this performance is that adsorption is restricted to a surface layer one molecule thick. In type II the adsorption curve is S-shape and increases to infinity as the relative saturation approaches unity. The explanation of this behavior is the formation of a multimolecular layer of indefinite thickness. In type III the curvature of the adsorption isotherm is convex toward the side of abscissas. The second derivative of the curve is thus always positive. The amount of gas adsorbed increases without limit as its

where V = concentration of adsorbate on the adsorbent, gm. adsorbed/
gm. solid.

x = Relative saturation (p^*/P) = Equilibrium partial pressure
of vapor/Saturated vapor pressure.

Fig. 5. Types of adsorption isotherms

relative saturation approaches unity. In this case as in type II an infinite molecular layer is possible. Type IV is similar to type II in the low and intermediate ranges of relative saturation, but the values of V (the concentration of adsorbate on the adsorbent) approach a maximum finite value at a relative saturation of unity. The high values of V are accounted for by capillary condensation, the maximum value corresponding to complete filling of the capillaries. Type V is similar to type III at low and intermediate ranges of relative saturation but approaches a maximum finite value for V at relative saturation of unity. This behavior is accounted for by capillary condensation and the building up of a layer of finite thickness at saturation. The initial convex curvature can be accounted for by the heat of adsorption of the first layer becoming less than the heat of normal condensation due to interaction.

There is no general equation suitable for all types of adsorption isotherms which has been developed from theoretical consideration. On a theoretical basis, Langmuir (20) developed an equation for type I, the simplest type of adsorption isotherm which is restricted to single molecular layer, assuming: 1) at any pressure less than saturation the amount of gas adsorbed is proportional to the partial pressure of the gas and to the fraction of the surface left uncovered, 2) the adsorbed gas has not dissociated nor interacted. On this basis, he developed the following equation:

$$V = \frac{V_m bp}{1 + bp} \quad [2]$$

where V = volume of gas (0°C, 760 mm Hg) adsorbed per unit mass of adsorbent.

V_m = volume of gas (0°C, 760 mm Hg) adsorbed per unit mass of adsorbent to cover surface with a layer one molecule thick.

b = empirical constant, in reciprocal pressure units.

Bienstock et. al. (2) had developed a satisfactory method in the application of exponential equations for adsorption of atmospheric sulfur dioxide.

In this method the Freundlich equation was applied to express the adsorption of the gas by a variety of solid materials and has the following general form:

$$M_g/M_s = KC^n \quad [3]$$

where M_g = the mass of gas retained by the adsorbent, μg .

M_s = the mass of adsorbent in bed, g.

K, n = proportionality constant

C = concentration of adsorbate gas in the effluent from the adsorbent, $\mu\text{g./liter}$

4. Calculation for the process of adsorption

4.1 Calculation of gas adsorbed on the solid material (25,36). The amount of gas adsorbed by the adsorbent bed in time dt can be expressed as follows:

$$dM_g = (C_b - C_a) V \cdot dt \quad [4]$$

$$\text{or} \quad M_g = V \int_0^t (C_b - C_a) dt$$

where M_g = the mass of gas adsorbed

C_b = the adsorbate concentration in the influent gas

C_a = the adsorbate concentration in the effluent gas

V = gas flow rate

and the change of capacity of adsorbent, dG , within the time dt is

$$dG = dM_g/M_s \quad [5]$$

Combining Eq. [4] and [5], we have

$$\frac{dG}{C_b - C_a} = \frac{V}{M_s} dt$$

Put into boundary conditions, $t = 0$, and $G = 0$, then we have

$$\int_0^{G_c} \frac{dG}{C_b - C_a} = \frac{V \cdot t}{M_s} \quad [6]$$

or

$$t = \frac{M_s}{V} \int_0^{G_c} \frac{dG}{C_b - C_a} = \frac{M_s G_c}{V (C_b - C_a)} \quad [7]$$

where M_s = the mass of adsorbent in bed

G_c = cumulative amount of adsorbate on the adsorbent

Integrating Eq. [6] and solving it in explicit form for C_a , we obtain

$$C_a = C_b (1 - \exp(-kVt/M_s)) \quad [8]$$

4.2 Estimation of adsorber

There are several criteria proposed as guidelines for adsorber design:

4.2.1 The pseudo gas velocity should be as high as the adsorber height restrictions and pressure drop limitations will permit in order to achieve efficient mass transfer possibly on the order of 45 feet per minute.

4.2.2 Adsorbent mesh size should be as small as the pressure drop limitations, granule strength and screen size will permit.

4.2.3 The adsorbent bed should be at least as long as the transfer zone length for the key component in the recovered product.

4.2.4 The length-diameter ratio (L/D) of the adsorbent bed should be as large as the height restrictions, pressure drop and fabrication economics will permit.

4.2.5 The saturation time interval must be at least as long as the minimum time required to regenerate and cool the alternate adsorber.

4.2.6 Optimum control of adsorber switching time must be based on continuous

monitoring of the key component concentration in the effluent gas.

In the light of above-mentioned criteria of adsorption design, Campbell, et. al (7) have developed an equation for the diameter of required adsorbent bed:

$$D = [25(W_g)(T_f)/(P_f)(V_g)]^{1/2} \quad [9]$$

where D = required adsorbent bed diameter, ft.

W_g = gas flow rate, million cu. ft. per day

T_f = Temperature in adsorber, °R

P_f = Pressure in adsorber, psia

V_g = linear gas velocity, ft./min.

The diameter of the adsorber used in the experiments has been checked, according to equation [9] in Appendix II.

CHAPTER IV

EXPERIMENTAL PROCEDURES

This experiment used woodchips as an adsorbent to remove sulfur dioxide from a gas stream by an adsorption process. The overall experimental process was carried out in the Air Pollution Laboratory of Portland State University and was initiated in the following ways:

1. A process flow diagram for the experiment was set up.
2. The required equipments were collected and the experimental train was assembled.
3. The kind of wood to be used as the adsorbent was determined, and an adequate size of woodchips was selected, dried and stored.
4. A calibration curve was prepared and an SO_2 monitor was calibrated.

The procedures for this experiment are stated in detail as follows:

1. For the flow diagram of the adsorption of sulfur dioxide on Douglas fir woodchips, see Fig. 6.
2. The following equipment was used in this experiment:
 - 2.1 Flowmeter: Predictable flowmeters manufactured by Manostat Corp., New York, Cat. No. 36-541-14, were used for measurement of gas flow ranging from 7.5 to 2,120 ml./minute.
 - 2.2 Thermometer: Ordinary thermometers were used in the range of -10°C to 100°C .
 - 2.3 SO_2 distribution apparatus:

As shown in Fig. 7, the SO_2 apparatus is a side-connected U-tube with one side filled with glass beads and the other side with one or more SO_2

Fig. 6. Flow diagram for the adsorption of sulfur dioxide on Douglas fir woodchips

Fig. 7. SO₂ distribution apparatus

permeation tubes.

2.4 SO₂ permeation tube: These tubes are made with plastic and filled with liquid SO₂ and both ends of the tube sealed. After initial conditioning, the permeation rate of SO₂ in a section of plastic tubing proceeds at a constant rate which depends on the temperature. The length of tube needed to produce the desired gas concentration can be estimated (22) by the following equations:

$$C = (K \times P_t \times L)/F \quad [10]$$

and
$$L = (C \times F)/(K \times P_t) \quad [11]$$

where C = SO₂ concentration in gas stream, ppm by volume

K = variable conversion factor depending on gases used,
for SO₂, K = 0.382 @ 1 atm. and 25°C.

P_t = permeation rate for stated operation temperature, t
(see Fig. 8).

L = active permeation tube length, cm.

F = Flowrate of carrier gas past the tube, cm³/min.

2.5 Adsorber:

An ordinary plastic or glass gas dryer was used as the adsorber. The size of the adsorber used was 1.7 cm. diameter X 15 cm. length with a 3.1 cm. diameter bulge. The volume estimated is about 41.6 cu. cm. Calculations of the required diameter of the adsorber, according to Campbell, et. al, are presented in Appendix II.

2.6 Sampling bubbler:

A series of all-glass midget impingers, which can be supplied by Ace Glass Company or Gelman Instrument Company, was used for sampling of SO₂ in the carrier gas before and after the adsorber.

Fig. 8. SO₂ nominal permeation rates for "Dynacal" tubes

2.7 Vacuum pump:

An oilless air compressor with 1/12 h.p., 1,725 rpm, Model No. LG, Identification No. GH, was used to draw the gas through the system. This pump is manufactured by Bell & Gossett Co., Morton Grove, Ill.

2.8 Spectrophotometer:

This experiment used a method of colorimetric analysis (West and Gaeke Method) to detect the trace amount of SO_2 that existed in a solution. A type of spectrophotometer, made by B & L Company was employed.

2.9 SO_2 monitor:

A Davis SO_2 Monitor, Model 70A1, was used to obtain continuous readings. This SO_2 monitor operates on the principle of electrical conductance caused by ionization of dissolved material.

3. Procedure for obtaining of results:

Data were obtained both by wet analysis and SO_2 monitor readings. The readings of the SO_2 monitor were occasionally checked by the West and Gaeke Method (16,17,34) (see Appendix III), in which SO_2 reacts with sodium tetrachloromercurate to form the dichlorosulfitomercurate ions, then reacts with acid-bleached para-rosaniline and formaldehyde to produce a red purple color. A spectrophotometer set at a wavelength of 560 m μ is then used to detect the different concentrations of SO_2 in the samples. In the overall study, about two-thirds of the results were obtained directly by the West & Gaeke method because of its great accuracy.

4. Adsorbent used: Douglas fir

4.1 The adsorbent used in this experiment was Douglas fir. Douglas fir (*Pseudotsuga taxifolia*) was named after the Scottish botanist, David Douglas. It is not a true fir, but belongs, botanically, to a separate species. The Douglas fir is regarded as the principal timber tree in the Northwest,

and comprises over 70% of the lumber produced in that area. The Douglas fir of the coast region is more widely used than any other American softwood. Due to contemporary framing and structural techniques, Douglas fir has become increasingly important as a building material for engineering structures. Its constituents make this species ideal for such usages as light framing for residential construction, and heavy framing for durable railway and highway bridges, and also for marine structures. Other uses for this wood include: railway ties, mine timbers, boxes, crates, silos, pulp, cooperage, car construction, furniture, containers for corrosive chemicals, and general mill-work.

4.2 There is a great amount of sawdust or woodchips produced in the processing of forest products. Most of these woodchips are considered to be waste material, and are used as land-fills. Some, of course, are utilized by pulp mills, or exported to other countries. However, the quantity is limited. According to Brown (4) and a U.S. Department of Agriculture report (33), 6,828 million cu. ft. of sawdust were produced in 1952. Since Douglas fir is a main timber cut in the U.S., selection of Douglas fir as an experimental adsorbent approaches both problems of air pollution and solid waste disposal.

4.3 Selection of adsorbent size:

Douglas fir was screened to separate an adequate and homogeneous materials for the experiment. Some physical and chemical properties of Douglas fir are given in tables IV and V. U.S. Standard sieves (ASTM E-11) No. 4 (Opening: 0.187 in. or 4.76 mm.) and No. 8 (Opening: 0.0937 in. or 2.38 mm.) were used for selection of sawdust sizes. Reasons for selection of uniform size are: 1) Larger solids do not give enough contacting surfaces between carrier gas and adsorbent. 2) Fine sawdust packed in the adsorber would produce a greater drop in pressure and could, therefore, be blown out through

TABLE IV

SOME PHYSICAL PROPERTIES OF DOUGLAS FIR

1. Color:

Heartwood: Orange red to red, sometimes yellow
 Sapwood: White to pale yellow

2. Weathering: Weathers to dark gray color with little or no sheen.

3. Growth: Growth rings delineated by pronounced band of dark summerwood.

4. Decay resistance: Heartwood is moderately durable, sapwood of species is non-durable.

5. Weight (Average):

Moisture content %	lb./ft ³	Density g./cm ³	Linear wt. lb./1,000 board ft.
8	33.1	0.53	2,760
16	34.3	0.55	2,860
20	35.1	0.561	2,920
24	35.8	0.572	2,980

6. Shrinkage and swelling:

Moisture content %	Reduction from size fiber saturation (unseasoned)		
	Vertical grain face %	Flat	grain face %
8	3.7		5.6
16	2.4		3.5
20	1.7		2.6

7. Moisture equilibrium:

Moisture content %	Relative humidity at	
	30°C	100°C
8	40 %	46 %
10	52 %	59 %
12	63 %	69 %
16	78 %	85 %
20	87 %	90.5 %
24	93 %	95.5 %

TABLE IV

**SOME PHYSICAL PROPERTIES OF DOUGLAS FIR
(CONTINUED)**

8. Moisture content in heartwood, sapwood and chips

	Moisture content (Average for fresh sawn lumber)
Heartwood	37 %
Sapwood	115 %
Chips	56.4%

- 9. Thermoconductivity:** 1 inch of net thickness
 Average $K = 1.0$ at 15% moisture content
 $K = 0.76$ at 0% moisture content

- 10. Thermal expansion:** In unit of length or width for 1 °F of
 temperature change

Longitudinal: 1.7×10^{-6} to 2.5×10^{-6}
 Vertical grain face: 1.43×10^{-5}
 Flat grain face: 2.07×10^{-5}

- 11. Specific gravity:**

	Sp. gr. .
Unseasoned	0.45
Air dry	0.48
(12 % moisture content)	

- 12. Electrical properties:**

Moisture content	Megaohms of resistance @ 80°F
%	
8	4,780
12	120
16	11.2
20	2.14
24	0.60

TABLE V

SOME CHEMICAL PROPERTIES OF DOUGLAS FIR

1. Chemical Compositions:

1.1 Soluble matters:

1.1.1 In alcohol: 4.20%

1.1.2 In hot water: 3.20% (This extraction made on residues after alcohol extraction).

1.2 Lignin content: 25.8%

1.3 Holocellulose (Carbohydrate fraction of extractive-free cell wall substance): 65.95%

2. Water effect:

Residue strength after soaking
in water

At room temperature

102 %

Boiling

76 %

3. Chemical effect: Residue strength after soaking in chemicals compared to water soaking

Chemicals	Room temperature		Boiling	
	Residue strength	Solution	Residue strength	Solution
HCl acid	67%	5%	59%	1%
H ₂ SO ₄ acid	91%	20%	67%	1%
HNO ₃ acid	65%	5%	59%	1%

the outlet tubing.

4.4 Measurement of the moisture content in the sawdust:

4.4.1 Separately weigh a container before and after filling with sawdust.

4.4.2 Place the sawdust in an oven and dry at 100°C to constant weight.

4.4.3 The moisture content of the sawdust is calculated in the following equations:

$$W = W_o (1 - M/100) \quad [12]$$

$$M = 100 (W - W_o)/W_o \quad [13]$$

where W = the weight at initial moisture.

W_o = the oven-dry weight.

M = the percentage of moisture in the sample based on oven-dry weight.

4.5 Classification and preparation of sawdust moisture content in the experiment:

In order to determine the adsorptivity of sulfur dioxide on woodchips, different moisture contents in sawdust were employed. First, dry sawdust samples were obtained as mentioned previously. Moistened sawdust samples were prepared in the following steps:

4.5.1 An empty dry flask was weighed and the dry sawdust was added.

4.5.2 A volume of distilled water equivalent to the moisture content required to make the required percentage of moisture was added to the dry wood.

For instance, exactly 1 ml. of distilled water was pipetted into the flask for 5 grams of dry sawdust to make a 20% moisture sample assuming that the density of water is equal to 1.

4.5.3 The flask was stopped and shaken to distribute the water homogeneously.

4.5.4 Immediately after preparing the samples of woodchips, the adsorber was filled and packed. The flask was weighed to determine if any of the sawdust or residue remained in the flask.

4.5.5 Five moisture levels were used:

4.5.5.1 Dry wood (0% of moisture content).

4.5.5.2 11% of moisture content.

4.5.5.3 20% of moisture content.

4.5.5.4 50% of moisture content

4.5.5.5 Saturated moisture content.

5. Recording of the experiment:

5.1 The temperature (dry bulb and wet bulb temperature), pressure, and the relative humidity of the supplied air and the vacuum pressure of the pump were recorded.

5.2 The weight of dry woodchips used for the adsorption, the moisture added, and the residues left in the preparation apparatus were measured before the woodchips were packed into the adsorber.

5.3 When samples were taken continuously, the temperature of the water bath (or the thermostat) of the SO_2 -distributor, total inlet of air flow, the flowrate in each branch, and the sampling time were recorded.

5.4 When the SO_2 -monitor was used, readings were obtained every half minute.

CHAPTER V

EXPERIMENTAL RESULTS

1. Three atmospheric SO_2 concentrations, 1.12 ppm., 1.83 ppm., and 4.60 ppm., were used. To each of the three concentrations, the selected Douglas fir woodchips were used for the experiments. These woodchips were matched, according to Chapter IV, Section 4.5.5, to five moisture levels. The results of these 15 combinations are presented in Appendix Table 1 to 15 and are shown in figures 9 through 23. The data were plotted in accordance with the calculated results presented in those tables. The experimental time including the preparation of the experiments, ranged from two hours for the shortest experiment to 20 hours for the longest one. For an influent SO_2 concentration of 1.12 ppm., 6.25 g., 7.00 g., 6.81 g., 6.64 g., and 6.00 g of woodchips were used. For an influent SO_2 concentration of 1.83 ppm., 6.15 g., 6.83 g., 5.85 g., 6.72 g and 7.00 g of woodchips were used, and for an influent SO_2 concentration of 4.60 ppm., 6.40 g., 6.71 g., 7.16 g., 6.93 g. and 6.89 g. of woodchips were used. For the above-mentioned quantities of woodchips, moisture levels of 0%, 11%, 20%, 50% and saturated were employed.

2. For additional testing of dry wood adsorptivity, concentrations of SO_2 of 0.675 ppm., 0.775 ppm., 0.85 ppm. and 3.60 ppm. were employed. Comparison of the adsorption of sulfur dioxide on dry wood for all SO_2 influent concentrations is shown in Fig. 24. It is clear from the experimental results that the dry woodchips do have some features in the adsorption of sulfur dioxide.

3. Comparisons of SO_2 saturation rates in the different moisture con-

Fig. 9. The adsorption of SO_2 on dry wood at an influent SO_2 concentration of 1.12 ppm.

Fig. 10. The Adsorption of SO_2 on wood with 11% H_2O at an influent SO_2 concentration of 1.12 ppm.

Fig. 11. The adsorption of SO₂ on wood with 20% H₂O at an influent SO₂ concentration of 1.12 ppm.

Fig. 12. The adsorption of SO_2 on wood with 50% H_2O at an influent SO_2 concentration of 1.12 ppm.

Fig. 13a. The adsorption of SO_2 on wood with saturated moisture at an influent SO_2 concentration of 1.12 ppm.

Fig. 13b. The adsorption of SO_2 on wood with saturated moisture at an influent SO_2 concentration of 1.12 ppm.

Fig. 14. The adsorption of SO_2 on dry wood at an influent concentration of 1.83 ppm.

Fig. 15. The adsorption of SO_2 on wood with 11% H_2O at an influent SO_2 concentration of 1.83 ppm.

Fig. 16. The adsorption of SO_2 on wood with 20% H_2O at an influent SO_2 concentration of 1.83 ppm.

Fig. 17. The adsorption of SO_2 on wood with 50% H_2O at an influent SO_2 concentration of 1.83 ppm.

Fig. 18. The adsorption of SO_2 on wood with saturated moisture at an influent SO_2 concentration of 1.83 ppm.

Fig. 19. The adsorption of SO_2 on dry wood at an influent SO_2 concentration of 4.60 ppm.

Fig. 20. The adsorption of SO_2 on wood with 11% H_2O at an influent SO_2 concentration of 4.60 ppm.

Fig. 21. The adsorption of SO_2 on wood with 20% H_2C at an influent SO_2 concentration of 4.60 ppm.

Fig. 22. The adsorption of SO₂ on wood with 50% H₂O at an influent SO₂ concentration of 4.60 ppm.

Fig. 23. The adsorption of SO_2 on wood with saturated moisture at an influent SO_2 concentration of 4.60 ppm.

Fig. 24. Comparison of the saturation rate of sulfur dioxide on dry wood at different influent SO_2 concentrations

tents of wood for influent SO_2 concentrations of 1.12 ppm., 1.83 ppm., and 4.60 ppm. are shown in Fig. 25 to 27 respectively. It was found that the higher the moisture content in the wood, the longer the time needed to reach saturation for SO_2 in the wood. At an influent SO_2 concentration of 1.12 ppm., the saturation time of SO_2 for dry wood was 45 minutes. This increased to 210 minutes for 11% moisture; to 240 minutes for 20%; to 720 minutes for 50%; and to 1080 minutes for the saturated wood. For an influent concentration of 1.83 ppm., the time it took to reach saturation was 8 minutes for dry wood; 16 minutes for 11%; 18 minutes for 20%; 35 minutes for 50%; and 300 minutes for the saturated wood. For an influent SO_2 concentration of 4.60 ppm., the time taken to reach saturation was 9 minutes for dry wood; and increased to 30 minutes for 11%; to 80 minutes for 20%; to 93 minutes for 50%; and 125 minutes for the saturated wood.

4. For each of the three influent SO_2 concentrations, Table VI to VIII give the adsorption efficiencies of the woodchips at 0 time, the 5th minute, the 10th minute and the final wood adsorptivity at different moisture content of wood samples. For an influent SO_2 concentration of 1.12 ppm., the adsorption efficiency was 66% for the first minute of the experiment with dry wood; it decreased to 47.3% after 5 minutes; to 45.5% after 10 minutes; and the overall efficiency was 22.2%. However, for the wood with moisture content the adsorption efficiencies reached 100% in the first minute and decreased slowly with respect to time. The overall adsorption efficiencies were 33.1% for 11% moisture wood; 42.5% for 20% wood; 64.4% for 50% wood; and 65.9% for saturated wood. For an influent concentration of 1.83 ppm., the overall efficiencies were 7.34, 34.1, 48.4, 32.8 and 20.6 percent for dry wood, 11% moisture wood, 20%, 50% and saturated wood respectively. For an influent concentration of 4.60 ppm., the overall efficiencies were 5.7%, 18.9%, 22.8%,

Fig. 25. Adsorption of SO_2 by Douglas Fir woodchips for an influent SO_2 concentration of 1.12 ppm.

Fig. 26. Adsorption of SO_2 by Douglas fir woodchips for an influent SO_2 concentration of 1.83 ppm.

Fig. 27. Adsorption of SO_2 by Douglas Fir woodchips for an influent SO_2 concentration of 4.60 ppm.

TABLE VI

ADSORPTION EFFICIENCIES AND ADSORPTIVITY OF WOOD FOR AN INFLUENT SO₂
CONCENTRATION OF 1.12 PPM. (2.94 µG./L.)

Moisture content of wood,		%	0	11	20	50	Saturated	
Weight of wood used,		g.	6.25	7.00	6.81	6.64	6.00	
Water added on wood,		ml.	0	0.77	1.37	3.32	11.50	
Time to reach the saturation of SO ₂ on wood,		min.	45	210	240	720	1080	
SO ₂ removed by wood	At zero time	Removed conc.	ppm.	0.74	1.12	1.12	1.12	1.12
		Removed effic.	%	66	100	100	100	100
		Quantity of SO ₂ removed	µg.	1.94	2.94	2.94	2.94	2.94
		Wood adsorptivity	ug/g.	0.31	0.42	0.43	0.44	0.49
	5 minutes	Removed conc.	ppm.	0.53	1.09	1.12	1.12	1.12
		Removed effic.	%	47.3	97.4	100	100	100
		SO ₂ cumulated on wood	µg.	11.51	20.14	20.60	20.6	20.6
		Cumulated wood adsorptivity	µg/g.	1.84	2.88	3.02	3.09	3.43
	10 minutes	Removed conc.	ppm.	0.51	1.08	1.12	1.12	1.12
		Removed effic.	%	45.5	96.5	100	100	100
		SO ₂ cumulated on wood	µg.	15.53	34.34	38.2	38.2	38.2
		Cumulated wood adsorptivity	µg/g.	2.48	4.92	5.61	5.74	6.35
Total SO ₂ retained on wood		µg.	29.37	203.93	299.9	1364.7	2090.5	
Total wood adsorptivity,		µg/g.	4.69	29.13	43.97	205.8	348.0	
Total volume of air sampled,		liters	45	210	240	720	1080	
Total quantity of SO ₂ passed through adsorbent bed,		µg.	132.1	617.5	705.5	2118	3179	
Overall adsorption efficiency,		%	22.2	33.1	42.5	64.4	65.9	

TABLE VII

ADSORPTION EFFICIENCIES AND ADSORPTIVITY OF WOOD FOR AN INFLUENT SO₂
CONCENTRATION OF 1.83 PPM. (4.79 µg./L.)

Moisture content of wood,			%	0	11	20	50	Saturated
Weight of wood used,			g.	6.15	6.83	5.85	6.72	7.00
Water added on wood,			ml.	0	0.75	1.17	3.36	14.0
Time to reach the saturation of SO ₂ on wood,			min.	8	16	18	35	300
SO ₂ removed by wood	At zero time	Removed conc.	ppm.	1.07	1.50	1.55	1.58	1.63
		Removed effic.	%	58.7	82.0	84.7	86.3	89.1
		Quantity of SO ₂ removed	µg.	1.76	9.83	5.07	5.18	26.7
		Wood adsorptivity	µg/g.	0.29	1.37	0.87	0.77	3.79
	5 minutes	Removed conc.	ppm.	0.05	0.94	1.33	1.08	1.52
		Removed effic.	%	2.8	51.3	72.7	59.0	83.1
		SO ₂ cumulated on wood	µg.	7.63	52.0	79.3	101.6	76.5
		Cumulated wood adsorptivity	µg/g.	1.24	7.61	13.54	15.11	10.84
	10 minutes	Removed conc.	ppm.	0	0.26	0.96	0.95	1.42
		Removed effic.	%	0	14.2	52.5	51.9	77.6
		SO ₂ cumulated on wood	µg.	7.73	63.39	98.13	114.0	123.0
		Cumulated wood adsorptivity	µg/g.	1.26	9.38	16.79	17.96	17.58
Total SO ₂ retained on wood,			µg.	7.73	65.26	107.24	143.23	745.15
Total wood adsorptivity,			µg/g.	1.26	9.56	18.35	21.35	106.38
Total volume of air sampled,			liters	21.88	40	46.3	91.3	756.3
Total quantity of SO ₂ passed through adsorbent bed,			µg.	105.3	191.9	221.9	437.5	3623.0
Overall adsorption efficiency,			%	7.34	34.1	48.4	32.8	20.6

TABLE VIII

ADSORPTION EFFICIENCIES AND ADSORPTIVITY OF WOOD FOR AN INFLUENT SO₂
CONCENTRATION OF 4.60 PPM. (12.05 µG./L.)

Moisture content of wood,			%	0	11	20	50	Saturated
Weight of wood used,			g.	6.40	6.71	7.16	6.93	6.89
Water added on wood,			ml.	0	0.74	1.44	3.47	13.8
Time to reach the saturation of SO ₂ on wood,			min.	9	30	80	93	125
SO ₂ removed by wood	At zero time	Removed conc.	ppm.	1.75	3.33	3.88	3.96	4.15
		Removed effc.	%	38.0	72.4	84.5	86.2	90.3
		Quantity of SO ₂ removed	µg.	5.75	11.0	24.8	26.0	27.2
		Wood adsorptivity	µg/g.	0.90	1.64	3.46	3.75	3.94
	5 minutes	Removed conc.	ppm.	0.1	2.10	3.69	3.96	4.15
		Removed effc.	%	2.0	45.6	80.2	86.2	90.3
		SO ₂ cumulated on wood	µg.	13.85	90	142.6	159.75	163.3
		Cumulated wood adsorptivity	µg/g.	2.17	13.42	20.21	28.5	23.64
	10 minutes	Removed conc.	ppm.	0	1.19	3.33	3.96	3.95
		Removed effc.	%	0	25.8	72.4	86.2	83.6
		SO ₂ cumulated on wood	µg.	15.26	139.8	261	338	343.1
		Cumulated wood adsorptivity	µg/g.	2.38	20.82	36.47	48.78	49.76
Total SO ₂ retained on wood,			µg.	15.26	215.8	548.3	1168.1	1446.2
Total wood adsorptivity,			µg/g.	2.38	32.2	76.7	168.56	209.56
Total volume of air sampled,			liters	22.5	750	200	232.5	312.5
Total quantity of SO ₂ passed through adsorbent bed			µg.	301.25	1205	2410	2800	3770
Overall adsorption efficiency,			%	5.7	18.9	22.8	41.7	40.9

41.7% and 40.9% for dry wood, 11%, 20%, 50% and saturated wood respectively. It is very clear that the adsorptvity of SO_2 on wood increased with increasing moisture content in wood.

5. For an influent SO_2 concentration of 1.12 ppm., the SO_2 retained in wood ranged from 29.37 μg . of SO_2 in the dry wood to 203.93 μg . in 11% wood; to 299.9 μg . in 20%; 1364.7 μg . in 50%; and to 2090.5 μg . in the moisture saturated wood. For an influent SO_2 concentration of 1.83 ppm., the SO_2 adsorbed in wood ranged from 7.734 μg . for the dry wood to 65.26 μg . for 11% wood; to 107.24 μg . for 20%; to 143.23 μg . for 50%; to 745.15 μg . for the saturated wood. For an influent concentration of 4.60 ppm., SO_2 adsorbed in wood were 15.26 μg . for the dry wood; 215.8 μg . for 11%; 548.3 μg . for 20%; 1168.13 μg . for 50%; and 1446.2 μg . for the saturated wood. The influence of moisture content on the adsorption of sulfur dioxide on wood at the different influent SO_2 concentrations is shown in Fig. 28.

6. The proportionality constants "K" and "n" in the Freundlich equation obtained by substituting the experimental data into the equation are presented in Table IX. For an influent SO_2 concentration of 1.12 ppm., the values of "K" increased from 1.1 for the dry wood to 235.0 for the moisture saturated wood. However, the constant "n" decreased from 1.38 to 0.373. For an influent concentration of 1.83 ppm., the constant "K" increased from 0.13 to 14.0 while the values of "n" decreased from 1.47 to 0.82. And for an influent concentration of 4.60 ppm., the constant "K" increased from 0.1 for dry wood to 33.0 for the saturated wood while the constant "n" decreased from 1.13 down to 0.777. Referring to the above data, the Freundlich adsorption isotherms are plotted for the sulfur dioxide on three different influent SO_2 concentrations in log-log papers as shown in Fig. 29 to 31.

Fig. 28. Influence of moisture on the adsorption of SO₂ by wood at the different influent SO₂ concentrations.

TABLE IX

LIST OF THE VALUES OF THE CONSTANTS "K" AND "n" IN FREUNDLICH
EQUATION FOR THE ADSORPTION OF SULFUR DIOXIDE ON
DOUGLAS FIR WOODCHIPS

Percent of moisture on wood	Influent SO ₂ concentration, ppm.					
	1.12		1.83		4.60	
	K	n	K	n	K	n
0	1.1	1.38	0.13	1.47	0.10	1.13
11	14.5	0.64	1.6	1.12	0.76	1.55
20	34.2	0.184	6.3	1.0	15.5	0.654
50	160.0	0.388	9.0	0.82	59.0	0.514
200 (Saturated)	235.0	0.373	14.0	1.3	33.0	0.777

Fig. 29. Freundlich Adsorption Isotherm for Sulfur Dioxide on wood for an Influent SO_2 Concentration of 1.12 ppm.

Fig. 30. Freundlich Adsorption Isotherm for Sulfur Dioxide on wood for an Influent SO_2 Concentration of 1.83 ppm.

Fig.31. Freundlich Adsorption Isotherm for Sulfur Dioxide on wood for an Influent SO_2 Concentration of 4.60 ppm.

CHAPTER VI

DISCUSSION

1. The results of the experiment show that Douglas fir woodchips do have the ability to adsorb sulfur dioxide. However, the adsorptivity, which has been considered to be low on dry wood, is proportional to the moisture content of wood. The higher the moisture content in wood, the greater the adsorptivity of SO_2 and also the longer the time required to reach saturation. This is obviously shown in the figures from Fig. 9 to Fig. 27. For instance, at an influent concentration of SO_2 of 1.12 ppm., the dry wood adsorptivity was 4.69 $\mu\text{g. SO}_2$ per g. wood, while it increased to 43.97 on the woodchips with 20% moisture and to 348.0 on woodchips which were saturated. The time needed to reach the saturation of SO_2 on wood was 45 minutes for the dry wood, up to 240 minutes for the wood with 20% of moisture and 1,080 minutes for the wood with saturated moisture.

2. In the process of adsorption, gas flowrate through the adsorption bed has an important effect on the adsorption efficiencies. The adsorptivity was greatly reduced by increasing the flowrate of the passing gases to the point where adsorbate had inadequate contact with adsorbent. If the time of retention and adsorption efficiencies are compared with the same moisture content at two different flowrates, it is found that the retention time of the lower flowrate is longer than that of the higher flowrate and the adsorption efficiencies of the low-rate are also higher than that of high-rate. For example, comparisons of an influent SO_2 concentration of 1.12 ppm. (1 liter per minute of flowrate) and 1.83 ppm. (2.5 liter per minute of flow-

rate) in Tables VI and VII, we find that it took 45 minutes for the flowrate of 1 liter/min. to reach the end point on dry wood, but at the same conditions, it took only 8 minutes for the flowrate of 2.5 liter/min. to do so. The adsorption efficiencies for the flowrate of 1 liter/min. were also higher than those of flowrate of 2.5 liter/min.

3. The quantity of sulfur dioxide adsorbed at different conditions of wood moisture is shown on Figure 28. The adsorption of SO_2 on different moisture content of wood can be predicted from these values. For instance, if the influent concentration of SO_2 of 1.12 ppm. is employed it can be predicted from Fig. 28 that about 6 grams of woodchips with 100% of moisture content will retain approximately 1,630 micrograms of SO_2 .

4. The temperature and humidity in the laboratory, adjusted by the air conditioner, were kept constant. After five measurements at different times, it was found that the dry-bulb temperature in the laboratory was 26°C (78.8°F) and the wet-bulb temperature was 19°C (66.2°F). According to humidity chart, the relative humidity is 50% and the absolute humidity is 0.011 lb. water per lb. dry air when the dry-bulb temperature is 26°C and the wet-bulb temperature is 19°C . In other words, the air in the laboratory was drier than the saturated air at the same temperature. The effluent temperature of the adsorber also measured about 26°C , i.e., the effluent gas was partially saturated by carrying over some moisture from the wood. Assuming the relative humidity (R. H.) of the effluent gas was raised to 80%, the water requirements for the influent gas are then $0.0169 - 0.011 = 0.0058$ lb. H_2O per lb. dry air. If 100 liters of sampled air are pumped through the adsorber, assuming that the air is at 1 atm. and 26°C , the quantities of air can, according to the idea gas law, be estimated as follows:

$$W = PVM/RT = (29 \times 1 \times 100)/(0.082 \times 299.2) = 118.2 \text{ g.}$$

and thus the water carried over by air = $118.2 \times 0.0058 = 0.686\text{g}$ per 100 liter of dry air. This means that the moisture in the woodchips was substantially reduced by the carrier gas. Of course, the quantities of moisture lost in the carrier gas are determined by the flowrate of the gas. A low flowrate of gas was applied, it did not cause great difference between the relative humidity of the effluent gas and that of the influent gas. The reason is that the higher flowrate will produce larger forces on the adsorbent from which more moisture will be removed.

5. The total quantities of sulfur dioxide adsorbed on wood were increased with a reduction of the flowrate of sampled air. As shown in Fig. 28, the total SO_2 retained on the wood having 1 liter/min. as the flowrate and 1.12 ppm. SO_2 concentration is greater than the other two higher concentrations with higher flowrates. For example, when the quantities of SO_2 retained on wood were compared, it was found that there were 2090.5 $\mu\text{g.}$ of SO_2 retained on the wood with saturated moisture content for the influent SO_2 concentration of 1.12 ppm. with a flowrate of 1 liter/min. However, there were 745.15 $\mu\text{g.}$ and 1446.2 $\mu\text{g.}$ of SO_2 retained on the wood at the same conditions for the two higher concentrations with higher flowrates. Three reasons are proposed to explain this phenomena: First, the adsorbent cannot be kept in good condition to retain adsorbate when the larger forces of carrier gas are applied to it. Second, the adsorptivity and absorptivity of wood (with moisture) is greatly affected by the moisture in wood, being gradually carried over by drier carrier gas. Third, the sulfur dioxide originally dissolved in the water and retained in the wood pores was re-entrained back to the carrier gas as the moisture was gradually transferred from the wood to the carrier gas at the final stage of the experiment.

6. The difference between the maximum influent SO_2 concentration used in this experiment, 4.60 ppm. (11.6 mg/M^3), and that of most industrial plants is very large. There is no doubt, however, that the higher the concentration of SO_2 in the flue gas, the more sulfur dioxide would be removed by wood and moisture.

7. It was found by taking samples without the adsorbent in the system that no sulfur dioxide was adsorbed by the adsorber or by any adsorption equipment. In other words, there was no SO_2 lost in the adsorption system caused by the tubings and the materials of the adsorber.

8. By substituting the observed results in the Freundlich equation, it was found that most of the data fit the equation. The straight lines in Fig. 29 to 31 show that the Freundlich equation can be used to describe the adsorption of sulfur dioxide on wood. As presented in Table IX and Section 6 of Chapter V, the values of the constant "K" in the Freundlich equation, Eq. [3], increase with increasing moisture content in wood. On the contrary, the slope "n" decreased with an increase in the moisture content in wood. Also, it was found that the values of "K" of the dry wood samples 1.1, 0.13 and 0.10, were all much lower than those of wood containing moisture. The adsorptivity of sulfur dioxide between dry and wet wood was greatly different. This situation was, however, reduced when more water was added to the wood as shown in Fig. 29, etc. Therefore, we can predict that the adsorptivity of sulfur dioxide on wood has a limit no matter how much moisture it contains, because it changes into the absorption of sulfur dioxide in water and the absorptivity is increased when the wood retains the extra moisture. By means of the Freundlich equation, it is possible to closely calculate the adsorption phenomena of the sulfur dioxide

on wood at various moisture contents.

9. The accuracy of Eq. [7] has been confirmed by substituting and checking most of the data from Appendix Table 1 to 15. The constant k in Eq. [8] can, therefore, easily be obtained if the values of C_a and C_b are measured and evaluated. For example, $C_b = 1.12$ ppm., $V = 1$ liter/min., $M_g = 6.25$ g.,

when $t = 18$ minutes, $C_a = 0.91$ ppm., substituting into Eq. [8], we have

$$0.91 = 1.12 (1 - \exp(-k \times 1 \times 18 / 6.25))$$

$$k = 0.592$$

Therefore, when $t = 5$ min., the theoretical value of C_a should be

$$C_a = 1.12 (1 - \exp(-0.592 \times 1 \times 5 / 6.25)) = 0.43 \text{ ppm.}$$

This is compared to the experimental result of 0.59 ppm. By the same method of calculation, when $t = 40$ min., C_a is obtained to be 1.09 ppm., which is compared to the experimental value of 1.07 ppm.

Another example, $C_b = 1.83$ ppm., $V = 2.5$ liter/min., $M_g = 6.15$ g., when $t = 3$ min., $C_a = 1.72$ ppm., constant k is determined to be 2.3.

By the same format of calculation mentioned above, when $t = 7$ min., we have $C_a = 1.828$ ppm. compared to the experimental result of 1.825 ppm. Also, when $t = 1$, the C_a is calculated to be 1.12 ppm. compared to the experimental result of 1.30 ppm.

The third example, $C_b = 4.60$ ppm., k is determined to be 3.0 when $V = 2.5$ liter/min., $M_g = 6.40$ g., and $t = 3$ min., $C_a = 4.47$ ppm. We then obtain $C_a = 4.59$ ppm (when $t = 7$) compared to the experimental value of 4.56 ppm and $C_a = 3.18$ ppm. (when $t = 1$) compared to the experimental value of 3.96 ppm.

Moreover, the adsorptivity and the retention time of wood on the adsorption of sulfur dioxide to any concentration of sulfur dioxide may, according to the same equation developed, be estimated.

CHAPTER VII

SUMMARY AND CONCLUSION

1. Summary

1.1 The study of the adsorption of sulfur dioxide on Douglas fir woodchips has shown that the wood can be used as an adsorbent to selectively remove sulfur dioxide from a dilute gaseous air-SO₂ stream. The moisture content in wood played an important part in the adsorption of SO₂. The adsorption efficiencies were very satisfactory for moistened wood especially for saturated wood. The Freundlich equation can be used to describe the adsorption of sulfur dioxide on woodchips. Other equations were developed to predict the amount of sulfur dioxide accumulated in wood, to predict the time needed to reach saturation of sulfur dioxide on wood, and to predict the effluent concentrations from the adsorbent bed.

1.2 At an influent concentration of SO₂ of 1.12 ppm. (2.94 µg. SO₂ per liter) and with a flowrate of 1 liter/minute, dry Douglas fir woodchips were found to have an adsorptivity of 4.69 µg. of SO₂ per gram of wood; 11 percent moisture of woodchips increased the adsorptivity to 29.13; 20 percent to 43.97; 50 percent to 205.8; and saturated woodchips to 348.0. The time of the experiment taken to reach saturation of sulfur dioxide on wood was 45 minutes for dry wood. It was increased to 210 minutes for 11 percent moisture; to 240 minutes for 20 percent; to 720 minutes for 50 percent; and to 1,080 minutes for the saturated wood.

1.3 At an influent concentration of SO₂ of 1.83 ppm. (4.79 µg. SO₂ per liter) and with a flowrate of 2.5 liter/minute, dry wood was found to

give an adsorptivity of 1.26 $\mu\text{g. SO}_2$ per gram of wood, which increased to 9.56 for 11 percent moisture; 18.35 for 20 percent; 21.35 for 50 percent; and 106.38 for saturated wood. The time needed to reach saturation was 8 minutes for the dry wood. Eleven percent moisture increased it to 16 minutes; 20 percent to 18 minutes; 50 percent to 35 minutes; and saturated was 300 minutes.

1.4 At an influent concentration of SO_2 of 4.60 ppm. (12.05 $\mu\text{g. SO}_2$ per liter) and with a flowrate of 2.5 liter/min, dry wood was found to have an adsorptivity of 2.38 $\mu\text{g. SO}_2$ per gram of wood; 11 percent moisture increased the adsorptivity to 32.2; 20 percent to 76.7; 50 percent to 168.56; and saturated to 209.56. The time required to reach saturation was 9 minutes for the dry wood, and then increased to 30 minutes for the wood with 11 percent of moisture; to 80 minutes for 20 percent; 93 minutes for 50 percent; and 125 minutes for saturated wood.

2. Conclusion

Wood can adsorb sulfur dioxide at least at high concentrations. This has already been shown in some sources which mentioned that the sulfur dioxide in a solution of 2 to 10 percent of SO_2 can be adsorbed either by sprucewood or hemlock chips. For lower ranges of sulfur dioxide concentrations, this study has shown that Douglas fir woodchips can be used as the adsorbent to remove traces of sulfur dioxide from a gas stream regardless of its low adsorptivity on dry wood.

The adsorptivity of the sulfur dioxide on wood is closely related to the moisture content of wood and is reduced with an increase in the flowrate of the carrier gases. More research is needed to determine an optimum gas flowrate through an adsorber to obtain a maximum adsorption equilibrium.

Extensive emission of sulfur dioxide is a problem in many industries.

It was found in this study that traces of sulfur dioxide in the air can be adsorbed on wood especially on those with sufficient moisture. The efficiencies of sulfur dioxide removal by moistened wood reached 100 percent during the first minute in some experiments. The Pacific Northwest is one of the main lumber producing areas in the United States and a great amount of waste woodchips and sawdust are produced from the lumber industry. Using woodchips to treat the residual sulfur dioxide in the waste gases of the plants may not only solve the problem of air pollution but the problem of some solid waste disposal.

Sulfur dioxide retained in wood may present further research topics of how to treat the woodchips which contain SO_2 , how to utilize and/or recover the chips and how to apply to the industrial production. In spite of the problems of treatment of the woodchips, this report may at least bring about an idea to some of the industries such as sulfite pulp industry for providing a means of control of sulfur dioxide pollution and the recovery of raw material. It also reveals that some other pollutants, for instance, hydrogen sulfide, carbon monoxide, ammonia, nitrogen oxides, etc. may be considered as the adsorbate and using wood for further adsorption studies.

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APPENDICES

APPENDIX I

APPENDIX I

SOLUBILITY OF SULFUR DIOXIDE IN WATER

Weight of SO ₂ per 100 wt. of water	Partial pressure of SO ₂ , mm. Hg.							
	0°C	7°C	10°C	15°C	20°C	30°C	40°C	50°C
20	646	657						
15	474	637	726					
10	308	417	474	567	698			
7.5	228	307	349	419	517	688		
5.0	148	198	226	270	336	452	665	
2.5	69	92	105	127	161	216	322	458
1.5	38	51	59	71	92	125	186	266
1.0	23.3	31	37	44	59	79	121	172
0.7	15.2	20.6	23.6	28.0	39.0	52	87	116
.5	9.9	13.5	15.6	19.3	26.0	36	57	82
.3	5.1	6.9	7.9	10.0	14.1	19.7		
.2	2.8	3.7	4.6	5.7	8.5	11.8	...	31.0
.15	1.9	2.6	3.1	3.8	5.8	8.1	12.9	20.0
.10	1.2	1.5	1.75	2.2	3.2	4.7	7.5	12.0
.05	0.6	0.7	0.75	0.8	1.2	1.7	2.8	4.7
.02	.25	.3	.3	.3	0.5	0.6	0.8	1.3

APPENDIX II

APPENDIX II

ESTIMATION OF ADSORBER DIAMETER

Campbell, et. al. (7) developed an equation for the diameter of required adsorbent bed as shown in equation (9) of the text:

$$D = [25(W_g)(T_f)/(P_f)(V_g)]^{\frac{1}{2}}$$

where D = required adsorbent bed diameter, ft.

W_g = gas flowrate, million cu. ft. per day (MMCFD)

T_f = Temperature in adsorber, $^{\circ}\text{R}$

P_f = Pressure in adsorber, psia

V_g = linear gas velocity, ft./min.

Assume that the gas flowrate through the adsorbent bed is 1 liter/min.,

then $W_g = 1 \text{ liter/min.} = 0.0353 \text{ cu. ft./min.} = 50.8 \text{ ft}^3/\text{day}$
 $= 50.8 \times 10^{-6} \text{ MMCFD}$

Diameter of adsorber used is, $D = 1.7 \text{ cm.} = 0.0558 \text{ ft.}$

Cross-sectional area of adsorber, $A = (0.0558)^2 \pi / 4 = 2.47 \times 10^{-3} \text{ ft.}^2$

Gas linear velocity, $V_g = 0.0353 / 2.47 \times 10^{-3} = 14.3 \text{ ft./min.}$

$T_f = 26^{\circ}\text{C} = 78.8^{\circ}\text{F} = 538.8^{\circ}\text{R}; \quad P_f = 14.7 \text{ psia}$

Thus the diameter of required adsorbent is

$$D = [25 (50.8 \times 10^{-6}) (538.8) / (14.7) (14.3)]^{\frac{1}{2}} = 5.68 \times 10^{-2} \text{ ft.}$$

$$= 1.73 \text{ cm.}$$

The diameter of adsorber used, according to the calculation, is just marginal for having 1 liter/min. of gas flow through the adsorbent bed. If the maximum linear velocity of the gas remained unchanged at 14.3 ft./min., and the flowrate increases to 2.5 liter/min. while other conditions remaining at constant, the required adsorber diameter will then be

$$D = (2.5/1)^{\frac{1}{2}} \times 1.73 = 2.73 \text{ cm.}$$

APPENDIX III

APPENDIX III

DETERMINATION OF SULFUR DIOXIDE BY
WEST AND GAEKE METHOD

1. Principle:

Sulfur dioxide reacts with tetrachloromercurate to form the dichlorosulfitomercurate ion, which reacts with acid-bleached para-rosaniline and formaldehyde to produce a red purple color. A spectrophotometer, which sets the exact wavelength, is used to distinguish the samples from the different concentration of sulfur dioxide.

2. Preparation of required reagents:

2.1 Absorbing reagent: 0.1 M. sodium tetrachloromercurate

Dissolve 27.2 g. (0.1 mole) of mercuric chloride and 11.7 g. (0.2 mole) of sodium chloride in 1 liter of distilled water.

2.2 Para-rosaniline hydrochloride (0.04%), acid bleached

2.2.1 Dissolve 0.2 g. of para-rosaniline hydrochloride in 100 ml. of distilled water and filter it after 48 hours.

2.2.2 Pipette 20 ml. of the filtered solution into 100-ml volumetric flask and add 6 ml. of concentrated HCl acid.

2.2.3 Allow the mixture to stand for 5 minutes, then dilute to mark with distilled water. This solution is a pale yellow in color with a greenish tint. It can be stored for about 2 weeks if refrigerated.

2.3 Formaldehyde, 0.2%

Dilute 5 ml. of 40% of formaldehyde to 1 liter with distilled water.

2.4 Standard sulfite solution, 3.0 ul. SO_2 per ml. of solution

Dissolve 59.7 mg. of sodium metabisulfite (assay 67% as SO_2) in 100 ml. of distilled water. This yields a solution of 0.40 mg SO_2 per ml.

3.7.3 Add 1.0 ml. of acid-bleached para-rosaniline solution and 1.0 ml. of the 0.2% formaldehyde solution to each tube and mix.

3.7.4 Allow 20 minutes for maximum color development and use the blank as the reference to read the absorbance of each samples at 560 mμ.

3.7.5 Plot the absorbance (optical density) as the abscissa against the ul. of SO₂ per 10 ml. of absorbing solution on rectangular coordinate paper (Appendix Figure 1). Compute the slope of the straight line.

4. Calculation of the SO₂ concentration:

4.1 Convert the volume of air sampled to the volume at standard conditions of 25 °C and 760 mm Hg. The equation is

$$V_s = V \times (P - P_m) \times (298.2) / (760) \times (t-273.2) \quad [14]$$

where V_s = volume of air in liters at standard conditions

V = volume of air in liters as measured by the meter

P = barometric pressure in millimeter of mercury

P_m = suction at meter in millimeter of mercury

t = temperature of sample air in °K

Generally, the correction for pressure is very small and may be overlooked.

4.2 Compute the microliters (ul.) of SO₂ in the sample by multiplying the absorbance by the slope of the calibration curve.

4.3 The concentration of sample can be calculated by

$$\text{ppm. of SO}_2 \text{ by volume} = \text{ul. SO}_2 / V_s \quad [15]$$

Appendix Fig. 1. Calibration curve in the analysis of SO₂ by West and Gaeke Method

APPENDIX TABLES

Appendix Table 1. Calculation of cumulative amount of SO_2 on dry wood for an influent SO_2 concentration of 1.12 ppm.

Dry wood used = 6.25 g.

Gas flowrate through the adsorber = 1 liter/min.

Time t min.	Sampling time min.	Vol. l.	Effl. SO_2 conc. ppm.	SO_2 adsorbed on wood ppm. $\mu\text{g/l}$.		p^*/p	Quantity of SO_2 on wood @ t, Cum. @t, μg .		Wood Adsorptivity $\mu\text{g. SO}_2/\text{g. wood}$
0	1	1	0.38	0.74	1.94	0.340	1.94	1.94	0.31
3	3	3	0.47	0.65	1.70	0.410	5.10	7.04	1.13
5	3	3	0.59	0.53	1.49	0.527	4.47	11.57	1.84
9	3	3	0.61	0.51	1.34	0.545	4.02	15.53	2.48
12	3	3	0.68	0.44	1.15	0.607	3.45	18.98	3.19
15	3	3	0.32	0.30	0.79	0.731	2.37	21.35	3.42
18	3	3	0.91	0.21	0.55	0.812	1.65	23.00	3.68
21	3	3	0.95	0.17	0.45	0.848	1.35	24.35	3.89
24	3	3	0.97	0.15	0.39	0.866	1.17	25.52	4.08
27	3	3	1.00	0.12	0.31	0.895	0.93	26.45	4.24
30	3	3	1.02	0.10	0.26	0.911	0.78	27.23	4.35
35	5	5	1.04	0.08	0.21	0.930	1.05	28.28	4.53
40	5	5	1.07	0.05	0.13	0.956	0.65	28.93	4.63
45	4	4	1.08	0.04	0.11	0.965	0.44	29.37	4.69

Appendix Table 2. Calculation of cumulative amount of SO_2 on wood with 11% H_2O for an influent SO_2 concentration of 1.12 ppm.

Dry wood used = 7.0 g.

Water added = 0.77 ml.

Gas flowrate through the adsorber = 1 liter/min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood	p*/P	Quantity of SO_2 on wood		Wood
min.	min.	l.	ppm.	ppm.	ng/l.	@ t,	Cum. @ t,	Adsorptivity
						ng.	ng.	ng. SO_2 /g.wood
0	1	1	0	1.12	0.94	0	2.94	0.42
3	6	6	0.029	1.091	2.86	0.026	17.20	2.88
10	5	5	0.032	1.088	2.85	0.035	14.20	4.92
15	5	5	0.066	1.054	2.77	0.059	13.85	6.89
20	5	5	0.20	0.92	2.41	0.179	12.1	8.61
25	5	5	0.34	0.78	2.04	0.302	10.2	10.06
30	5	5	0.35	0.77	2.01	0.312	10.0	10.50
35	5	5	0.41	0.71	1.86	0.365	9.3	12.82
40	5	5	0.43	0.69	1.81	0.383	9.1	14.12
50	10	10	0.44	0.68	1.78	0.392	17.8	16.58
60	10	10	0.59	0.53	1.39	0.526	13.9	19.45
70	10	10	0.62	0.50	1.31	0.553	13.1	20.58
80	10	10	0.68	0.44	1.15	0.607	11.5	22.17
90	10	10	0.76	0.36	0.94	0.680	9.4	23.45
100	10	10	0.95	0.17	0.44	0.850	4.4	24.18
110	10	10	0.78	0.34	0.89	0.700	8.9	25.31
120	10	10	0.85	0.27	0.71	0.760	7.1	26.42
130	10	10	0.97	0.15	0.39	0.866	3.9	26.89
140	10	10	0.98	0.14	0.37	0.875	3.7	27.58
160	20	20	1.04	0.08	0.21	0.928	4.2	28.05
180	20	20	1.05	0.07	0.18	0.937	3.6	28.65
190	10	10	1.08	0.04	0.11	0.963	1.1	28.74
200	20	20	1.09	0.03	0.08	0.974	1.44	29.13

Appendix Table 3. Calculation of cumulative amount of SO_2 on wood with $11\% \text{H}_2\text{O}$ for an influent SO_2 concentration of 1.12 ppm.

Dry wood used = 6.81 g.

Water added = 1.37 ml.

Gas flowrate through the adsorber = 1 liter/min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood	p^*/p	Quantity of SO_2 on wood		Wood
min.	min.	l.	ppm.	ppm.	$\mu\text{g/l.}$	$\mu\text{g.}$	$\mu\text{g.}$	$\mu\text{g. SO}_2/\text{g. wood}$
0			0					
10			0					
20			0					
35			0					
45	50	50	0	1.12	2.94	0	117.0	21.57
60	15	15	0.11	1.01	2.64	0.098	39.6	27.28
75	15	15	0.53	0.59	1.55	0.47	23.2	30.64
90	15	15	0.78	0.34	0.89	0.70	13.3	32.73
100	10	10	0.65	0.47	1.23	0.58	12.3	34.45
115	15	15	0.87	0.25	0.66	0.78	9.9	35.97
125	20	20	0.73	0.39	1.02	0.65	20.4	38.92
150	15	15	0.88	0.24	0.63	0.78	9.5	40.38
160	15	15	0.95	0.17	0.44	0.85	6.6	41.25
180	20	20	0.97	0.15	0.39	0.86	7.8	42.38
200	20	20	1.014	0.106	0.28	0.90	5.6	43.35
220	20	20	1.053	0.067	0.18	0.94	3.6	43.72
240	10	10	1.08	0.04	0.11	0.97	1.1	43.97

Appendix Table 4. Calculation of cumulative amount of SO_2 on wood
with 50% H_2O for an influent SO_2 conc. of 1.12 ppm.

Dry wood used = 6.64 g.

Water added = 3.32 ml.

Gas flowrate through the adsorber = 1 l./min.

Time t, min.	Sampling time min.	Effluent Volume liter	SO_2 conc. ppm.	SO_2 adsorbed on wood ppm. $\mu\text{g}/\text{l.}$	p^*/P	Quantity of SO_2 on wood @ t, Cum. @ t, $\mu\text{g.}$ $\mu\text{g.}$	Wood Adsorptivity $\mu\text{g. SO}_2/\text{g. wood}$
0			0				
30			0				
60	75	75	0	1.12	2.94	0	210 210.0 31.6
90	30	30	0.03	1.09	2.86	0.027	85.7 295.7 44.4
120	30	30	0.03	1.09	2.86	0.027	85.7 381.4 57.4
150	30	30	0.04	1.08	2.82	0.036	84.5 465.9 70.1
180	30	30	0.06	1.06	2.78	0.054	83.4 549.3 82.7
210	30	30	0.04	1.08	2.82	0.036	84.5 632.8 95.2
230	20	20	0.07	1.05	2.75	0.063	55.0 687.8 103.4
260	40	40	0.09	1.03	2.70	0.080	108.0 795.8 120.0
300	30	30	0.14	0.98	2.56	0.125	76.8 872.6 131.4
330	30	30	0.18	0.94	2.46	0.160	73.8 946.4 142.5
360	30	30	0.25	0.87	2.28	0.22	68.4 1014.8 152.9
390	30	30	0.29	0.83	2.17	0.26	65.0 1079.8 162.5
420	30	30	0.38	0.74	1.94	0.34	58.0 1137.8 171.3
450	30	30	0.47	0.65	1.70	0.42	51.0 1188.8 179.0
480	30	30	0.61	0.51	1.34	0.55	40.2 1229.0 185.0
510	30	30	0.65	0.47	1.23	0.58	36.9 1265.9 190.5
540	30	30	0.78	0.34	0.89	0.70	26.7 1292.6 194.7
570	30	30	0.84	0.28	0.73	0.75	21.9 1314.5 197.4
600	30	30	0.93	0.19	0.50	0.83	15.0 1329.5 199.9
630	30	30	0.96	0.16	0.42	0.86	12.6 1342.1 202.0
660	35	35	0.98	0.14	0.37	0.88	13.0 1355.1 204.0
720	40	40	1.03	0.09	0.24	0.92	9.6 1364.7 205.8

Appendix Table 5. Calculation of cumulative amount of SO₂ on wood with saturated H₂O for influent SO₂ conc. of 1.12 ppm.

Dry wood used = 6.0 g.

Water added = 11.50 ml.

Gas flowrate through the adsorber = 1 l./min.

Time t, min.	Sampling time min.	Effluent Volume liter	SO ₂ conc. ppm.	SO ₂ adsorbed on wood ppm. µg/l.	p*/P	Quantity of SO ₂ on wood @ t, µg.	Cum. @ t, µg.	Wood Adsorptivity µg.SO ₂ /g.wood
0			0					
60	80	80	0	1.12	2.94	0	236.2	39.33
90	20	20	0.02	1.10	2.88	0.018	57.5	48.87
120	30	30	0.02	1.10	2.88	0.018	86.4	63.42
150	30	30	0.03	1.09	2.86	0.027	85.6	75.59
180	30	30	0.03	1.09	2.86	0.027	85.6	91.83
210	30	30	0.04	1.08	2.82	0.036	84.6	106.43
240	30	30	0.05	1.07	2.80	0.045	84.0	119.74
270	30	30	0.04	1.08	2.82	0.036	84.6	133.96
300	30	30	0.07	1.05	2.75	0.063	82.5	147.59
330	30	30	0.06	1.06	2.78	0.054	83.4	163.04
360	30	30	0.03	1.09	2.86	0.027	85.6	176.28
390	30	30	0.07	1.05	2.75	0.063	82.5	189.54
420	30	30	0.14	0.98	2.56	0.125	71.9	201.84
450	30	30	0.17	0.95	2.49	0.152	74.7	214.37
480	30	30	0.18	0.94	2.46	0.160	73.9	226.05
510	30	30	0.28	0.84	2.20	0.250	66.0	237.81
540	30	30	0.25	0.87	2.28	0.220	68.5	248.17
570	30	30	0.30	0.82	2.15	0.268	64.5	259.74
600	60	60	0.32	0.80	2.10	0.294	126.0	280.08
660	60	60	0.39	0.73	1.91	0.347	114.6	299.53
720	60	60	0.44	0.68	1.78	0.392	108.8	317.85
780	60	60	0.56	0.56	1.47	0.50	30.0	322.10
840	60	60	0.77	0.35	0.92	0.69	41.4	329.74
900	60	60	0.83	0.29	0.76	0.74	44.4	337.05
930	30	30	0.86	0.26	0.68	0.77	20.2	340.08
960	30	30	0.92	0.20	0.52	0.82	15.6	342.47
990	30	30	0.98	0.14	0.37	0.87	11.1	345.63
1020	30	30	1.02	0.10	0.26	0.91	7.8	345.89
1050	30	30	1.03	0.09	0.24	0.92	7.2	347.29
1080	20	20	1.05	0.07	0.18	0.94	5.4	348.00

Appendix Table 6. Calculation of cumulative amount of SO_2 on dry wood for an influent SO_2 concentration of 1.83 ppm.

Dry wood used = 6.15 g.

Water added = None

Gas flowrate through the adsorber = 1 liter/min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood		p^*/P	Quantity of SO_2 on wood		Wood Adsorptivity
min.	min.	l.	ppm.	ppm.	$\mu\text{g}/\text{l.}$		@ t, $\mu\text{g.}$	Cum.@t, $\mu\text{g.}$	$\mu\text{g. SO}_2/\text{g. wood}$
0	0.25	0.625	0.756	1.074	2.82	0.413	1.762	1.762	0.29
0.5	0.5	1.25	1.305	0.525	1.375	0.713	1.719	3.481	0.57
1	1	2.5	1.62	0.21	0.550	0.885	1.375	4.856	0.79
2	1	2.5	1.67	0.16	0.418	0.912	1.045	5.901	0.96
3	1	2.5	1.72	0.11	0.288	0.939	0.720	6.621	1.08
4	1	2.5	1.725	0.105	0.275	0.942	0.688	7.309	1.19
5	1	2.5	1.78	0.05	0.131	0.972	0.328	7.637	1.24
6	1	2.5	1.82	0.01	0.026	0.994	0.065	7.702	1.25
7	1	2.5	1.825	0.005	0.013	0.997	0.032	7.734	1.26
8	1	2.5	1.83	0	0	1.0	0	7.734	1.26

Appendix Table 7. Calculation of cumulative amount of SO_2 on Wood with 11% H_2O for an influent SO_2 concentration of 1.83 ppm.

Dry wood used = 6.83 g.

Water added = 0.75 ml.

Gas flowrate through the adsorber = 2.5 liter/min.

Time t	Sampl- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood		p^*/P	Quantity of SO_2 on wood @ t, Cum.@ t		Wood Adsorptivity
min.	min.	l.	ppm.	ppm.	$\mu\text{g}/\text{l.}$		$\mu\text{g.}$	$\mu\text{g.}$	$\mu\text{g. SO}_2/\text{g. wood}$
0	1	2.5	0.33	1.50	3.93	0.180	9.83	9.83	1.37
1	1	2.5	0.47	1.36	3.30	0.257	8.25	18.08	2.65
3	2	5.0	0.65	1.18	3.09	0.356	15.45	33.53	4.91
5	3	7.5	0.89	0.94	2.46	0.487	18.46	51.99	7.61
8	2	5.0	1.22	0.61	1.60	0.667	8.00	59.99	8.78
10	2	5.0	1.57	0.26	0.68	0.858	3.40	63.39	9.38
12	1	2.5	1.68	0.15	0.39	0.918	0.98	64.37	9.42
13	1	2.5	1.75	0.08	0.21	0.957	0.53	64.90	9.51
14	1	2.5	1.78	0.05	0.131	0.973	0.33	65.23	9.55
15	1	2.5	1.81	0.02	0.053	0.990	0.03	65.26	9.56
16	1	2.5	1.83	0	0	1.0	0	65.26	9.56

Appendix Table 8. Calculation of cumulative amount of SO_2 on wood with 20% H_2O for an influent SO_2 concentration of 1.83 ppm.

Dry wood used = 5.85 g.

Water added = 1.17 ml.

Gas flowrate through the adsorber = 2.5 liter/min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood		p*/P		Quantity of SO_2 on wood		Wood
min.	min.	l.	ppm.	ppm.	µg/l.			@ t, µg.	Cum. @t, µg.	Adsorptivity µg. SO_2 /g.wood
0	0.5	1.25	0.28	1.55	4.061	0.153		5.07	5.07	0.87-
1	1	2.5	0.28	1.55	4.061	0.153		10.14	15.21	2.59
2	2	5.0	0.28	1.55	4.061	0.153		20.28	35.49	6.07
4	1	2.5	0.46	1.37	3.589	0.251		8.97	44.46	7.61
5	4	10.0	0.50	1.33	3.485	0.273		34.85	79.31	13.54
10	3	7.5	0.87	0.96	2.510	0.475		18.82	98.13	16.79
12	1	2.5	1.15	0.68	1.732	0.628		4.46	102.59	17.65
13	1	2.5	1.38	0.45	1.179	0.755		2.95	105.54	18.14
14	1	2.5	1.61	0.22	0.576	0.880		1.44	106.98	18.26
15	1	2.5	1.81	0.02	0.053	0.990		0.13	107.11	18.30
16	2	5.0	1.82	0.01	0.026	0.991		0.13	107.24	18.35
18	1	2.5	1.83	0	0	1.0		0	107.24	18.35

Appendix Table 9. Calculation of cumulative amount of SO_2 on wood with 50% H_2O for an influent SO_2 concentration of 1.83 ppm.

Dry wood used = 6.72 g.

Water added = 3.36 ml.

Gas flowrate through the adsorber = 2.5 liter/min.

Time t, min.	Samp- ling time min.	Vol. l.	Effl. SO_2 conc. ppm.	SO_2 adsorbed on wood		p^*/P	Quantity of SO_2 on wood		Wood Adsorptivity
				ppm.	$\mu\text{g./l.}$		@ t, $\mu\text{g.}$	Cum. @t, $\mu\text{g.}$	$\mu\text{g. SO}_2/\text{g. wood}$
0	0.5	1.25	0.25	1.58	4.14	0.137	5.18	5.18	0.77
1	2	5.0	0.28	1.55	4.05	0.153	20.30	25.48	3.79
2	3	7.5	0.36	1.47	3.92	0.197	29.40	54.88	8.17
3	3	7.5	0.53	1.30	3.40	0.290	25.50	80.38	11.95
5	3	7.5	0.75	1.08	2.84	0.410	21.22	101.60	15.11
10	2	5.0	0.88	0.95	2.48	0.481	12.40	114.00	17.96
12	2	5.0	1.24	0.59	1.54	0.677	7.70	121.70	18.10
15	4	10.0	1.40	0.43	1.13	0.765	11.30	133.00	19.80
18	2	5.0	1.56	0.27	0.71	0.852	3.55	136.55	20.30
20	2	5.0	1.61	0.22	0.58	0.880	2.90	139.45	20.79
22	3	7.5	1.72	0.11	0.29	0.940	2.18	141.63	21.08
25	4	10.0	1.77	0.05	0.13	0.966	1.30	142.93	21.26
30	4	10.0	1.82	0.01	0.03	0.995	0.30	143.23	21.35
35	2	5.0	1.83	0	0	1.0	0	143.23	21.35

Appendix Table 10. Calculation of cumulative amount of SO_2 on wood with saturated moisture content for influent SO_2 concentration of 1.83 ppm.

Dry wood used = 7.0 g.

Water Added = 14.0 ml.

Gas flowrate through the adsorber = 2.5 l/min.

Time t, min.	Sampling time min.	Effluent Volume liter	SO_2 conc. ppm.	SO_2 adsorbed on wood ppm.	SO_2 adsorbed on wood $\mu\text{g}/\text{l}.$	p^*/P	Quantity of SO_2 on wood @ t, $\mu\text{g}.$	Cum. @ t, $\mu\text{g}.$	Wood Adsorptivity $\mu\text{g}.\text{SO}_2/\text{g}.\text{wood}$
0	2.5	6.25	0.20	1.63	4.27	0.109	26.70	26.70	3.79
5	5	12.50	0.31	1.52	3.98	0.169	49.80	76.50	10.84
10	5	12.50	0.41	1.42	3.72	0.224	46.50	123.00	17.58
15	5	12.50	0.54	1.29	3.38	0.295	42.30	165.30	23.60
20	10	25.00	0.79	1.04	2.72	0.432	68.00	233.30	33.24
30	10	25.00	1.03	0.80	2.10	0.563	52.50	285.80	40.85
40	10	25.00	1.09	0.74	1.94	0.595	48.40	334.20	47.78
55	15	37.50	1.15	0.68	1.78	0.628	66.80	401.00	57.25
60	15	37.50	1.26	0.57	1.49	0.688	55.80	456.80	65.00
75	15	37.50	1.33	0.50	1.31	0.727	49.20	506.00	72.23
90	15	37.50	1.39	0.44	1.15	0.760	43.10	549.10	78.52
105	15	37.50	1.46	0.37	0.97	0.798	36.40	585.50	83.50
120	15	37.50	1.52	0.31	0.81	0.830	30.40	615.90	88.07
135	15	37.50	1.57	0.26	0.68	0.857	25.50	641.40	91.48
150	10	25.00	1.57	0.26	0.68	0.857	17.00	658.40	93.97
160	5	12.50	1.57	0.26	0.68	0.857	8.50	666.90	95.21
165	15	37.50	1.60	0.23	0.60	0.874	22.50	689.40	98.36
180	10	25.00	1.60	0.23	0.60	0.874	15.00	704.40	100.25
190	10	25.00	1.62	0.21	0.55	0.885	13.75	718.15	102.38
200	10	25.00	1.70	0.13	0.34	0.928	8.50	726.65	103.74
210	10	25.00	1.73	0.10	0.26	0.945	6.50	733.15	104.82
240	30	75.00	1.79	0.04	0.11	0.978	8.25	741.40	106.03
300	50	125.00	1.82	0.01	0.03	0.995	3.75	745.15	106.38

Appendix Table 11. Calculation of cumulative amount of SO_2 on dry wood for the influent SO_2 conc. of 4.60 ppm.

Dry wood used = 6.40 g.

Flowrate of Gas through the adsorber = 2.5 l./min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood			Quantity of SO_2 on wood		Wood Adsorptivity
min.	min.	l.	ppm.	ppm.	$\mu\text{g/l}$	p^*/P	@ t, $\mu\text{g.}$	Cum. @ t, $\mu\text{g.}$	$\mu\text{g. SO}_2/\text{g. wood}$
0	0.5	1.25	2.85	1.75	4.60	0.620	5.75	5.75	0.90
0.5	0.5	1.25	3.96	0.64	1.78	0.861	2.23	7.98	1.25
0.75	0.5	1.25	4.20	0.40	1.05	0.913	1.31	9.29	1.45
1	0.5	1.25	4.36	0.24	0.63	0.949	0.79	10.08	1.56
1.5	0.5	1.25	4.36	0.24	0.63	0.949	0.79	10.87	1.69
2	0.5	1.25	4.44	0.16	0.42	0.966	0.52	11.39	1.78
2.5	0.5	1.25	4.44	0.16	0.42	0.966	0.52	11.91	1.83
3	0.5	1.25	4.47	0.13	0.34	0.972	0.43	12.34	1.93
4	1	2.5	4.47	0.13	0.34	0.972	0.86	13.20	2.06
5	1	2.5	4.50	0.10	0.26	0.980	0.65	13.85	2.17
6	1	2.5	4.50	0.10	0.26	0.980	0.65	14.50	2.27
7	1	2.5	4.56	0.04	0.11	0.991	0.38	14.88	2.32
8	1	2.5	4.56	0.04	0.11	0.991	0.38	15.26	2.38
9	1	2.5	4.60	0	0	1.0	0	15.26	2.38

Appendix Table 12. Calculation of cumulative amount of SO_2 on wood with 11% H_2O for an influent SO_2 conc. of 4.60 ppm.

Dry wood used = 6.71 g.

Water added = 0.74 ml.

Gas flowrate through the adsorber = 2.5 l./min.

Time t	Samp- ling time	Vol.	Effl. SO ₂ conc.	SO ₂ adsorbed on wood	p*/P	Quantity of SO ₂ on wood @ t,	Wood Adsorptivity Cum. @ t,		
min.	min.	l.	ppm.	ppm.	μg/l	μg.	μg.SO ₂ /g.wood		
0	0.5	1.25	1.27	3.33	8.70	0.276	11.0	11.0	1.64
1	0.5	1.25	1.35	3.25	8.50	0.294	10.6	21.6	3.22
2	1	2.5	1.50	3.10	8.10	0.326	20.3	41.9	6.11
3	1	2.5	1.82	2.78	7.25	0.396	18.3	60.2	8.97
4	1	2.5	2.11	2.46	6.42	0.465	16.0	76.2	11.35
5	1	2.5	2.50	2.10	5.50	0.514	13.8	90.0	13.42
6	1	2.5	2.66	1.94	5.06	0.578	12.7	102.7	15.29
7	1	2.5	2.93	1.67	4.36	0.638	10.9	113.6	16.93
8	1	2.5	3.10	1.50	3.92	0.574	9.8	123.4	18.37
9	1	2.5	3.25	1.35	3.52	0.707	8.6	132.0	19.69
10	1	2.5	3.41	1.19	3.10	0.742	7.8	139.8	20.83
12	3	7.5	3.73	0.87	2.27	0.812	24.6	164.4	24.51
15	3	7.5	3.88	0.72	1.88	0.845	14.1	178.5	26.57
18	3	7.5	4.18	0.42	1.09	0.910	8.1	186.6	27.83
20	3	7.5	4.24	0.36	0.94	0.922	7.2	193.8	28.78
22	3	7.5	4.28	0.32	0.84	0.931	6.3	200.1	29.81
25	3	7.5	4.32	0.28	0.73	0.940	5.4	205.5	30.59
30	3	7.5	4.44	0.16	0.42	0.966	3.3	208.8	30.99
33	3	7.5	4.50	0.10	0.26	0.980	2.0	210.8	31.32
35	3	7.5	4.50	0.10	0.26	0.980	2.0	212.8	31.87
40	3	7.5	4.56	0.04	0.11	0.991	3.0	215.8	32.20

Appendix Table 13. Calculation of cumulative amount of SO_2 on wood with $11\% \text{H}_2\text{O}$ for the influent SO_2 conc. of 4.60 ppm.

Dry wood used = 7.16 g.

Water added = 1.44 ml.

Gas flowrate through the adsorber = 2.5 l./min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood		p^*/p	Quantity of SO_2 on wood		Wood Adsorptivity
min.	min.	l.	ppm.	ppm.	µg/l		@ t, µg.	Cum. @t, µg.	µg. SO_2 /g. wood
0	1	2.5	0.715	3.885	9.93	0.155	24.8	24.8	3.46
2	2	5	0.795	3.805	9.90	0.173	45.5	70.3	9.83
5	3	7.5	0.910	3.69	9.65	0.198	72.3	112.6	20.21
8	3	7.5	0.99	3.61	9.45	0.215	70.9	213.5	29.80
10	2	5	1.27	3.33	8.73	0.276	47.5	261.3	36.47
12	1	2.5	1.59	3.01	7.90	0.345	19.8	280.8	39.38
13	1	2.5	1.74	2.86	7.50	0.377	18.8	299.6	41.92
15	2	5	2.14	2.46	6.45	0.465	32.2	331.8	46.43
18	4	10	2.38	2.22	5.82	0.516	58.2	390.0	54.50
21	2	5	2.82	1.78	4.66	0.613	23.2	413.2	57.63
25	4	10	3.25	1.35	3.54	0.706	35.4	448.6	62.50
30	5	12.5	3.89	0.71	1.86	0.844	23.2	471.8	65.84
35	5	12.5	4.05	0.55	1.44	0.880	18.0	489.8	68.45
38	4	10	4.17	0.43	1.13	0.905	11.3	501.1	69.99
42	6	15	4.24	0.36	0.94	0.920	14.2	513.3	72.03
50	6	15	4.36	0.24	0.63	0.946	9.5	524.8	73.46
55	4	10	4.40	0.40	0.52	0.957	5.2	530.0	74.13
60	10	25	4.44	0.16	0.42	0.964	10.5	540.5	75.62
70	6	15	4.48	0.12	0.31	0.973	4.7	545.2	76.47
75	4	10	4.52	0.08	0.21	0.982	2.1	547.3	76.56
80	5	12.5	4.57	0.03	0.08	0.992	1.0	548.3	76.70

Appendix Table 14. Calculation of cumulative amount of SO_2 on wood with 50% H_2O for influent SO_2 conc. of 4.60^2 ppm.

Dry wood used = 6.93 g.

Water added = 3.47 ml.

Gas flowrate through the adsorber = 2.5 l./min.

Time t	Sampling time	Vol. l.	Effl. SO_2 conc. ppm.	SO_2 adsorb. on wood		p^*/P	Quantity of SO_2 on wood		Wood Adsorptivity $\mu\text{g. SO}_2/\text{g. wood}$
							@ t, $\mu\text{g.}$	Cum. @ t $\mu\text{g.}$	
0	1	2.5	0.635	3.965	10.4	0.138	26.0	26.0	3.75
10	12	30	0.635	3.965	10.4	0.138	312.0	338.0	48.78
17	5	12.5	0.675	3.925	10.3	0.147	128.0	466.0	67.05
20	2	5	0.80	3.80	10.0	0.174	50.0	516.0	74.46
22	2	5	0.95	3.65	9.65	0.207	48.3	564.3	78.72
25	4	10	1.15	3.45	9.05	0.250	90.5	654.8	94.34
30	4	10	1.59	3.01	7.90	0.346	79.0	733.8	105.48
35	6	15	2.06	2.54	6.65	0.448	99.5	833.3	120.04
42	8	20	2.62	1.98	5.20	0.548	104.0	937.3	135.07
48	4	10	2.70	1.90	4.97	0.587	49.7	987.0	142.25
50	4	10	2.94	1.66	4.35	0.638	43.5	1030.5	148.37
55	4	10	3.41	1.19	3.12	0.741	31.2	1061.7	153.07
58	2	5	3.61	0.99	2.60	0.784	13.0	1074.7	154.84
60	4	10	3.73	0.87	2.28	0.810	22.8	1097.5	158.18
65	4	10	3.89	0.71	1.86	0.846	18.6	1116.1	160.07
70	6	15	4.05	0.55	1.44	0.880	21.6	1137.7	164.10
75	4	10	4.20	0.40	1.05	0.912	10.5	1148.2	165.47
80	6	15	4.30	0.30	0.78	0.935	11.7	1159.9	167.43
85	4	10	4.40	0.20	0.53	0.956	5.3	1165.2	168.12
90	4	10	4.52	0.08	0.21	0.982	2.1	1167.3	168.43
93	3	7.5	4.56	0.04	0.11	0.991	0.83	1168.13	168.56

Appendix Table 15. Calculation of cumulative amount of SO_2 on wood with saturated moisture content for an influent SO_2 conc. of 4.60 ppm.

Dry wood used = 6.89 g.

Water added = 13.8 ml.

Gas flowrate through the adsorber = 2.5 l./min.

Time t	Samp- ling time	Vol.	Effl. SO_2 conc.	SO_2 adsorbed on wood	p^*/P	Quantity of SO_2 on wood		Wood Adsorptivity
min.	min.	l.	ppm.	ppm.	$\mu\text{g}/\text{l}$	@ t, $\mu\text{g}.$	Cum. @ t, $\mu\text{g}.$	$\mu\text{g}.\text{SO}_2/\text{g}.\text{wood}$
0	1	2.5	0.445	4.155	10.9	0.097	27.2	3.94
5	5	12.5	0.445	4.155	10.9	0.097	136.1	23.64
7.5	3	7.5	0.595	4.005	10.5	0.129	78.8	35.05
10	4	10	0.754	3.846	10.1	0.164	101.0	49.76
15	4	10	1.19	3.41	8.94	0.258	89.4	62.43
20	6	15	1.43	3.17	8.30	0.311	124.5	80.69
25	4	10	1.82	2.78	7.29	0.396	72.9	91.32
30	6	15	2.10	2.50	6.55	0.456	98.4	105.41
35	4	10	2.30	2.30	6.02	0.500	60.2	114.28
40	10	25	2.50	2.10	5.50	0.543	137.5	134.37
50	10	25	2.65	1.95	5.10	0.576	127.5	152.78
60	6	15	2.85	1.75	4.58	0.620	68.6	162.51
65	4	10	3.17	1.43	3.74	0.689	37.4	168.05
70	10	25	3.37	1.23	3.22	0.732	80.5	179.95
80	10	25	3.42	1.18	3.09	0.743	77.3	190.82
90	6	15	3.50	1.10	2.88	0.761	43.2	197.35
95	4	10	3.60	1.00	2.62	0.783	26.2	200.17
100	10	25	3.90	0.70	1.83	0.847	45.7	207.46
110	10	25	4.44	0.16	0.41	0.965	10.3	209.14
120	6	15	4.52	0.08	0.20	0.982	3.0	209.43
125	2	5	4.56	0.04	0.10	0.991	0.5	209.56