

AN ABSTRACT OF THE THESIS OF

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Title: THE CHARACTERIZATION AND PHYSICAL-CHEMICAL  
TREATABILITY OF LOG POND WATERS

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/s/ Frank D. Schaumburg

The treatability of waters from four log ponds in Oregon by physical and chemical treatment methods was investigated. Treatment processes included sand filtration, activated carbon contact and coagulation with aluminum sulfate.

Preliminary studies were made at each log pond to determine the homogeneity of the pond water for sampling purposes and to examine the effects of storage time and type of timber stored on water quality. In general the waters throughout each pond were found to be of uniform character.

The treatment of log pond water by activated carbon was found to be the most effective method studied. The ultimate capacity of the carbon employed was determined by adsorption isotherms and was found to range between 272 and 485  $\frac{\text{mg COD}}{\text{gram carbon}}$ .

The jar test procedure was employed to investigate the

feasibility of coagulating log pond waters with aluminum sulfate.

Alum concentrations ranging from 125 to 175 mg/l were found to be effective in removing up to 96% of the suspended solids and 68% of the COD.

Sand filtration appears to be impractical as a sole method of treating log pond waters.

The concentration of lignin-like substances extracted from logs appears to be higher in ponds storing Douglas fir than in those storing ponderosa pine. This observation is primarily based upon the results obtained from the nitroso test (PBI).

The Characterization and Physical-Chemical  
Treatability of Log Pond Waters

by

Guy Ivan Blanton, Jr.

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# THE CHARACTERIZATION AND PHYSICAL-CHEMICAL TREATABILITY OF LOG POND WATERS

## INTRODUCTION

Oregon and Washington together produce 42% of the softwood sawtimber and 35% of the sawtimber in the nation even though only 9% of the total commercial forest land in the United States is contained in these states (Timber Resource Statistics..., 1965). In 1966 the timber harvest in Oregon alone was 8.9 billion board feet (Wall, 1967).

Due to climatic conditions in the Pacific Northwest, only a part of the year is suitable for timber harvest. As a result, during this period lumber companies receive far more timber than they can process at any one time and are forced to store logs from a few weeks to several years in some instances.

Unless proper precautions are taken, stored logs are subject to end splitting, checking and fungal or insect attack which can greatly reduce their commercial value. Checks and splits are separations or ruptures in the wood tissues along the longitudinal plane which result from non-uniform drying. These conditions affect the strength of wood by reducing its resistance to shear and also act as channels for fungal or insect infections.

The most essential conditions for fungal growth in wood are

suitable temperature, available oxygen and proper moisture content. Fungi develop best in a temperature range from 75 to 85 degrees F. Temperatures below 50 degrees F greatly reduce the activity of the organisms (Dobie, 1965). If the wood is completely saturated or if the moisture content is less than 20% of saturation, fungal growth cannot develop (Graham and Miller, 1967).

Dobie (1965) reported that the use of water is the most widely accepted means of preventing wood decay. Water inhibits fungal and insect attack by lowering the temperature, restricting the flow of oxygen around logs and saturating the timber. It also retards end splitting (Dobie, 1965).

Water saturation can be accomplished by storing logs in a body of water (such as a lake, slough, river, estuary, or log pond), or by an adequate sprinkling system. Storage of timber in log ponds is widely practiced in the Pacific Northwest. Oregon has approximately 12,000 acres of log ponds and 2,000 acres of sloughs and canals used for this purpose. Log ponds range in size from less than 1 to more than 400 acres (McHugh et al., n.d.). They are created by excavation or by damming a small stream. Depending on the source of water, log ponds may overflow continuously, semi-continuously, or not at all.

## PURPOSE AND SCOPE

At present very little is known concerning the effect of log storage ponds on water quality. However, the few investigations that have been made (Hendriksen and Samdal, 1966; McHugh et al., n.d.; Ellwood and Ecklund, 1959) indicate that waters receiving log pond overflows may show an increase in COD, BOD and color content; create taste and odor problems; and may be toxic to aquatic life.

The present study was undertaken to evaluate the physical and chemical treatability of water from four log ponds in Oregon. Both overflowing and non-overflowing log ponds were investigated. The ponds contained Douglas fir or ponderosa pine logs. Each pond was characterized by determination of total and suspended solids, nitrogen and phosphorus content, alkalinity, chemical and biochemical oxygen demand and the Pearl-Benson Index (PBI).

The methods of treatment employed were sand filtration, activated carbon contact and coagulation with aluminum sulfate.

The feasibility of carbon treatment was investigated by evaluating adsorption isotherms using COD as the waste strength parameter.

Coagulation with aluminum sulfate consisted of determining the optimum pH and alum concentration for each log pond. COD, BOD, suspended solids and PBI were used in evaluating the effectiveness of coagulation. The volume of sludge produced during chemical coagulation was determined for each log pond.

## LITERATURE REVIEW

### Wood Chemistry

The chemical composition of log pond water has not as yet been investigated in great detail. An investigation primarily concerned with mosquitoes in log ponds was conducted by the Oregon State Board of Health (McHugh et al., n. d.). The main objective of the chemical analyses in the study was to determine an expression, such as total solids, COD, etc., which would be a good indicator of the degree of pollution of the log pond water. Due to the lack of facilities available for analyzing organic constituents, identification of the material leached or dissolved from logs during storage was not made.

Many textbooks have devoted considerable space to wood and cellulose chemistry. An examination of the primary wood and bark components and some of their chemical properties will give a better insight as to what material is most likely present in log pond waters.

Wood is predominantly composed of holocellulose (cellulose and hemi-cellulose) and lignin. Other substances such as tannins, simple sugars, gums and pectins are present to a lesser degree. Wood can be categorized as coniferous (softwoods) and deciduous (hardwoods). Softwoods contain 70-75% holocellulose and 25-30% lignin, whereas hardwoods contain 75-82% holocellulose and 18-25% lignin (Stamm, 1964).

Cellulose is the principal component of the cell wall. It is a long rigid molecule and its composition is expressed by the formula  $(C_6H_{10}O_5)_n$  where  $n$  is approximately 1500. Cellulose is highly insoluble in most solvents, including water, which is important in the pulp-making processes (Kice and Marvell, 1966).

The hardening and strengthening of the wood cell wall is known as lignification and is the result of lignin combining with cellulose and other carbohydrates. Lignin is located primarily between the cell walls. It is aromatic in character and is almost totally insoluble in most solvents except for hot solutions of sodium hydroxide, sulphurous acid and sulphites (Norman, 1937). Lignins contained in softwoods are very homogeneous, whereas those contained in hardwoods are much more reactive and vary between different species (Browning, 1963).

The ratio of the concentrations of lignin to holocellulose is generally greater in the bark than in the wood. Douglas fir bark, for example, on an extractive-free basis contains approximately 45% lignin and 55% holocellulose (Browning, 1963), as compared to a lignin content of 25-30% in the wood, stated above.

The presence of lignin or cellulose to any appreciable extent in log ponds is doubtful since both are highly insoluble in water. Both lignin and cellulose are very resistant to biological degradation; however, certain organisms are capable of attacking these complex

molecules at a slow rate. Ellwood and Ecklund (1959) in a study of bacterial attack of pine logs in pond storage stated that the strong odors produced in ponds are due to the production of organic acids as a result of carbohydrate breakdown.

The extraneous materials in wood and bark referred to as extractives, are generally those substances which are soluble in neutral solvents. Included in this group are: volatile oils, terpenes, fatty acids, unsaponifiables, carbohydrates, polyhydric alcohols, nitrogen compounds, aromatic compounds and inorganic constituents (Browning, 1963).

In a study by Zellner and co-workers the bark from 30 species of trees was analyzed for its solubility in organic solvents and water. It was reported that of the extractives from bark, those soluble in water are tannins, simple sugars, glycosides, polysaccharides, gums and pectins (Browning, 1963).

Tannins, pigments and phlobaphenes are the important color components of wood. Tannins, being soluble in water and making up more than 50% of the extractible material of bark (Kurth et al., 1949), are probably responsible for the dark color of most log ponds. This is substantiated by the fact that bark which has been left in the woods or in log ponds is low in tannin content (Kurth, 1953).

### Waste Water Treatment Methods

Chemical coagulation is used extensively for the removal of suspended and colloidal materials from waste waters. This method of treatment is widely used to treat highly colored wastes from the textile industry. In some instances coagulation has removed up to 99% of the color-producing material (Parsons, 1965).

Chemical coagulation is brought about by the addition of flocc-forming chemicals to the waste water to bring together slow settling or non-settleable material with a relatively fast settling floc. The chemicals most commonly used include alum,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ; copperas,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; ferric sulfate,  $\text{Fe}(\text{SO}_4)_3$ ; ferric chloride,  $\text{FeCl}_3$ ; and chlorinated copperas, a mixture of ferric sulfate and chloride. Aluminum sulfate is considered to be more effective in coagulating carbonaceous material, while iron sulfates are more effective for wastes which are high in protein content (Nemerow, 1963).

Even though chemical coagulation may increase removal of suspended material from log pond waters, it is ineffective for the removal of dissolved organics. Log pond waters high in sugars, soluble polysaccharides and glycosides may not be treatable by chemical coagulation.

Many organic compounds found in industrial wastes are difficult

or impossible to treat biologically or by chemical coagulation. Detergents, insecticides and herbicides are included in this group.

Activated carbon has been successfully employed to remove these contaminants from water. Activated carbon shows a preference for organic compounds and therefore has also been used extensively for controlling taste and odor problems produced by decaying organic matter, algae and other microscopic organisms (Flentje and Hager, 1964).

The removal of organic substances by activated carbon is a process known as adsorption. This is a process by which molecules of a substance are accumulated on the surface of the adsorbing material. The large surface area of activated carbon makes it ideal for this purpose.

In 1957 E. A. Sigworth conducted a survey for the American Water Works Association concerning water treatment plants serving populations greater than 10,000. The results of this survey showed that of 450 trials of activated carbon treatment on various types of taste and odor problems, 86% reported complete success, 12% indicated partial success and 2% reported no success (Sigworth, 1968).

Sand filtration is used extensively for the treatment of surface waters. Its use for the treatment of waste water, however, has been somewhat limited. A very low percentage of the waters containing color are treatable by filtration without the aid of coagulants. Water



with low turbidity is readily treated with slow rate filters (1-10 mgad); however, water with turbidities in excess of 40 Jackson Candle Units clog these filters so quickly that this method of treatment is impractical unless preceded by coagulation and sedimentation. Large microorganisms such as algae and diatoms are readily removed by sand filters but taste and odor producing substances associated with these organisms may be unaffected unless filtration is accompanied by other treatment methods specifically designed for their removal (Fair and Geyer, 1958).

## ACTIVATED CARBON ADSORPTION

Activated carbon removes pollutants from a gas or liquid by a process known as adsorption, whereby impurities become attached to the carbon surface. Adsorptive forces are physical or chemical in nature. Because of the weak forces involved, physical adsorption is quite reversible and of little significance. The forces of chemical adsorption are similar to those of a chemical reaction and therefore are much stronger and irreversible.

During the process of adsorption a single layer of adsorbate, one molecule thick, is formed on the surface of the adsorbent and as a result the adsorptive powers of a material are dependent on its surface area. Due to the large ratio of surface area to mass, activated carbon is used extensively by industry for adsorptive purposes. The surface area of one gram of activated carbon may be as high as 1,500 square meters. Over 95% of this area is accounted for by the holes or pores produced by activation of carbon, and as a result pulverizing this material to a fine powder will have very little effect on its total surface area or adsorptive capacity. Adsorption is limited by the rate at which particles diffuse into the interior of the carbon; therefore crushing carbon will greatly decrease the time required to reach equilibrium.

Adsorption is also affected by molecular size and chemical

nature of the material adsorbed and pH if in solution. As the size of molecules increases, the distance they are able to diffuse into the pores is decreased, thus reducing the available surface area. In mixtures of different sized molecules, the movement of smaller particles into the pores is not affected by the larger molecules because of the greater mobility of smaller particles and the fact that the particles and pores are irregular in shape and the larger molecules would not seal the pore.

The affinity of a non-polar (organic) adsorbent will be greater for an organic adsorbate than for an inorganic one. Activated carbon, being organic in nature, is efficient in removing organic pollutants causing taste and odor problems.

The pH of a solution may affect its adsorption. Generally the adsorption of organic molecules is more efficient at their isoelectric point, that is, the pH at which the molecules are electrically neutral.

The feasibility of carbon treatment for a particular waste can be determined by analysis of its adsorption isotherm. In a liquid phase the adsorption isotherm would show the amount of adsorbate in the adsorbent and that in solution. Graphically, an adsorption isotherm is a plot of impurity adsorbed per unit weight of carbon versus the amount of impurity remaining in solution.

For liquids, straight line isotherm plots can generally be obtained on log · log graph paper using the empirical Freundlich

equation given in the following expression:

$$\frac{x}{m} = kc^{1/n}$$

where

$x$  = amount of impurity adsorbed

$m$  = weight of carbon

$\frac{x}{m}$  = amount of impurity adsorbed per unit weight of carbon

$c$  = equilibrium concentration in solution after adsorption

$k$  and  $n$  are constants (The Laboratory Evaluation. . . , 1966).

The amount of impurity adsorbed can be measured by reduction in color, turbidity, COD, TOC, or any other suitable parameter.

The ultimate adsorptive capacity of the carbon can be estimated from the isotherm plot (Figure 1) in the following manner:

1. A vertical line is drawn from a point on the abscissa representing the influent concentration ( $c_o$ ).
2. The isotherm is extrapolated to intersect the constructed line.
3. The ultimate capacity of carbon,  $(\frac{x}{m})_{c_o}$ , can then be read from the ordinate.

From the ultimate capacity,  $(\frac{x}{m})_{c_o}$ , the capacity in terms of volume of liquid purified per unit weight of carbon can be calculated (Laboratory Evaluation of. . . , 1966).

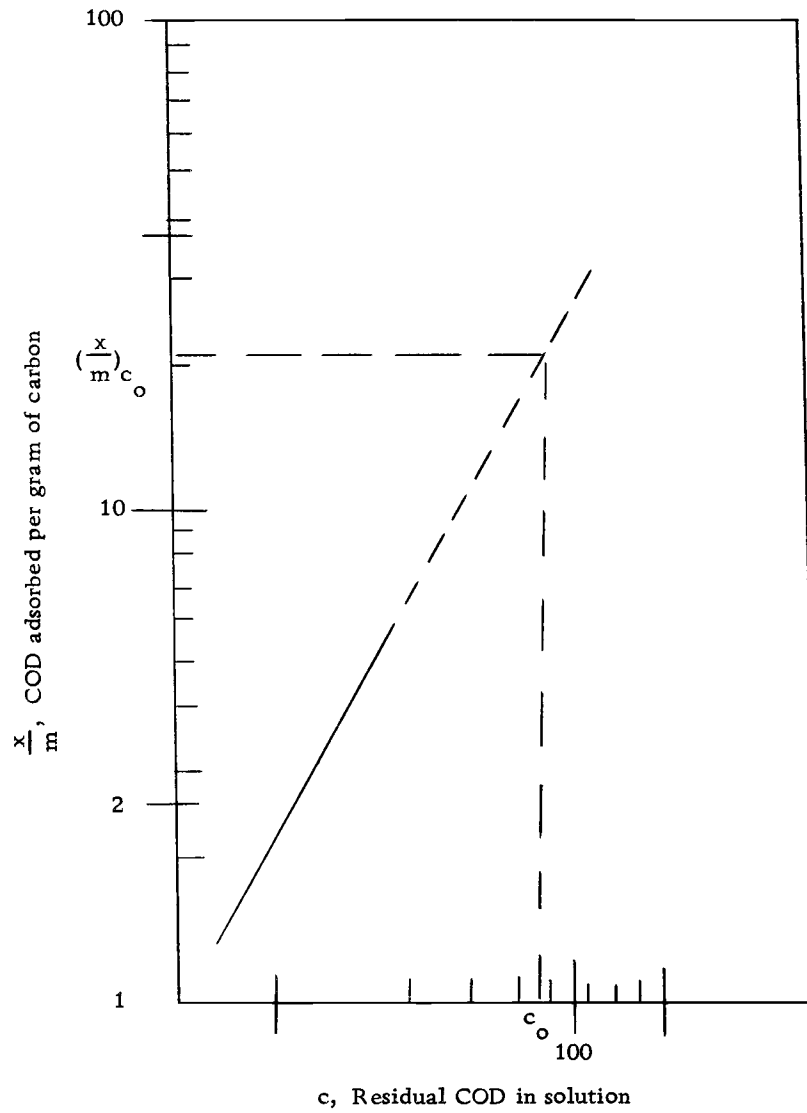


Figure 1. Typical adsorption isotherm.

For complete COD removal:

$$V_{c_o} = \frac{(\frac{x}{m})_{c_o}}{c_o} V$$

where

$V_{c_o}$  = theoretical volume of liquid purified per unit weight  
of carbon

$(\frac{x}{m})_{c_o}$  = capacity per unit weight of carbon at the influent concentration

$V$  = volume of liquid used in isotherm test

$c_o$  = influent concentration.

Where complete COD removal is impossible or where it is desired only to a concentration  $c_1$ , the following formula may be used (Laboratory Evaluation of. . . , 1966):

$$V_{c_1} = \frac{(\frac{x}{m})_{c_o}}{c_o - c_1} V$$

From an isotherm plot it can be determined whether or not a certain degree of treatment can be obtained and the ultimate adsorptive capacity of the carbon for the particular waste. With the above information a rough estimation of the quantity of carbon needed can be obtained. Isotherms also provide a convenient method of investigating the effects of temperature and pH on adsorption and comparing the adsorption of various types of carbon.

Before a full scale activated carbon column can be constructed and put into operation more information than that obtained from isotherm data is needed. The required flow rate and bed depth for

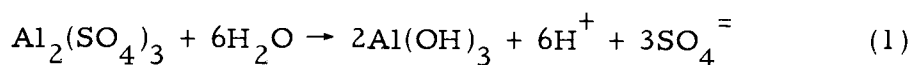
optimum performance will depend upon the rate at which impurities are removed from solution and can only be determined through an actual column study. Pilot plant studies must be conducted in columns with bed depths similar to those expected for plant operation, since it is impossible to extrapolate the results from a one- or two-foot bed depth to a ten-foot column.

## CHEMICAL COAGULATION

Chemical coagulation is a process by which finely divided suspended or colloidal material is removed from water. The various compounds formed by the addition of the coagulant destabilize the colloidal particles by reducing their electronic charge to a value at which agglomeration of these particles will occur. Color and turbidity in natural waters are most frequently negatively charged particles. Consequently, the salts of trivalent metals, usually aluminum or iron, are used as coagulants.

The reactions which occur during coagulation with aluminum sulfate and ferric sulfate are essentially the same. Since aluminum is considered to be more effective in coagulating carbonaceous material (Nemerow, 1963), its action will be discussed below in more detail.

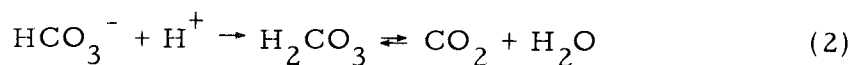
When aluminum sulfate is added to water, the following reaction occurs:



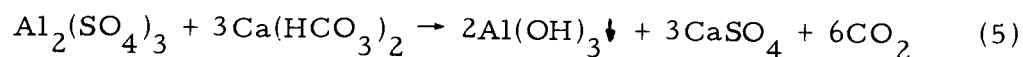
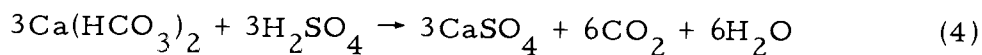
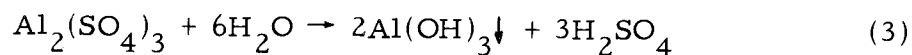
Equation 1 shows that during the formation of aluminum hydroxide, hydrogen ions are released. As a consequence, the pH is lowered to such an extent that the reaction cannot continue unless the hydrogen ions are neutralized with some form of alkalinity. Bicarbonates



present in natural waters neutralize the hydrogen ions in the following manner:



Rewriting Equations 1 and 2 in molecular form and combining gives Equation 5 as follows:



In the pH range of 4.8-7.6, the aluminum hydroxide complexes are essentially insoluble and form a chemical floc which is completely precipitated. Since aluminum hydroxide is positively charged in the stated pH range, it also combines with the negatively charged colloids. Colloids not initially adsorbed may be removed by enmeshment in the floc.

## EXPERIMENTAL PROCEDURES AND APPARATUS

### Pond Surveys

Preliminary investigations were made at each log pond site to characterize the water before any actual treatment was attempted. The survey consisted of an interview with each log pond supervisor to determine the surface area and depth of the log pond, the period of pond use, source of water, whether or not the pond was overflowing, type of timber stored, length of storage period and if the pond receives wastes from any other sources.

Homogeneity of the log pond water was determined by measuring dissolved oxygen, temperature, total and suspended solids, and COD at a depth of one foot below the water surface at various sampling points. However, at least one sample was taken at the bottom of each pond. A large homogeneous sample was taken from each pond to the laboratory to ascertain a more complete characterization and to investigate the treatability of the pond water. A ten-foot aluminum pram was used for sampling where cat-walks were not present.

All dissolved oxygen measurements were made with a YSI Model 54 Oxygen Meter.<sup>1</sup> This polarographic method was selected since problems were encountered by McHugh (n. d. ) using the Winkler

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<sup>1</sup> The oxygen meter was obtained from Van Waters and Rogers, Inc.

method on this type of water. The probe was standardized by direct calibration in air.

For ponds which were located at too great a distance to commute daily, a sufficient quantity of pond water for laboratory investigation was taken in plastic carboys and preserved with 5 mg/l mercuric chloride. Samples for BOD determinations were preserved by freezing with dry ice.

### Sand Filtration

Figure 2 shows the apparatus used for sand filtration. The sand column had a diameter of 1.5 inches and a bed depth of 15 inches. The effective size of the sand was 0.50 mm and the uniformity coefficient was 1.55. The ratio of column diameter to sand size was approximately 50:1, which is large enough to effectively minimize wall effects (Borchardt and O'Melia, 1961). Pond water was fed to the sand column through a constant head siphon at a rate of 2 gallons per minute per square foot ( $\text{gpm/ft}^2$ ). The filter was backwashed with distilled water.

### Chemical Coagulation

All coagulation experiments were conducted using a standard jar test procedure outlined by the Calgon Corporation (Coagulant Aids..., 1967). Preliminary experiments were made with various

coagulants including organic polymers to evaluate their effectiveness in coagulating log pond waters. Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (alum), was selected as the coagulant in these studies. A stock alum solution was prepared such that 1 ml of solution contained 50 mg of the active coagulant.

A Phipps and Bird variable speed multiple stirrer fitted with six, 2-liter containers was used in the jar tests. The containers were fabricated from plexiglass and had a square cross section (Figure 3). After addition of alum and pH adjustment with 1.0 normal solutions of NaOH and  $\text{H}_2\text{SO}_4$ , the following time and speed sequences for mixing and floc formation were utilized.

- a) 3 minutes @ 100 rpm, then
- b) 5 minutes @ 50 rpm, then
- c) 10 minutes @ 20 rpm.

After removal of the stirring paddles, a quiescent period of 45-60 minutes was provided prior to the withdrawal of samples one inch below the liquid surface. The samples were examined for waste strength reduction by COD, BOD, suspended solids and PBI measurements. Appropriate controls were set up using pond water with no coagulant added.

A first series of jar tests was run at a constant pH to determine the optimum alum concentration. Additional tests were run at constant alum concentrations to determine the optimum pH.

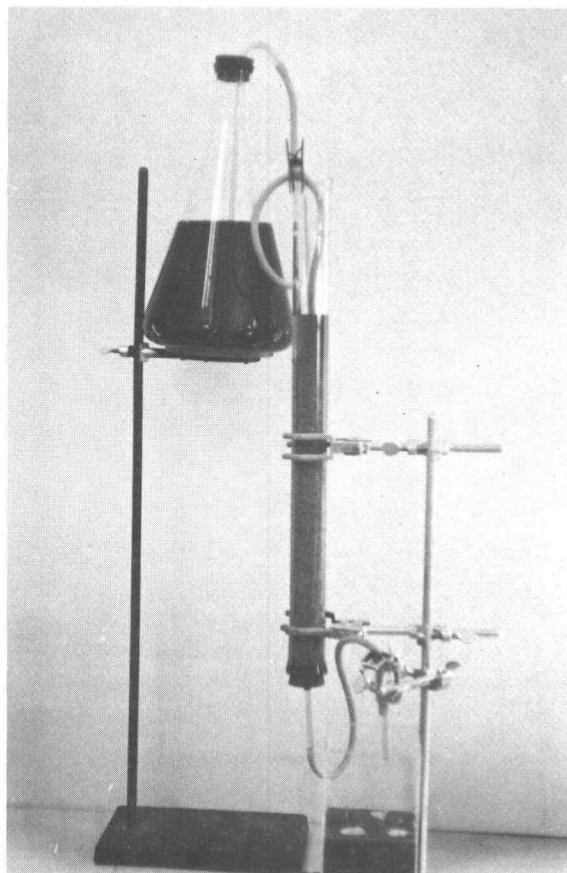


Figure 2. Sand filtration apparatus.

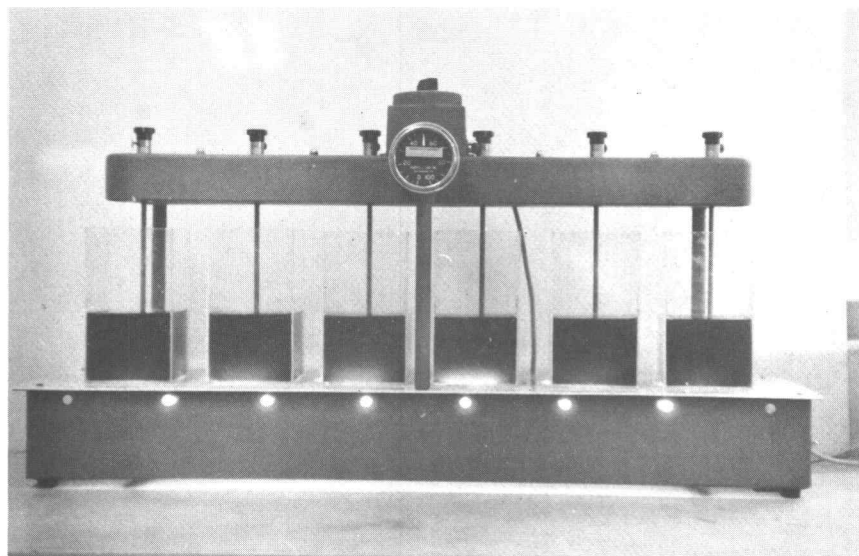


Figure 3. Phipps and Bird variable speed multiple stirrer.

### Adsorption Isotherms

A laboratory procedure outlined by the Pittsburgh Activated Carbon Company (The Laboratory Evaluation. . . , 1966) was followed to obtain data for the adsorption isotherms. The procedure consisted of treating fixed volumes of log pond water with a series of known quantities of activated carbon. To eliminate the need of pulverizing granular carbon, a finely powdered carbon, Aqua Nuchar,<sup>2</sup> was used in all experiments.

Prior to carbon contact, the carbon was predried at 150°C for three hours and water samples were passed through the sand filter described above to remove large particles. Two hundred milliliters (ml) of pond water were added to each of six 1,000 ml Erlenmeyer flasks containing measured amounts of activated carbon. Carbon concentrations ranged from 0.05 to 1.00 gm per 200 ml solution. The flasks were stoppered and placed on an Eberbach shaker, operating at 100 oscillations per minute, for a time sufficiently long to approach equilibrium. Preliminary tests were run to determine adequate contact times.

After carbon treatment the contents of the flasks were filtered with Millipore pressure filters through Whatman GF/C glass filters.

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<sup>2</sup>Aqua Nuchar was obtained from Van Waters and Rogers, Inc.

A sample of the untreated pond water was also filtered in order to determine waste strength reduction by activated carbon. COD evaluated by the rapid COD test (Jeris, 1967) was used as the waste strength parameter.

### Chemical Tests

The rapid COD test, developed by Jeris (1967), was used in all experiments because of its rapidity and reproducibility. A direct comparison of this rapid method with the standard COD test (Standard Methods..., 1965) on log pond waters showed very close agreement in results (see Appendix).

The standard BOD test (Standard Methods..., 1965) was followed throughout the investigation. Activated sludge acclimated to log pond water was used to seed the BOD dilution water. Dissolved oxygen measurements were made with the YSI oxygen meter.

The Brucine method (Standard Methods..., 1965) was used to quantitate the nitrates in pond water samples.

Total phosphate concentrations were determined with the Stannous Chloride method for orthophosphates (Standard Methods..., 1965). Polyphosphates were hydrolyzed to orthophosphate by heating for 30 minutes in an autoclave at 15 psi.

Total solids, suspended solids, settleable solids, nitrogen (total Kjeldahl), and alkalinity were determined as described in

Standard Methods (1965).

The Pearl-Benson or nitroso test (Barnes et al., 1963) was used to estimate the removal of phenolic material by the treatment methods employed. The test is recommended for estimating the concentration of spent sulfite liquor, which consists of approximately 65% lignin sulfonates; however, tannins from bark extractives, amines and certain inorganic substances are known interferences. Since tannins are most likely present in log pond waters, PBI results were expressed as apparent SSL concentrations. Due to the turbidity of the log pond waters, samples used in PBI determinations were prefiltered through Whatman GF/C glass filters. According to Barnes (1963) filtration may remove some of the lignin sulfonates; therefore the letter F is used to designate which samples were filtered.

A Beckman DU spectrophotometer was used in the determination of nitrates by the Brucine method, phosphates by the Stannous Chloride method and phenolic material by the Pearl-Benson test.



## RESULTS AND DISCUSSION

### Initial Pond Survey

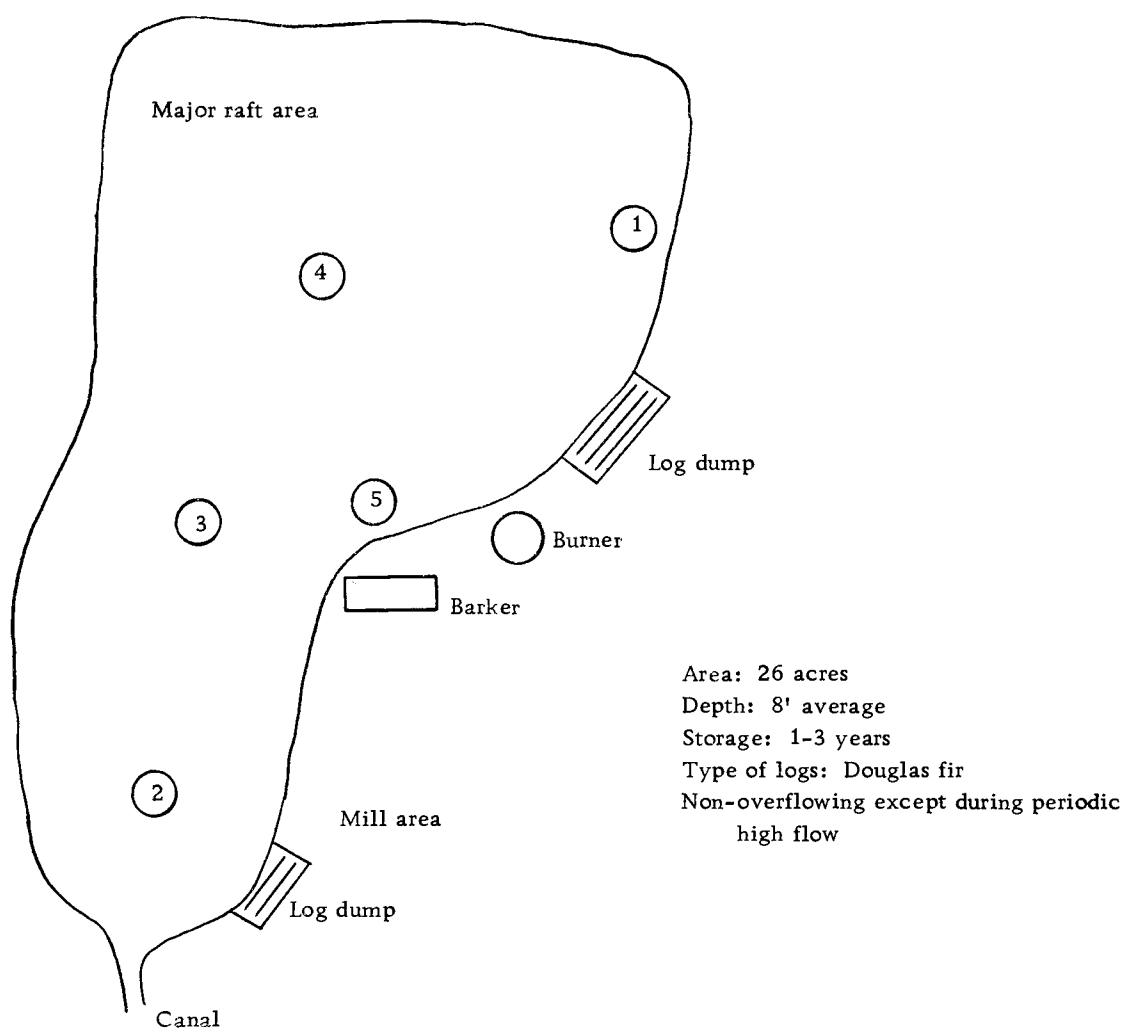
In order to adequately characterize the four ponds studied, a preliminary survey was conducted at each pond site to determine whether or not the pond water was homogeneous. The history of use and hydraulic characteristics of each pond were also investigated as possible factors affecting the chemical nature of the water. The results of these surveys follow.

#### Pond I

A 26-acre log pond situated near Corvallis, Oregon, was selected for the initial phase of this study (Figure 4). This pond has been in continuous use for 11 years. The pond, fed by a small creek, does not overflow except during periods of high precipitation during the winter months. Douglas fir logs are stored almost exclusively in this pond for a maximum period of one to three years.

Water samples were taken at a depth of one foot below the surface at the various points in the pond shown in Figure 4. Dissolved oxygen, temperature, COD, along with total, volatile and suspended solids measurements were made on the samples. The results of these tests are also included in Figure 4.

The COD ranged from 100 to 116 mg/l for the five sampling



Station	DO mg/l	Temp. °C	COD mg/l	Total solids mg/l	Volatile solids %	Suspended solids mg/l
1	0.1	22	116	254	59%	43
2	0.1	22	116	253	53%	38
3	0.4	22	104	230	49%	27
4	0.2	22	116	238	53%	14
			100*	301*	46%*	21*
5	0.2	22	116	260	56%	35

\* Bottom sample

Figure 4. Pond I: layout, sampling stations and results of initial survey.

stations. These results indicate that the pond was generally homogeneous in nature. Consequently, one large sample was taken at Station 1 for use in further characterization and subsequent treatment studies. A more comprehensive characterization of the pond water is discussed in a later section.

### Pond II

The second pond selected for investigation was located near Independence, Oregon, and contained primarily Douglas fir logs (Figure 6). Timber at this mill site is initially stored in cold decks until it is ready for processing. For ease of handling, logs are then dumped into the log pond, floated to the saw shed (Figure 5), cut to workable lengths in the water and floated to the barker. Logs are in the pond for approximately one week.

The 20-acre pond was excavated in 1955. The pond is non-overflowing and its surface level is maintained with water pumped from a nearby well. The location of the six sampling points and the results of the initial pond survey are shown in Figure 6.

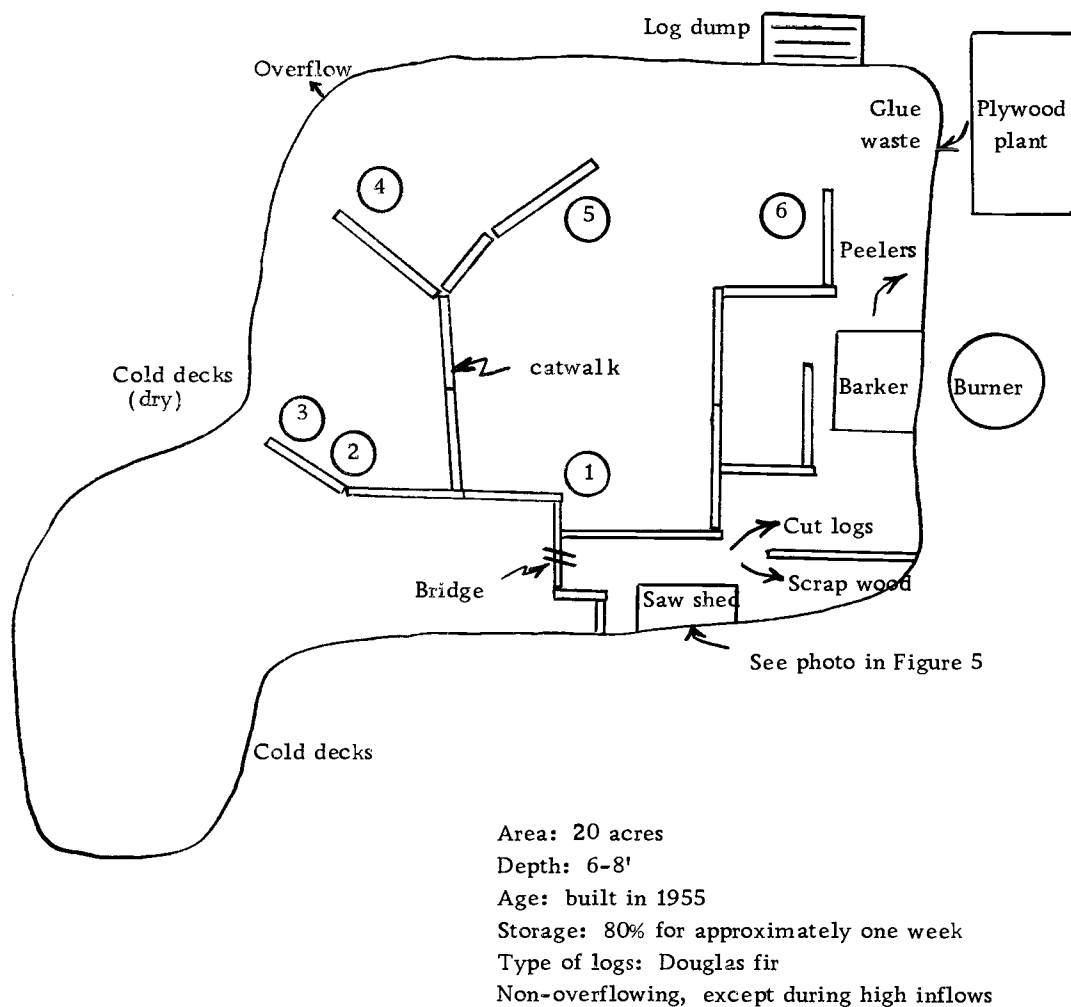
Unfortunately, glue wastes from an adjacent plywood plant are discharged into the log pond. Therefore, the exact composition and volume of this waste were not obtainable. This additional waste contribution to the pond tends to mask the effect of stored logs on the

pond water quality.



Figure 5. Pond II saw shed receiving Douglas fir.

The COD of the pond water ranged between 484 and 504 mg/l and total solids ran from 724 to 776 mg/l. Station 6 was located in the area of the pond where glue wastes were entering. The COD, total and suspended solids at Station 6 were generally slightly higher than the results obtained at the other stations. However, water pumps located at the saw shed were used to keep the logs moving in desired directions and this agitation allowed the glue wastes to be fairly well dispersed. As a result, all subsequent samples were taken at Station 2. Complete characterization is given in a following section.



Station	DO mg/l	Temp. °C	COD mg/l	Total solids mg/l	Volatile solids %	Suspended solids mg/l
1	0.3	21.5	496	747	55%	180
2	0.2	21.5	484	724	63%	162
3*	0.0*	21.0*	504*	776*	60%*	266*
4	0.2	22.0	488	720	61%	234
5	0.3	22.0	488	723	57%	248
6	0.1	22.0	504	755	56%	256

\* Bottom sample

Figure 6. Pond II: layout, sampling stations and results of initial survey.

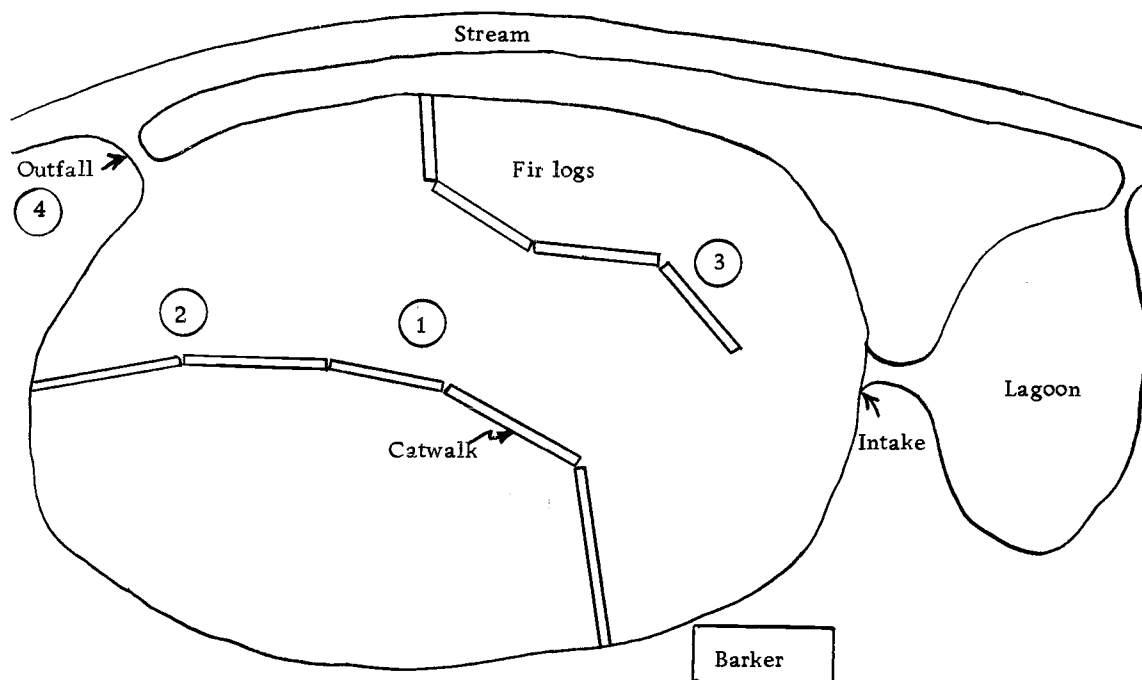
### Pond III

A 2 1/2-acre log pond located in Prineville, Oregon, was the third pond selected for this study. The pond has been in use since 1940. Eighty-five percent of the timber stored is ponderosa pine; the remainder is fir, which is stored separately at one end of the pond (Figure 7). Logs are stored in the water for approximately two weeks.

The log pond has an average depth of 12 feet. It is a flow-through type, receiving water from a nearby stream. The pond is emptied every two years to remove sinkers and bark deposits. Heated water from a boiler is discharged continuously into the pond to prevent the water from freezing over in the winter.

Pond III was evaluated for homogeneity in the same manner as Ponds I and II, and the results are shown in Figure 7. The COD of the water ranged from 20 to 26 mg/l and total solids varied between 352 and 360 mg/l. The very low COD precluded the necessity of any treatment for the waters of Pond III.

A fairly rapid exchange of water takes place in the log pond due to its small size and large inflow (400 gpm) and as a result, the dissolved oxygen concentration was found to be about 1.7 mg/l, the highest for any of the log ponds studied. This condition makes it possible for catfish and carp to survive in the water. A more



Area: 2 1/2 acres  
 Depth: 12'  
 Age: since 1940  
 Storage: 2 weeks  
 Types of logs: 85% ponderosa pine, 15% fir  
 Overflowing (400 gpm)

Station	DO mg/l	Temp. °C	COD mg/l	Total solids mg/l	Volatile solids %	Suspended** solids mg/l
1	1.5	23	20	352	30%	---
2	1.7	23	24	356	31%	---
3	2.0	23	26	360	32%	---
4	---	--	22	352	30%	4

\*\* Suspended solids were not run on frozen samples.

Figure 7. Pond III: layout, sampling stations and results of initial survey.

complete characterization of the pond is contained in a subsequent section.

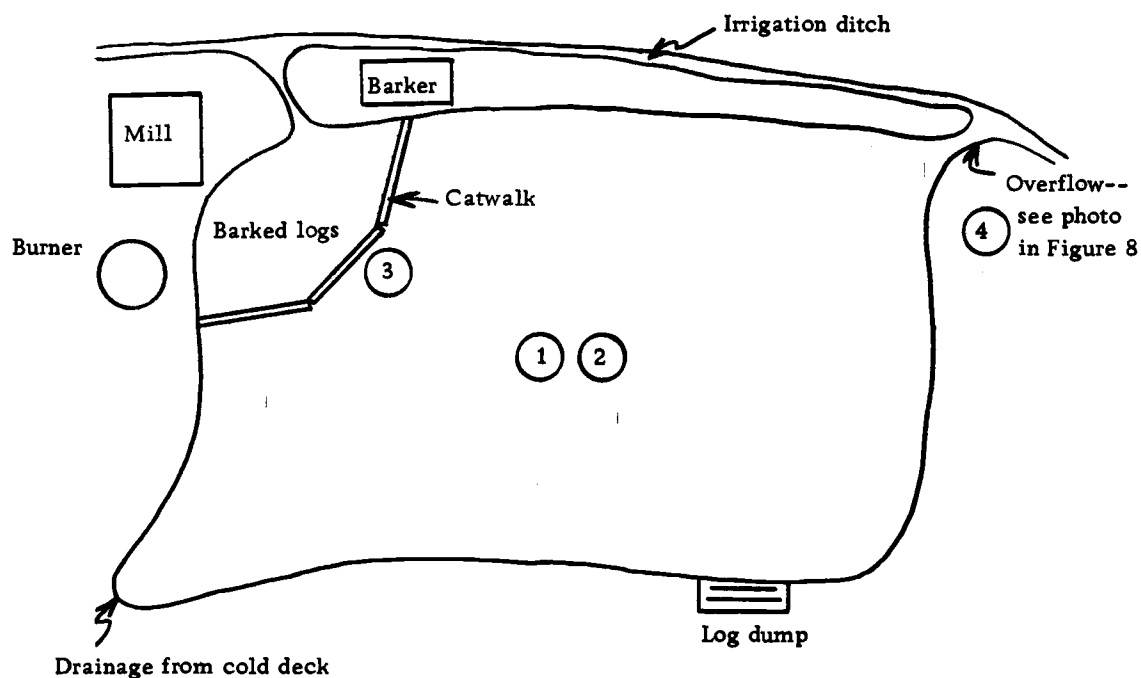
#### Pond IV

This 3-acre over-flowing pond, located near Prineville, Oregon, was excavated in 1920 and has been enlarged several times since (Figure 9). The pond is fed by an irrigation ditch and several springs. A 16 gpm overflow from the pond is directed back into the irrigation ditch (Figure 8).



Figure 8. Overflow of Pond IV, sampling Station 4.





Area: 3 acres

Depth: 4-5'

Age: Originally built in 1920, enlarged since

Storage: Approximately one week

Type of logs: Over 90% ponderosa pine, also white and Douglas fir

Station	DO mg/l	Temp. °C	COD mg/l	Total solids mg/l	Volatile solids %	Suspended solids** mg/l
1	0.4	21.0	312	550	40%	---
2*	0.2*	20.5*	316*	580*	50%*	---
3	0.5	21.0	310	530	44%	---
4	0.7	21.5	353	606	46%	122

\* Bottom sample

\*\* Suspended solids were not run on frozen samples

Figure 9. Pond IV: layout, sampling stations and results of initial survey.

Over 90% of the timber stored in the pond is ponderosa pine, and the remainder is made up of White fir and Douglas fir. Timber is stored in cold decks until it is ready for processing. The logs are then dumped into the pond and floated to the barker. Logs remain in the pond for approximately one week.

The results of the initial pond survey are shown in Figure 9. The COD at the overflow (353 mg/l) was approximately 11% greater than that found at the other stations. This result and the fact that any polluttional threat from the pond would be released through the outfall made this station the most logical choice for further sampling.

Due to long distances involved between the pond site and laboratory, four, 5-gallon polyethylene carboys were filled with pond water from the overflow, preserved against biological attack with 5 mg/l mercuric chloride and returned to Corvallis for further characterization and subsequent treatment studies.

#### Characterization of Log Pond Waters

A summary of the physical, chemical and biological characterization of the four log ponds investigated is given in Table 1. An attempt was made to relate the effects of type of logs stored and length of storage period on the nature of log pond water. However, the validity of these comparisons is limited somewhat since only four log ponds were involved in this study and since Pond II receives glue

Table 1. Summary of chemical, physical and biological characterization of log ponds investigated.

	Pond I	Pond II	Pond III	Pond IV
Flow-through nature	non-overflowing	non-overflowing	overflowing	overflowing
Major timber species stored	Douglas fir	Douglas fir	ponderosa pine	ponderosa pine
Length of storage	1-3 years	1 week	2 weeks	1 week
Total solids, mg/l	254	724	352	606
Volatile solids, %	59	63	30	46
Suspended solids, mg/l	43	162	4	122
pH	6.9	7.1	7.5	7.2
COD, mg/l	116	484	22	353
Alkalinity (Bicarbonate)				
mg/l CaCO <sub>3</sub>	99	255	212	218
BOD <sub>5</sub> , mg/l	29	54	6	68
BOD <sub>20</sub> , mg/l	48	167	10	116
k, day <sup>-1</sup>	0.08	0.03	0.08	0.08
Nitrogen (total Kjeldahl)				
mg/l N	2.4	10.4	<1.0	4.9
Nitrates, mg/l N	0.6	1.5	<1.0	0.7
Total Phosphate				
mg/l PO <sub>4</sub>	0.5	1.2	<1.0	2.0
PBI, apparent SSL*, ppm	175F**	545F**	35F**	338F**

\* Spent sulfite liquor

\*\* Filtered samples

wastes from an adjacent plywood plant.

### Type of Logs Stored

The effects of the type of timber stored on the composition of log pond waters were investigated using ponds with nearly equal storage periods. The ponds selected for this comparison were Pond II, storing Douglas fir, and Pond IV, storing ponderosa pine; both ponds have a one week holding period. Pond III was eliminated from this comparison due to the fact that the rapid exchange of water in the pond greatly dilutes the concentration of materials leached from the logs.

The most significant contrast in the chemical composition of Pond II and IV is the difference in the PBI results. The amount of phenolic or lignin-like material contained in Pond II (Douglas fir) was approximately 60% greater than that contained in Pond IV (ponderosa pine). The COD of the water from Pond II was nearly 40% greater than that from Pond IV. The COD results may be due in part to the presence of glue wastes in Pond II and/or the fact that Pond IV has a slight overflow. The PBI values would not be affected by the additional wastes since glue does not contain lignin-like material.

The ultimate BOD ( $BOD_{20}$ ) of Pond II water was approximately 45% greater than the ultimate BOD of the water from Pond IV, which agrees with the COD observation. The  $BOD_5$ , however, is somewhat

less for Pond II water than that found for Pond IV water. This indicates that the water from Pond II is more difficult to degrade. The lower BOD decay constant ( $k$ ) found in Pond II substantiates this finding.

### Storage Period

As the log storage period in a log pond decreases, the capacity of the pond in number of logs per acre per year increases proportionately. As a result, the concentration of substances leached from logs stored in waters may be expected to be greater for ponds with shorter storage periods. This argument is strengthened by the results given for Ponds I and II in Table 2. Both ponds store Douglas fir but have different storage periods.

The COD of the water from Pond I (storage period 1-3 years) is only 24% of that for Pond II (storage period 1 week). Similarly, the PBI and total solids for Pond I were approximately 35% of the respective results for Pond II. Although the differences in COD and total solids may be affected by the presence of glue wastes in Pond II, the PBI values would not.

### Sand Filtration

The sand filter described in the section entitled EXPERIMENTAL PROCEDURES AND APPARATUS (see Figure 2) was employed

to determine the feasibility of treating log pond waters by this physical treatment method. The filter was operated at a hydraulic flow rate of 2 gallons per minute per square foot of filter ( $\text{gpm/ft}^2$ ). The effectiveness of filtration was measured by the percent reduction in  $\text{BOD}_5$ , COD and suspended solids between raw and filtered water. Results of the filtration tests are given in Table 2.

These results demonstrate that sand filtration had no measurable effect on the waters from Pond I, which has a storage time of one to three years. However, there is some reduction of BOD, COD and suspended solids in pond waters with storage times from one to two weeks. Due to the small reduction in BOD and COD, sand filtration would not be feasible as the sole method of treatment. However, sand filtration might be employed ahead of an activated carbon treatment system to reduce filterable suspended solids.

### Chemical Coagulation

Chemical coagulation with aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) was investigated as a possible method for the clarification of log pond waters. This evaluation was made using the jar test outlined by the Calgon Corporation (Coagulant Aids . . . , 1967). This method is described in the section entitled EXPERIMENTAL PROCEDURES AND APPARATUS.

Prior to any evaluation of the effectiveness of chemical

Table 2. Waste strength reduction by sand filtration. \*

	BOD <sub>5</sub> inflow mg/l	BOD <sub>5</sub> outflow mg/l	BOD <sub>5</sub> reduction %	COD inflow mg/l	COD outflow mg/l	COD reduction %	S. S. inflow mg/l	S. S. outflow mg/l	suspended solids reduction %
Pond I	29	29	0	128	128	0	43	41	5
Pond II	41	35	15	476	397	16	194	139	28
Pond IV	**	**	**	328	279	15	123	60	50

\* Water from Pond III was too dilute for treatment.

\*\* Sample preserved with mercuric chloride.

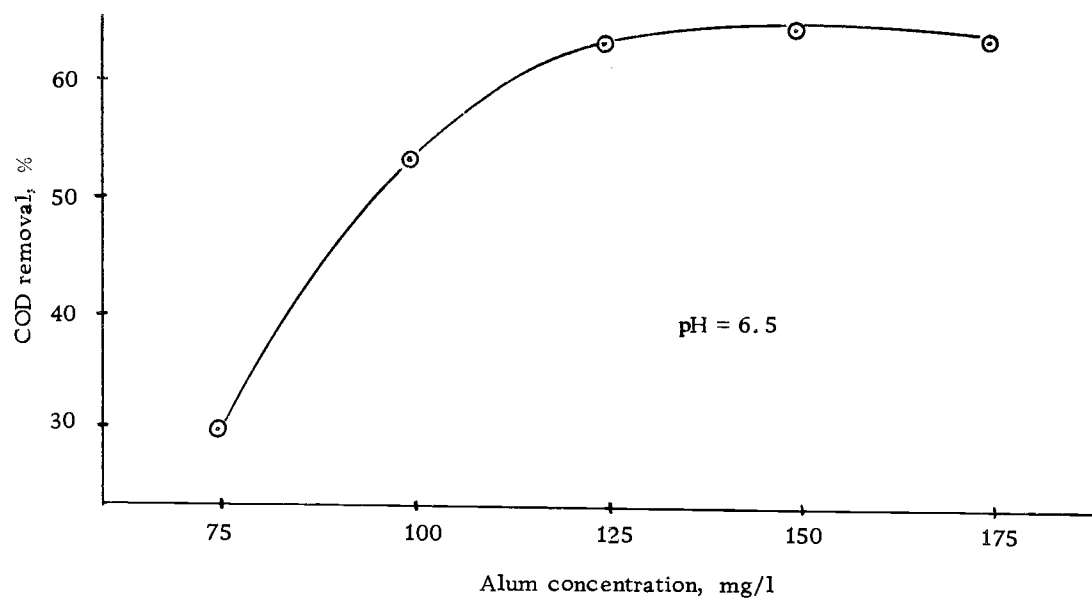
coagulation for the treatment of log pond waters, preliminary experiments were conducted on water from each log pond to determine the optimum pH and alum concentration.

The optimum alum concentration, expressed as  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , was determined for Pond I in the following manner. Various amounts of aluminum sulfate were added to six, 1-liter samples of pond water to given alum concentrations ranging from 75 to 175 mg/l. After the samples were thoroughly mixed, the pH of each solution was adjusted to 6.5 with 1.0 N solutions of  $\text{H}_2\text{SO}_4$  or NaOH. Jar tests were then run on the treated samples. The COD removal at each alum concentration was determined and a plot of the results is shown in Figure 10a. From the graph the optimum alum concentration at pH 6.5 was found to be 125 mg/l.

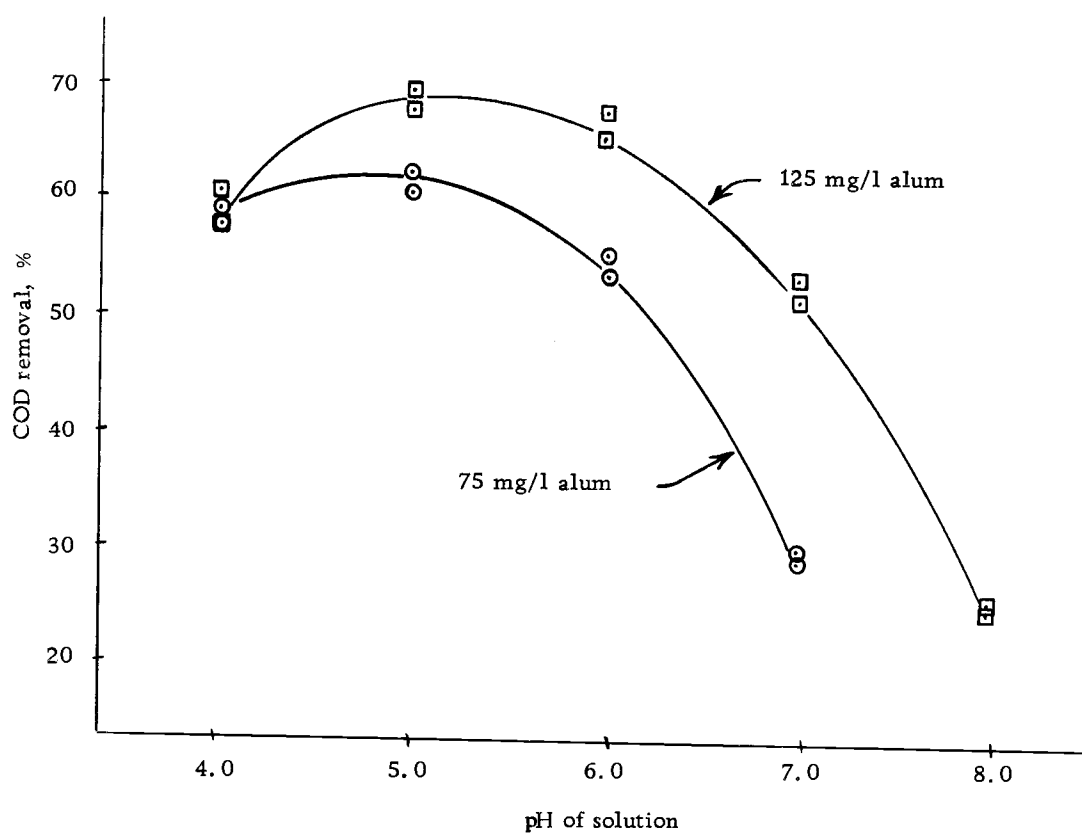
The optimum pH for coagulating the waters from Pond I was obtained by a second series of jar tests. A constant alum concentration of 125 mg/l was provided in each sample. The pH was then varied from 4.0 to 8.0 by the addition of  $\text{H}_2\text{SO}_4$  or NaOH as described above. Upon completion of the jar test, the reduction in COD at each pH was determined. A pH of 5.0 was found to be optimum.

Tests were run at an alum concentration of 75 mg/l to determine whether the coagulant dosage influenced the optimum pH. From the plot of the results shown in Figure 10b, the optimum pH at this alum dosage was again found to be 5.0, even though the magnitude of





(a)



(b)

Figure 10. Pond I: determination of (a) optimum alum concentration and (b) optimum pH for chemical coagulation.

COD removal was somewhat less.

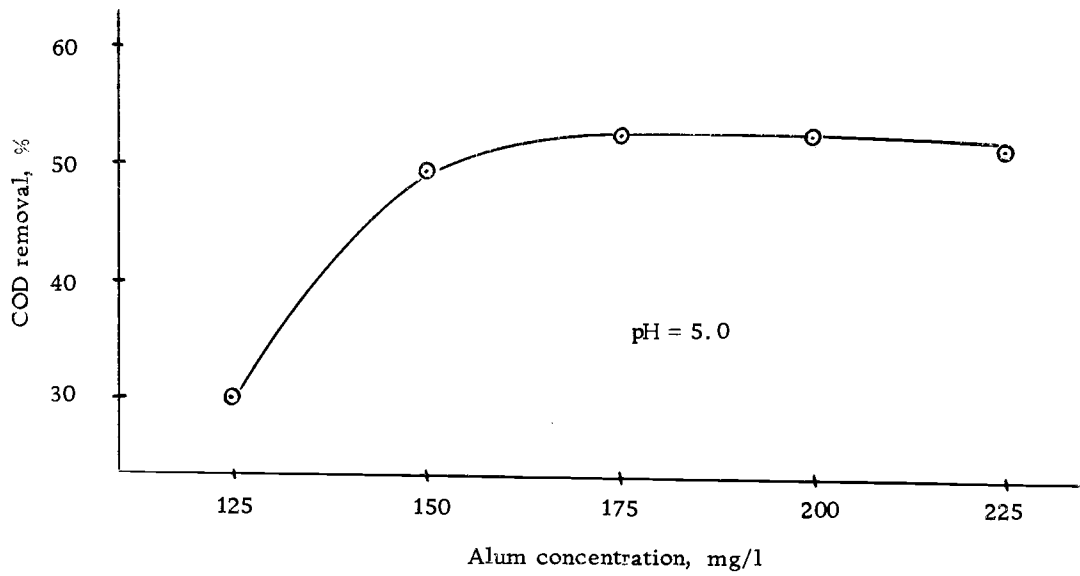
The optimum pH and alum concentrations for coagulation of the waters from Ponds II and IV were determined in a manner similar to that described for Pond I. The results are shown in Figures 11 and 12.

The optimum alum concentrations for coagulation of the waters from the ponds studied ranged between 125 and 175 mg/l. A pH of 5.0 was found to be optimum in all cases. The effective pH range for coagulation, however, was not consistent. For example, at an alum concentration of 175 mg/l and a pH of 6.0, a 53% COD reduction was obtained for Pond I water whereas at the same alum dosage and the same pH only 13% of the COD was removed from Pond II water.

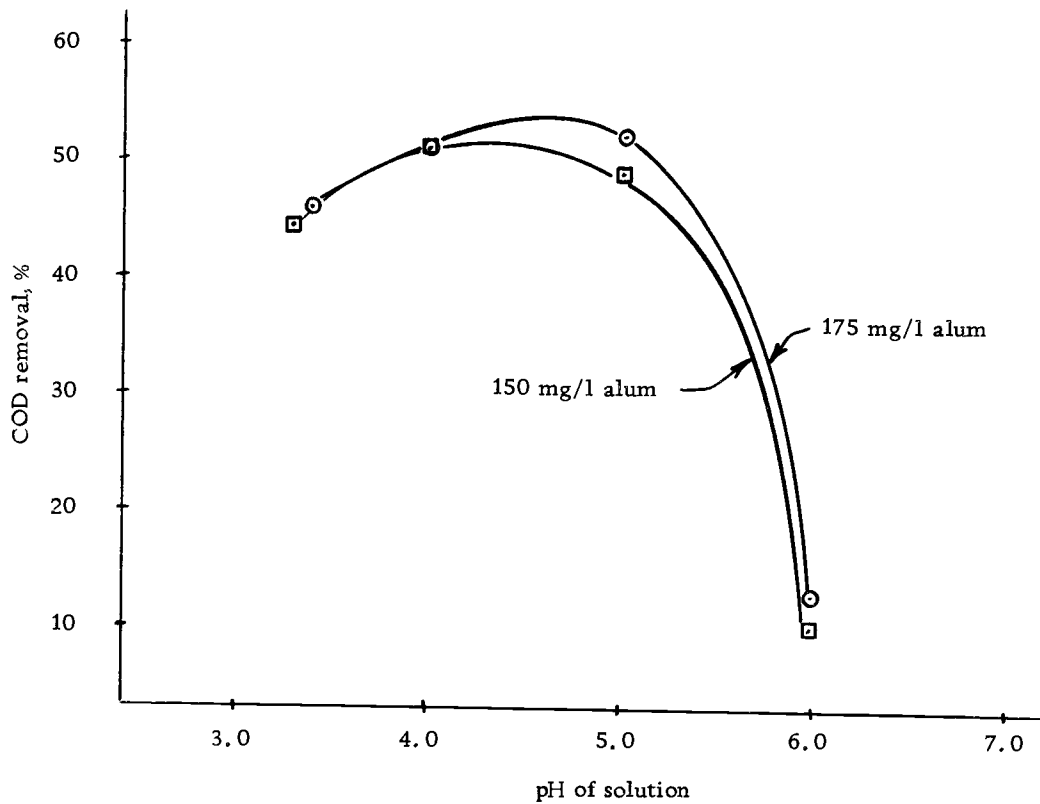
COD removal for pond waters treated with aluminum sulfate ranged from 52 to 68%. Reduction in suspended solids, PBI and  $BOD_5$  are given in Table 3. Also included in this table is an estimation of sludge produced during coagulation.

The percent reduction in COD by coagulation with alum does not appear to be significantly affected by the type of logs stored or the length of storage period. However, the validity of this assumption is questionable due to the presence of glue waste in Pond II and the small number of ponds investigated.

A greater reduction in lignin-like material through coagulation, as indicated by the PBI results, was observed for Pond IV, storing

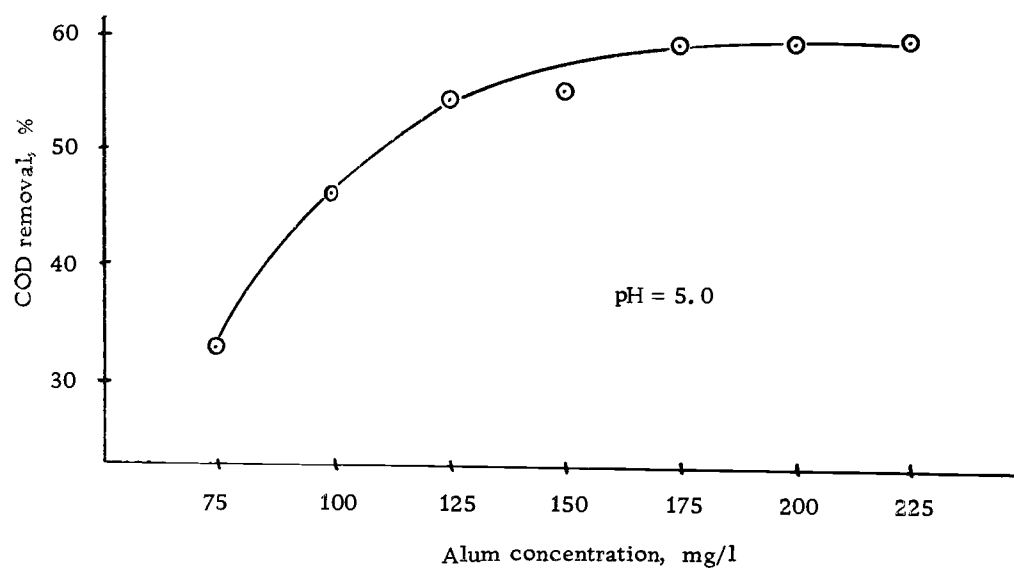


(a)

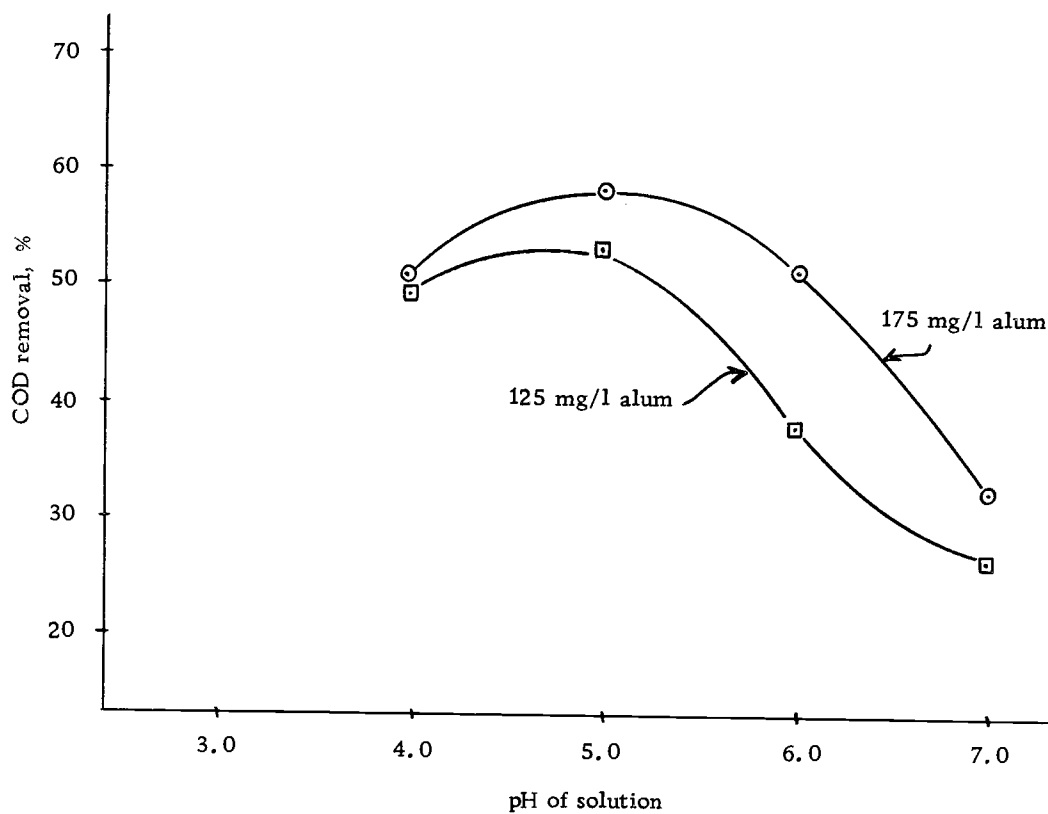


(b)

Figure 11. Pond II: determination of (a) optimum alum concentration and (b) optimum pH for chemical coagulation.



(a)



(b)

Figure 12. Pond IV: determination of (a) optimum alum concentration and (b) optimum pH for chemical coagulation.

ponderosa pine, than for those ponds storing Douglas fir.

Table 3. Waste strength reduction by chemical coagulation.

		Pond I	Pond II	Pond IV
BOD <sub>5</sub>	Inflow mg/l	29	41	*
	Outflow mg/l	27	21	*
	Reduction %	7	49	*
COD	Inflow mg/l	128	460	324
	Outflow mg/l	42	220	136
	Reduction %	67	52	58
Suspended solids	Inflow mg/l	43	180	126
	Outflow mg/l	3	48	5
	Reduction %	93	73	96
PBI**	Inflow mg/l		545F	338F
	Outflow mg/l		415F	118F
	Reduction %		24	65
Sludge volume produced ml/l		35	48	40

\* Samples preserved with mercuric chloride.

\*\* Filtered samples.

### Adsorption Isotherms

The adsorption isotherm technique, as outlined in the section entitled ACTIVATED CARBON ABSORPTION, was used to determine the treatability of log pond waters by activated carbon contact. Data for the isotherm plots were obtained by using COD as a waste strength parameter.

Figure 13 shows the adsorption isotherm for the waters of Pond I. The near-straight line plot indicates that the adsorption follows

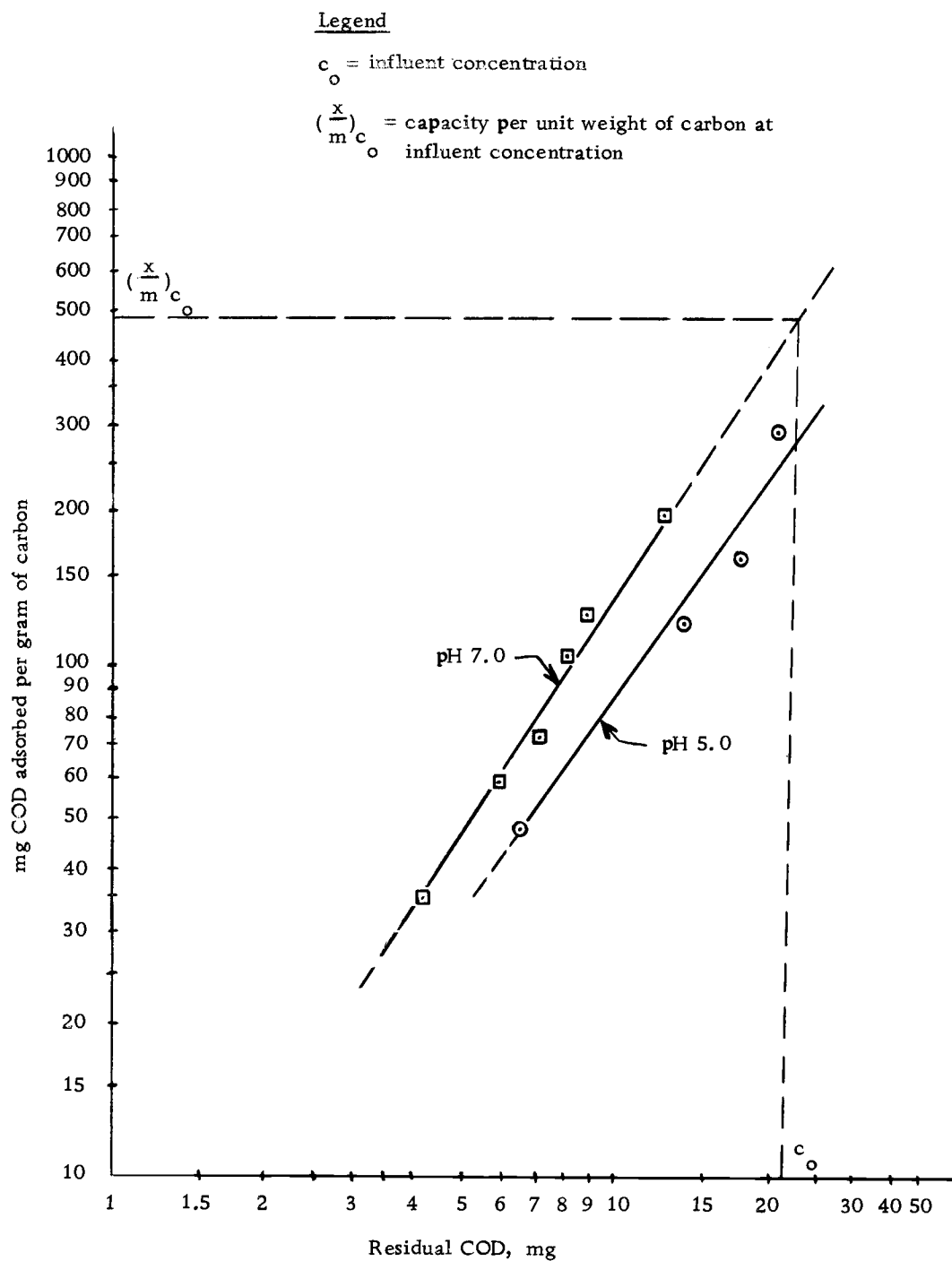


Figure 13. Adsorption isotherms for Pond I run at pH 5.0 and pH 7.0.

the empirical Freundlich equation. This is quite often the case for liquids which do not contain several wastes which are absorbed at different rates. The ultimate capacity of the carbon was found to be  $485 \frac{\text{mg COD}}{\text{gram carbon}}$ , i. e., 1 gram of carbon will absorb 485 mg COD at equilibrium. In terms of volume of water treated, the ultimate capacity was found to be  $4.33 \frac{\text{liters purified}}{\text{gram carbon}}$ .

A second isotherm evaluated at pH 5.0 showed a decrease in the carbon adsorption. Generally the adsorption of organic molecules is more efficient at their isoelectric point, or the pH at which they are most reactive.

The adsorption isotherm for the water of Pond II is shown in Figure 14. The change in slope indicates that the pond water may contain two or more different types of materials which are adsorbed at different rates. This may be the result of glue wastes in the log pond water. The ultimate capacity was found to be  $272 \frac{\text{mg COD}}{\text{gram carbon}}$  or  $1.97 \frac{\text{liters purified}}{\text{gram carbon}}$ . An isotherm run at pH 5.0 in this case showed an increase in adsorbance.

Figure 15 shows the adsorption isotherm for Pond IV water. The upper portion of the curve very nearly follows the Freundlich equation. The vertical segment at the lower end of the curve indicates that 4.8 mg COD is non-adsorbable. As a result, the ultimate capacity of the carbon is obtained by a vertical line drawn from the abscissa at a residual COD concentration of  $c_o = 4.8$ . The ultimate

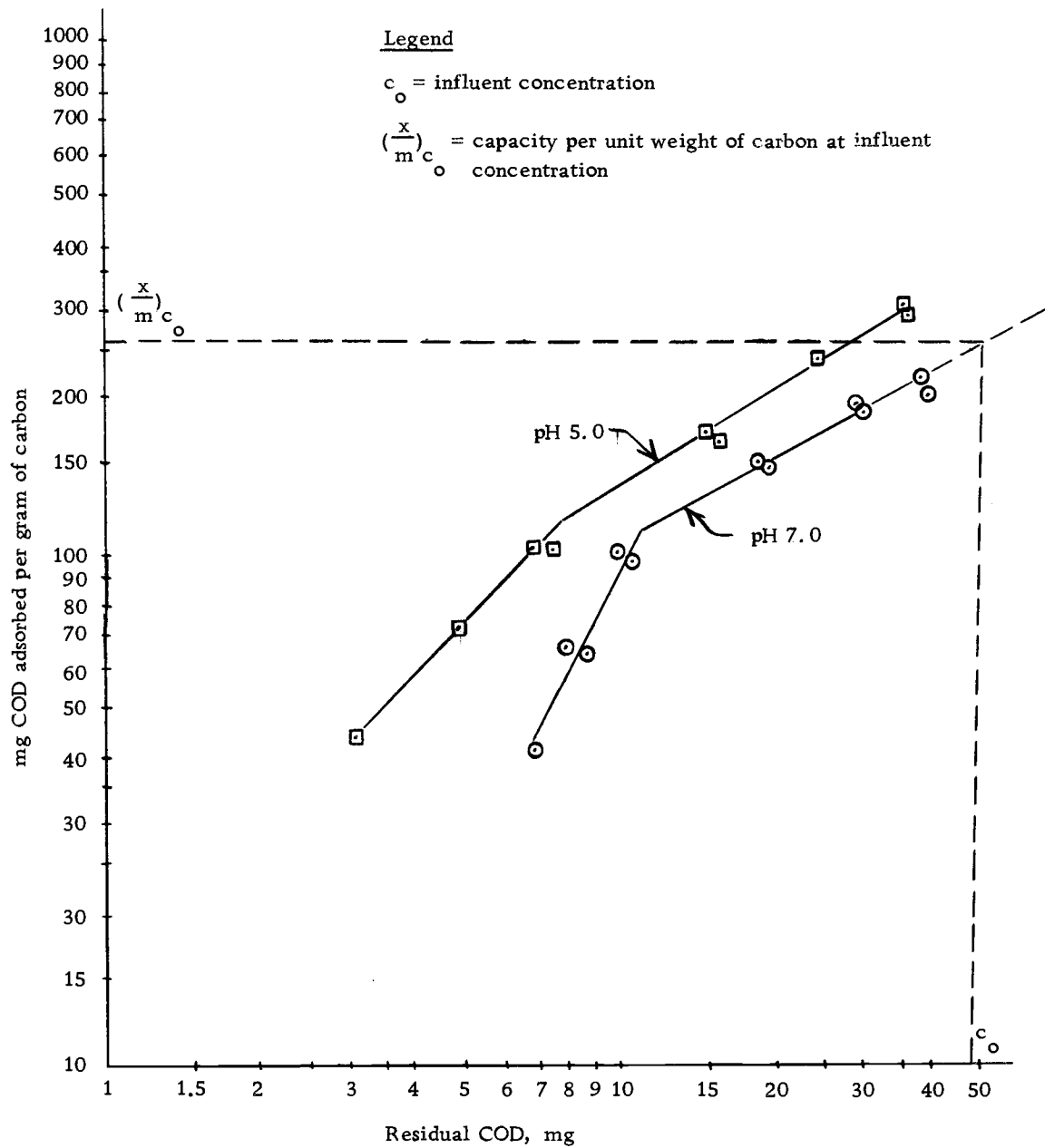


Figure 14. Adsorption isotherms for Pond II run at pH 5.0 and pH 7.0.



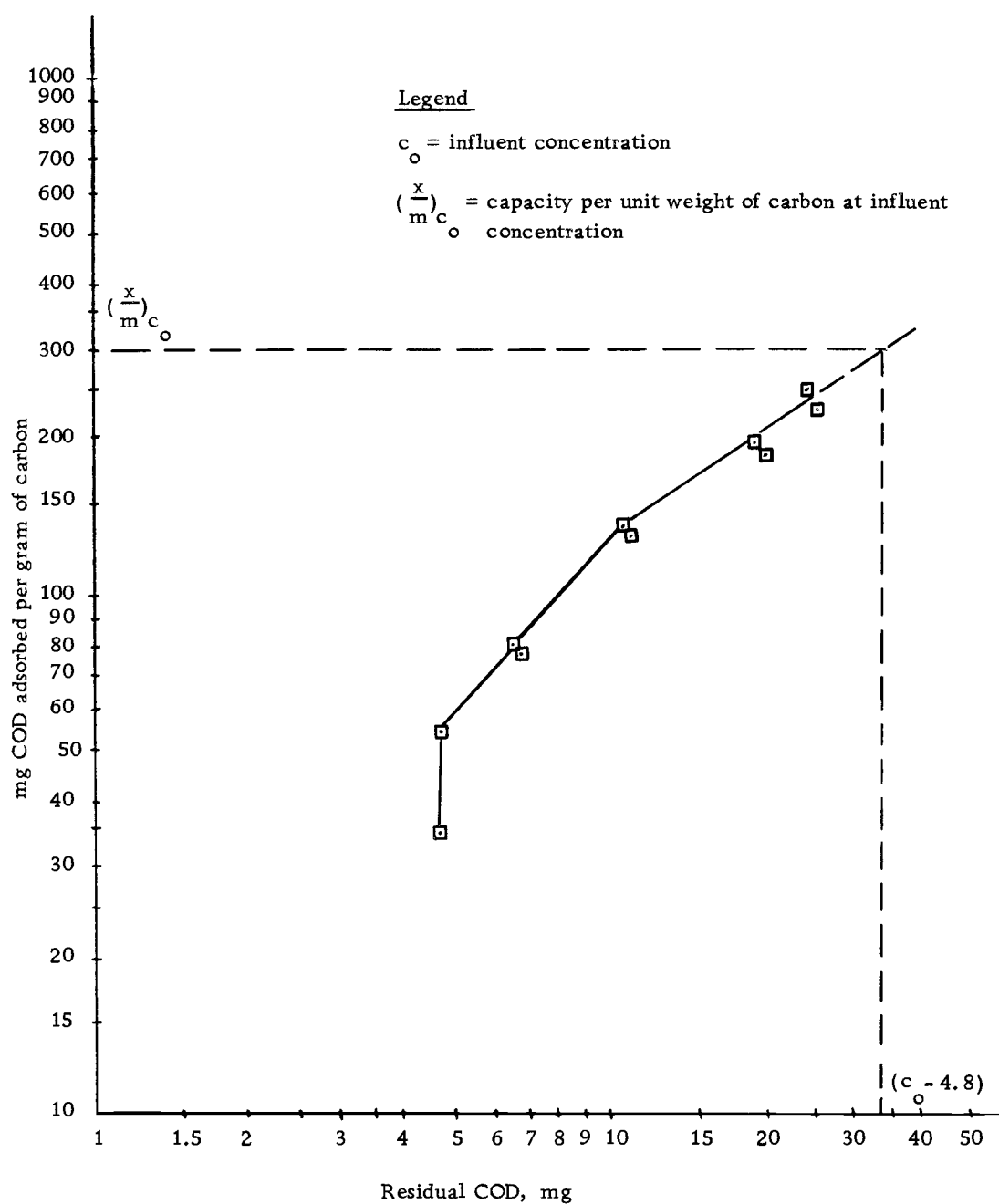


Figure 15. Adsorption isotherm for Pond IV run at pH 7.0.

capacity was found to be  $300 \frac{\text{mg COD}}{\text{gram carbon}}$ , or  $1.74 \frac{\text{liters purified}}{\text{gram carbon}}$ .

In comparing the results of the isotherm tests, the term " $\frac{\text{mg COD}}{\text{gram carbon}}$ " must be used instead of " $\frac{\text{liters purified}}{\text{gram carbon}}$ " since the COD per liter will vary considerably for each pond. The results indicate that there is no significant difference in the adsorptive capacity of carbon for pond waters storing pine and those storing fir for one to two weeks. However, it appears there may be a considerable increase in the ultimate capacity of the carbon with water from ponds having longer storage periods. Perhaps this is due to a more complete biodegradation of the material in Pond I water as a result of the increased storage time. This is consistent with the large difference in the composition of Pond I water compared to the waters of Ponds II and IV (Table 1).

The adsorption isotherm can be used to determine whether or not a particular COD removal can be achieved and the approximate ultimate capacity of the carbon for that application. For example, from the isotherm plot for Pond IV water (Figure 15) it is indicated that a residual COD of 4.8 mg for the 200 ml sample can be achieved. This corresponds to a COD concentration of 24 mg/l, and a COD reduction of 92%.

Before a full scale activated carbon column can be reliably designed, pilot plant studies should be conducted using columns with

bed depths similar to those expected for plant operation. This is necessary to determine flow rate and bed depth for optimum performance.

## CONCLUSIONS

The results of this investigation have led to the following conclusions:

1. Log pond waters are generally homogeneous in nature, based on the small number of ponds investigated.
2. Concentrations of lignin-like substances extracted from logs appear to be higher in ponds storing Douglas fir than in those storing ponderosa pine. This observation is primarily based upon the PBI results.
3. Sand filtration does not appear to be a feasible method of treating log pond waters. However, filtration might be employed to remove filterable solids ahead of other treatment processes.
4. Chemical coagulation of pond waters with aluminum sulfate at concentrations ranging from 125 to 175 mg/l was found to be effective in removing up to 96% of the suspended solids and as high as 68% of the COD.
5. Activated carbon contact was found to be the most effective method of clarifying log pond waters. The ultimate capacity of the carbon used in this study ranged from 272 to  $485 \frac{\text{mg COD}}{\text{gram carbon}}$ .

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## APPENDIX



Table A-1. Comparison of rapid and standard COD methods.

Source of log pond waste water	Rapid COD method mg/l	Standard COD method mg/l	Average % recovery
Pond I	112	124	97
	120	112	
	116	120	
Pond II	488	488	100
	488	488	