Ultrafiltration of Alkalignin

Ultrafiltration of Alkalilignin Through Dynamic Membranes Formed of Feed Constituents

By

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ABSTRACT

Membranes formed by constituents of ultrafiltration feed solutions on a support structure are called dynamic membranes. Lignin has the ability to form a self-rejecting membrane potentially useful for separating lignin from pulping wastes.

lignin solutions and pulp mill wastes were circulated past support tubes at different operating conditions. A typical product flux was about 7 gal/ft^{2}day with about 99% rejection. The effect of the feed solution concentration, the pore size of the support structure and the cross-flow velocity were small on the membrane performance. A temperature increase from 30°C to 70°C increased the product flux by 130%. A higher operating pressure increased the product flux only slightly above a critical pressure of about 80 psi. The product flux was highly dependent on the pH, being e.g. 30 gal/ft^{2}day at pH2 and 7.5 gal/ftday at pH//.

Some chemical additives, reported to alter liquid conformation, were tested and the best results were given by addition of formaldehyde. It increased the product flux at pH2 from 30 gal/ft^{2}day to 42 gal/ft^{2}day. A pretreatment of the carbon support tubes by hydrochloric acid

improved the product flux from 6 gal/ft^{2}day to 16 gal/ft^{2}day but the beneficial effect, in this case, was time dependent.

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1. INTRODUCTION

Ultrafiltration has had little practical significance until the development of anisotropic and dynamic membranes. In some cases waste water constituents form, on a support structure, a self-rejecting membrane. Pulp mill wastes are known to have this property. (Perona et al. 1967). If by studying operational parameters conditions could be found where a dynamic self-rejecting membrane would let through a high flux at moderate pressure and reasonable rejection, this technique might be a feasible alternative to treat effluents or recover lignin from effluents of the pulping industry.

The object of this study was to develop a dynamic self-rejecting ultrafiltration membrane composed of lignin and to test its potential usefulness for separating lignin from sulfate pulping waste waters. For this purpose the effect of the most important operating parameters on lignin membrane performance had to be studied, and means to improve product fluxes and rejection had to be tried with a synthetic lignin solution. Finally, samples of kraft mill effluent were ultrafiltered at the most promising operating conditions.

2. LITERATURE REVIEW

2.1 Membrane Processes

2.1.1 Reverse Osmosis

Osmosis is the spontaneous transport of solvent molecules from a dilute solution to a concentrated solution through a semipermeable membrane. This membrane prevents the passage of solute molecules but allows solvent molecules to pass through. Solvent flow can be induced by exerting pressure on the more concentrated side of the membrane. At a certain pressure, equilibrium is realized and the amount of solvent passing in each direction is equalized. This happens at the so called osmotic pressure which is a property of the solution only.

If the pressure in the more concentrated side of the membrane is increased above the osmotic pressure, the solvent flow reverses. This phenomen, called reverse osmosis, is the basis of many practical applications in water treatment.

Osmotic pressure can be calculated for a solution when the concentration of solute and the temperature are known (Tommila 1965):

$$\pi = \frac{n}{V} RT \tag{1}$$

where π = osmotic pressure
n = number of moles
V = volume
R = gas constant
T = temperature

Equation (1) is valid only for dilute solutions. For more concentrated solution it is modified with an osmotic pressure coefficient, ϕ, (Weber 1972), and equation (1) is rewritten as

$$\pi = \phi . \frac{n}{V} RT \tag{2}$$

The solvent flow is proportional to the pressure difference on both sides of the membrane minus the difference in osmotic pressure (Weber 1972)

$$F_w = W_p \ (\Delta P - \Delta \pi) \tag{3}$$

where F_w = solvent flux
W_p = solvent permeation coefficient
P = pressure

The solvent permeation coefficient depends on the following parameters (Weber 1972)

$$W_p = \frac{D_w C_w V_w}{R \ T \ \delta_m} \tag{4}$$

where D_w = diffusion coefficient of solvent
C_w = concentration of solvent
δ_m = thickness of the membrane
V_w = molar volume of solvent

Thus

$$F_w = \frac{D_w C_w V_w}{R \cdot T \; \delta_m} (\Delta P - \Delta \pi) \tag{5}$$

A small amount of solute passes through the membrane (Merton 1966) and

$$F_s = -D_s \frac{dC_{ms}}{dx} + C_{ms} u_m \tag{6}$$

where F_s = solute flux

D_s = diffusion coefficient of solute

C_{ms} = solute concentration in membrane

x = distance

u_m = velocity of solvent through the membrane

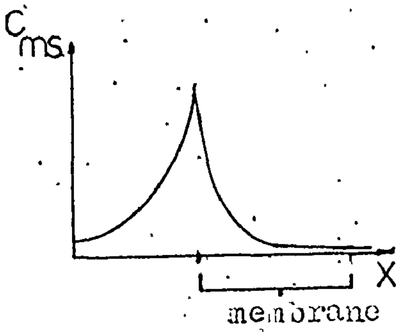
The first term is the solute diffusion terms and the second one is the solute transport by solvent flow term. If the second term is negligible, then

$$F_s = B(C_{1s} - C_{2s}) \tag{7}$$

B = solute mass transport coefficient

C_{1s} = concentration of solute on high pressure side of the membrane

C_{2s} = concentration of solute on low pressure side of the membrane



The primary and best criterion of the membrane performance, as is shown in Appendix I, are total flux through the membrane, usually given in gal/ft^{2}day and rejection of solute. Rejection is defined as

$$R = 1 - \frac{C_{2s}}{C_{1s}} \quad (8)$$

or

$$R = \frac{(C_{1s} - C_{2s})\ 100\%}{C_{1s}} \quad (9)$$

where R = rejection

2.1.2 Ultrafiltration

Ultrafiltration and reverse osmosis are related processes. They both rely on a pressure difference across a membrane for transport of solvent. Reverse osmosis membranes reject ionized salts and small molecules. If they can be considered to have pores, the pores are less than 20 A in diameter. For such tight membranes it is very difficult to distinguish between transport through pores and transport by diffusion. On the other hand, a typical ultrafiltration membrane has pores with a diameter between 20 A and 100 A. This is small enough to reject colloids and large molecules but large enough for laminar solvent flow of solvent. Because some membranes have pores belonging to both ultrafiltration and reverse osmosis regions, both processes can occur simultaneously.

In ultrafiltration the membrane screens out colloids and molecules larger than the pores. Thus a more concentrated solution is formed on the upstream side of the membrane. There is no sharp molecular weight or particle size cutoff because membranes usually have a distribution of pores sizes. Molecules with the same diameter as the pores, are rejected by the smallest pores but will pass through the larger ones.

Another theory (Harriot 1973) suggests that the concentration of solute varies from pore to pore at the same depth. If the concentration is low, most pores will have no solute molecules, some will have one and very few will have two or more. The flow of solution is assumed to be lower in pores containing solute molecules than in empty pores, hence, the concentration of solute on the low pressure side of the membrane will be lower.

The solvent flux can be described by equations analogi~~cal~~ to current, voltage and resistance relations in electricity, i.e.,

$$\Delta P = F_w R_m \quad \text{or} \quad F_w = \frac{\Delta P}{R_m} \tag{10}$$

where R_m = membrane flow resistance.

The membrane resistance is determined by porosity, pore radius, density of solvent, tortuosity, viscosity and membrane thickness as

$$R_m = \frac{8\tau^2 \mu \partial m}{\varepsilon a^2 \zeta \ell} \tag{11}$$

where τ = tortuosity

μ = viscosity of solvent

ε = porosity

a = pore radius

$\zeta\ell$ = density of solvent

Thus

$$F_w = \frac{\varepsilon a^2 \zeta \ell}{8\tau^2 \mu \delta_m} \quad \Delta P \qquad (12)$$

2.1.3 Membranes

Until the late 1950's, the lack of suitable membranes made reverse osmosis and ultrafiltration impractical processes. This changed with anisotropic membranes which were developed first by Loeb and Sourirajan (Michaels 1968). By properly adjusting polymer casting solution composition and properly controlling after treatment conditions they succeeded in preparing anisotropic cellulose acetate membranes with thin layers of varying structure. The superiority of these anisotropic membranes is based on their property not to become plugged or fouled by solutes. The reason seems to be that any particle small enough to enter a micropore in the skin layer of the membrane on the pressure side has no difficulties finding its way out from the opposite side through larger pores.

Cellulosic membranes suffer from some limitations. They can be used only in aqueous solutions since organic solvents either dissolve it or plasticize it sufficiently to cause its collapse. Most of them lose their permeability if allowed to dry. Also they cannot by operated at high or low pH or at temperatures above 50 - 60°C.

Other synthetic polymers have been used for producing anisotropic membranes. In many cases their physical and chemical properties are much better than those of cellulose membranes. Some membranes can be handled dry and they can be used with a variety of organic solvents as well as operated at temperatures up to 150°C without deterioration. Solvent flux and rejection can be controlled over a broad range. High molecular fluxes can be maintained through these membranes; e.g. 100-600 gal/ft^{2}day is possible for separation of compounds with a molecular weight of 100,000 at 100 psi (80-100% rejection). Typical values in the lower performance range for these membranes are 10 gal/ft^{2}day for raffiuose with molecular weight of 600 and 25 gal/ft^{2}day for dextran with a molecular weight of 100,000, both at 100 psi (Weber 1972).

Another important discovery was made in 1966 by Marcinkowsky and his co-workers (1966). They found that inorganic polyelectrolytes added to pressurized salt solutions form a salt rejecting membrane when the solutions were circulated past and through porous supports. This class of membranes are called "dynamically formed" or "dynamic" membranes. A very wide assortment of additives have been shown to form membranes this way; synthetic and natural organic polyelectrolytes, hydrous oxides of some metals, etc.

High water fluxes frequently one order of magnitude higher than with cellulose acetate membranes (Johnson et al 1972), are observed. For many water treatment problems the degree of filtration seems to be adequate. Typical values for hydrous zirconium oxide membranes, on a porous carbon tube with 0.36μ pore size are 79% rejection of NaBr (0.025 ml/l) and 80 gal/ft^{2}day at 400 psi.

With most dynamic membranes it is not necessary to add one or more membrane forming materials to the feed solution after the membrane has been formed. Also in some cases the feed solution contains already a membrane forming material without additives. The advantages of dynamic membranes are (Hachscheif et al 1972):

(a) Easy formulation
(b) High flux rates
(c) Low cost

The disadvantages are:

(a) Non-homogeneity
(b) Less selective rejection than with cast membranes.

2.1.4 Concentration polarization

Because there is little difference between ultrafiltration and reverse osmosis, their boundary layer effects are similar. Rejection of particles, solute molecules or ions creates a higher concentration layer at the membrane surface on the high pressure side. Concentration polarization is defined as the ratio of solute concentration at the membrane surface to the solute concentration in the bulk phase.

This phenomenon has a great effect on the applications of membrane processes (Stratmann 1972, 1973). The osmotic pressure that has to be compensated by the hydrostatic pressure becomes higher and the corresponding smaller difference between applied pressure and osmotic pressure decreases the flux. Furthermore, the rejection decreases because the solute flux is proportional to the concentration difference, as seen in equation (7), the rejection decreases. Concentration polarization can bring about precipitation on the surface of the membrane and this layer can act as another membrane completely changing the characteristics of the original membrane. This second film is actually an unwanted dynamic membrane.

To minimize the effect of concentration polarization cross-flow techniques are usually applied. Filtration is achieved by pumping suspension or solution under pressure past the membrane at sufficiently high tangential velocities (Darlheimer et al 1970, Johnson 1970). To increase the effect of velocity turbulence promoters have been recommended (Mixon 1968, Thomas et al. 1970). A detached promoter made of thin wire in spiral form with longitudianl wire runners seem to be most effective. This probably comes closest to the ideal promoter defined as one that neither blocks the surface of membrane nor provides stagnant regions where solids can accumulate or concentration or rejected salts can build up.

The effect of turbulence promoters is greatest at low Reynolds numbers (Thomas et al 1968). Up to 50% higher transmission rates have been observed by using a turbulence promoter compared to the values found in the same test with a portion of membrane containing no promoters. Similarly the rejection can more than double.

2.2 Important Operating Parameters

2.2.1 Temperature

Equations 1 and 5 show that product flux should decrease with increasing temperature. However, the diffusion coefficient and the membrane thickness are also dependent on the temperature thus complicating the product flux and temperature relations. It can be seen that equations 12 and 5 have the same kind of temperature dependancy by remembering that the diffusion coefficient is directly proportional to the temperature and inversely proportional to the viscosity (if the osmotic pressure term is negligible).

Collins et al (1973) studied the effect of temperature on lignosulfonate rejection using self-rejecting membranes built by spent sulfite liquor. Lower temperatures brought about higher rejection, e.g. 50% at 70°C and 90% at 10°C. The flux rate was also highly dependent on temperature, e.g. about 3 gal/ft^{2}day at 13°C and 24 gal/ft^{2}day at 65°C.

Wiley et al (1967) found that the effect of temperature on the product flux is about the same for pure water and spent sulfite liquor when the osmotic pressure is less than 70% of the applied pressure. The experiments were made using cellulose acetate membranes in the temperature range of 10°C - 35°C. The relationship between flux and temperature was linear. The flux rate was twice as much at 31°C (10 gal/ft^{2}day at 600 psi) as at 10°C (5 gal/ft^{2}day at 600 psi). They observed only a slightly improved rejection at lower temperatures.

Perona et al (Perona et al 1967) studied self-rejecting spent sulphite liquor membranes on porous carbon and ceramic tubes at temperatures between 17.5°C and 62.5°C. The increase in the product flux with temperature was found to be inversely proportional to the viscosity of water. With carbon support the product flux changed from 9 gal/ft^{2}day at 20°C to 19 gal/ft^{2}day at 60°C both at 400 psi. Ceramic supports showed a little higher fluxes and steeper temperature dependancy. For the above change of temperature the rejection decreased only slightly, from 97% to 97% for the ceramic tube and from 90% to 85% for the carbon tube.

2.2.2 Pressure

Johnson et al (1972) found that the rejection of chloride improved from 90% to 95% when the pressure was increased from 300 psi to 900 psi using a dilute sodium chloride solution and Hydrous Zirconium (11) Oxide dynamic membranes. At the same time product flux increased from 35 gal/ft^{2}day to 80 gal/ft^{2}day. When the system was returned to 300 psi, most of the original rejection and flux returned overnight.

Perona (1967) found three different kinds of effects of pressure on the flux divided by pressure or permeability when using self-rejecting spent sulphite liquor membranes and different concentrations of feed solution and ceramic and carbon supports. With ceramic support and 1% sulphite liquor at 63°C the permeability decreased by a factor of 2.3 as the pressure increased from 100 psi to 700 psi. At the same time the product flow increased by a factor of 3.1. A second type of behaviour was exhibited by a carbon tube at above conditions. Permeability was completely unaffected by pressure or product flux was linearity proportional to the pressure applied. A third type of relation was observed ith a ceramic tube having larger pore size than the first one. The feed solution was 10% and temperature 25°C. After a normal decrease in permeability it increased rapidly above a certain pressure.

Porter and Michaels (1971) explain that product flux and pressure relations depend on solute concentration. Product flux will increase with pressure until the concentration at the membrane surface reaches some critical concentration. High molecular weight solutes, such as proteins and colloidal dispensions when concentrated beyond a certain point form solid or thixotropic gels. The gel layer will thicken until the convective transport of solute toward the membrane is reduced to a value equal to the diffusive back transport of solute away from the gel layer into the bulk solution. Any increase of pressure will cause the gel layer to thicken or compact resulting in increased resistance. With more concentrated solutions the critical point for gel formation is reached at lower pressures. With very dilute solutions this point is reached at very high pressures if it can be observed at all.

2.2.3 Concentration of Feed Solution

Some effects of feed solution concentration were presented already under pressure effects. Generally an increase in feed solution concentration lowers the product flux (Porter and Michaels 1971).

According to Palmer, Hopfenberger and Felder (1973) the rejection of surfactants increases with solute concentration, whereas the rejection of non-surface active solutes decreases with increasing concentration. They explain the behaviour of surfactants as a consequence of micellar aggregation of these solutes.

Bhattacharyya, Bewley and Grieves (1974) found that during the ultrafiltration of laundry wastes through non-cellulosic membranes, the addition to the feed of a 0.2µ suspension over the broad concentration range of a 100 mg/l to 500 mg/l, caused no drop in water flux. The organic carbon content in the waste decreased the product flux as expected. Their synthetic laundry waste caused the membrane to swell when total solids concentration was increased from 300 ppm to 900 ppm and resulted in poorer rejecton. This could be reduced conceivably by using higher cross-flow velocities and by short intermittent flushing periods with solute-free water.

The relation between feed solution concentration and required cross-velocity will be discussed later.

2.2.4 pH

In many cases, a change in pH of the feed solution has an effect on membrane performance. Johnson et al (1972) observed a strong relationship between pH and rejection and pH and product flux with an NaCl solution Zr(IV)O_2 membrane probably due to the effect of pH on the properties of the ZrO_2.

Sometimes adjustment of feed solution pH is unavoidable. For example cellulose acetate membranes cannot be used at a pH less than 4 (Staude 1973).

Johnson et al (1974) also did some experiments with kraft mill bleach plant effluents using zirconium membranes improved with a polyacrylate surface membrane. This time they didn't observe any remarkable changes in rejection or product flux (about 80 gal/ft^2day at 950 psi) when pH was varied between 5.7 and 9.7. Colour rejection had a slight maximum at pH8, about 99%.

If a membrane has ion-exchange capacities which are changed by pH, the rejection also changes. Anion change capacity drops with increasing pH, while cation change capacity increases. The rejection of ions behaves the same way (Shor et al 1968). The rejection of anion increases at higher pH, whereas cations behave the opposite way.

2.2.5 Linear Velocity

Ammerlaan et al (1969) studied the effect of linear or cross-flow velocity on product flux using cellulose acetate membranes and spent sulfite liquors and kraft bleach effluents. The pattern was always the same: above a certain velocity (minimum linear velocity) the flux remained constant whereas below the minimum linear velocity the flux rate dropped off as a result of concentration polarization. Furthermore, the minimum linear velocity increased as a function of the feed solution concentration. Minimum linear velocities were between 30 and 105 cm/sec. for solids concentrations between 1.8 and 95 g/l.

The dynamic model of membrane formation suggests that increasing linear velocity should decrease the boundary layer thickness and cause an increase in product flux. Perona et al (1967) found that at velocities high enough to give Reynolds numbers above 2000 (near the transition point from laminar to unstable flow), product flux and rejection were independent of velocity for all systems they used, except one. Here velocities greater than 135 cm/sec (Reynolds number 1920) caused increasing product flux and decreasing rejection. At 460 cm/sec. no rejection was obtained. Obviously high velocities sheared off the dynamic membrane. At velocities smaller than 135 cm/sec both the product flux and the rejection were independent of cross-flow velocity.

Moore et al (1972) found that product flux is independent of cross-flow velocity at pressures up to 350 psi using dynamic Zr(IV) Oxide membranes. At 950 psi the product flux changed during the operation from linearly increasing to exponentially increasing as the cross-flow velocity was increased.

Turbulence promoters have been mentioned earlier in the chapter dealing with concentration polarization. By using turbulence promoters the critical velocity can be reached at lower Reynolds numbers. The effect of cross-flow velocity on concentration polarization is calculated in Appendix 2. Comparison to calculated osmotic pressures in Appendix 3 shows the small significance of this parameter in most cases.

2.2.6 Pore Size of the Membrane Support

In the case of dynamic membranes, support material pore size is very important. It determines whether or not a membrane forms on the support and some of the properties of the membrane.

Porous support for dynamic membranes can cause six kinds of membrane behaviour (Savage et al 1969, Perona et al 1967, Johnson 1968) in order of increasing pore sizes:

1. No flux goes through if the pores are too small for the solvent.
2. The supporting structure acts itself as a membrane and a secondary membrane may or may not form on it.

3. A membrane composed of solute molecules, colloids or solids on the surface of the support material is formed.
4. A membrane forms as in 3 but some pores in support material are plugged irreversibly. Product flux can decrease.
5. Membrane forms as in 3 but leaks at some places because the membrane is pushed through larger pores. Rejection decreases.
6. Pores are too large for the formation of a membrane and the feed solution passes through without rejection.

The actual limits for each type of membrane are different for different solutions and depend on operating parameters such as temperature and pressure. By using additives such as clay or polymers, a membrane can be formed on a support structure where the feed solution does not normally form a membrane.

According to Perona et al (1967) the critical (type 6) pore diameter for spent sulfite liquor membranes on ceramic support was 1.4μ. On carbon supports a leakage was observed already at an average pore diameter of 0.41μ (type 5) but a wide pore size distribution implied that here, also, the limiting pore size may be 1.4μ.

2.2.7 Membrane Aging

If no secondary membrane forms on cellulose-acetate or other stationary membranes, the properties of these do not change or change only little with time. When a secondary membrane forms on a stationary membrane the system behaves like a dynamic membrane.

Because the forming of a self-rejecting dynamic membrane starts in the beginning of the operation, product flux and rejection change initially rapidly with time. Rejection increases and product flux decreases until an equilibrium is reached. This time depends primarily on the solution properties. It can take anywhere from a few minutes to a couple of hundred hours before the equilibrium is reached.

The original conditions can be easily restored with dynamic membranes by backwashing. The direction of the flow through the support material is reversed for a period of time and the membrane is worked out. Because stationary membranes usually can resist pressure from only one side, they have to be cleared by other methods.

One of the weaknesses of membrane processes has been a short membrane life time. A required life expectancy of 12 or more months for industrial use is not easily reached with stationary membranes (Barsal 1975). Easily renewable dynamic membranes, however, can be reformed indefinitely.

2.3 Pulping Processes

There are basically two different processes used in pulping. One uses an alkali cooking liquor to separate cellulose and other wood constituents. It is called the sulfate or kraft process. The other one employs an acidic cooking liquor for the same purpose. It is called the sulfite process.

2.3.1 The Sulfate Process

In the sulfate or kraft process, an aqueous solution of mainly sodium hydroxide and sodium sulfide is cooked with wood chips 4 to 6 hours at 165 to 175°C. During the cooking process natural liquors are converted to alkali liquors which then dissolve in the cooking liquor. After cooking the fibrous cellulose is separated from the solvent (black liquor). Dissolved liquor in its sodium salt form, contributes approximately half of the organic matter in black liquor. Additional components include other organic substances arising from carbohydrate and resin dissolution during cooking, e.g. carboxylic acids and alcohols. Inorganic constituents come from wood and unreacted cooking chemicals (Rankin 1975).

In a modern unbleached kraft mill individual wastes are are discharged from almost every phase of the process. From 15,000 to 40,000 gallons (75 to 180 tons) of water are typically discharged per ton of product. The effluent volume depends to a large extent on the type of product, degree of recirculation and condenser system employed (Rudolfs 1961).

The BOD discharged from a modern unbleached kraft mill amounts to approximately 50 lb (25 kg) per ton of product. Suspended solids sewered generally amount to less than 0.5% of production. Improvements in recovery systems have reduced in recent years, the oxygen demand discharged and this trend is expected to continue. Even a completely recycled water system is possible and a full scale plant of the Great Lakes Pulp and Paper Company on Thunder Bay has recently started to operate on this basis.

According to Rudolfs (1961) a typical 24-hour composite sample of combined effluent from a modern unbleached kraft mill has

	Max	Min	Average
pH	9.5	7.6	8.2
Total alkalinity (ppm)	300	100	175
Total solids (ppm)	2000	800	1200
Volatile solids (%)	75	50	65
Total suspended solids (ppm)	300	75	150
Volatile (%)	90	80	85
BOD (5 day, ppm)	350	100	175
Colour (Hazen units)	500	100	250

Processes employed for pulp bleaching are varied in respect to the stages employed. But generally two wastes of dissimilar reaction are produced. One is a acid waste from chlorine and hypochlorite bleaching and the other is an alkaline waste from the caustic extraction stage. The acid wastes are characterized by their low concentration in terms of oxygen consuming substances and colour as well as their large volume. The caustic extract waste is high in oxygen demand and colour but much less in volume than the acid wastes. Combination of these two generally produces a waste substantially neutral in reaction with a volume of 30,000 to 60,000 gallons (150 to 250 tons) per ton of pulp bleached. The colour is due mainly to lignin salts. The lignin salts are, to a degree, indicative of the acidity of the waste, varying from pale yellow at low pH to dark brown at high pH. Analysis of combined bleaching discharge is generally within the range of the following values (Rudolfs 1961):

pH	4.5 - 8.0
Turbidity (Hazen)	60 - 300
Total Solids (ppm)	1000 - 2000
Volatile (%)	45 - 65
Suspended Solids (ppm)	50 - 75
Volatile (%)	40 - 70
BOD_5 (ppm)	50 - 100

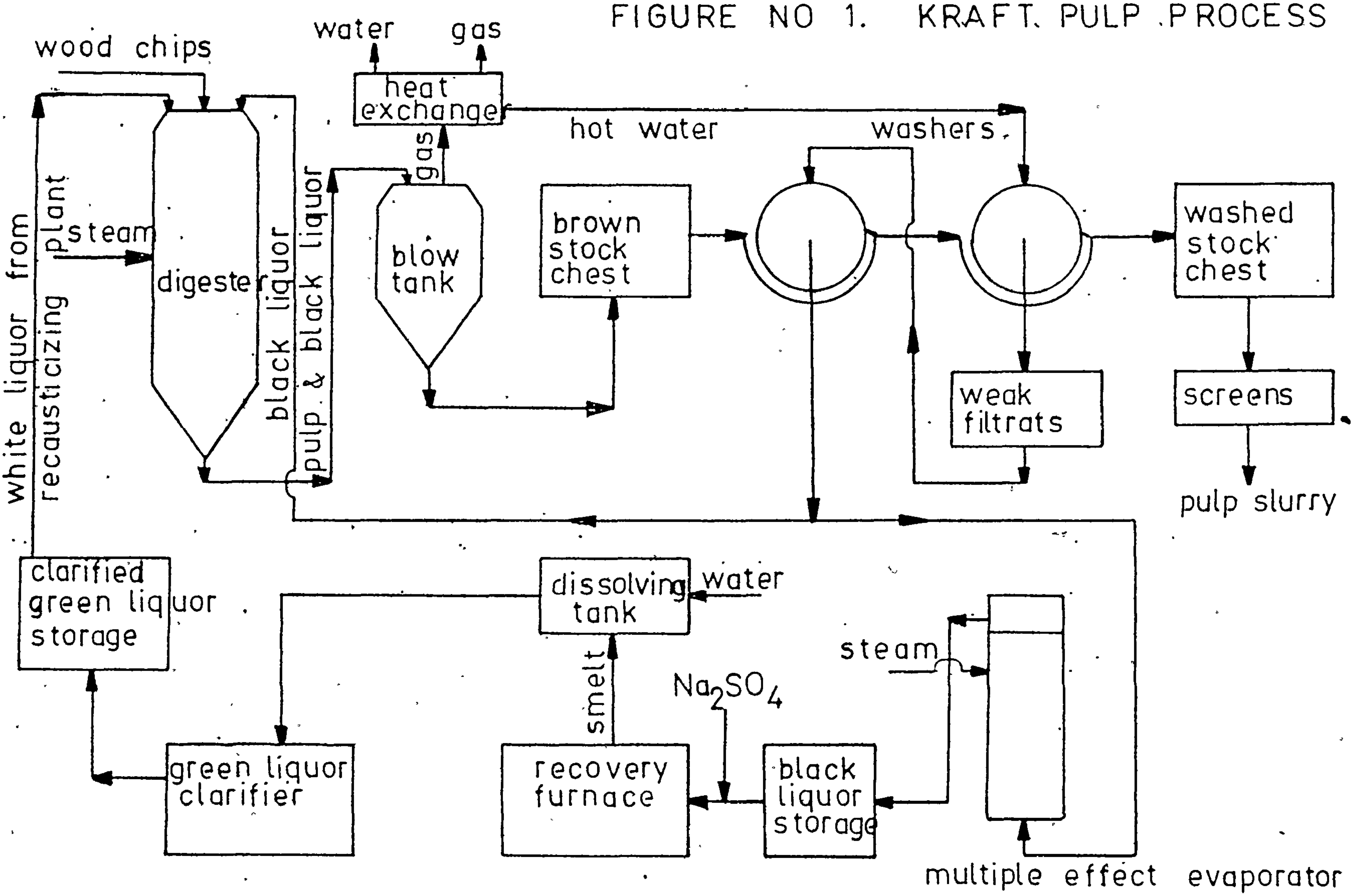
Because lignin is viturally non-biodegradable it doesn't contribute to BOD.

Diagrams of the kraft pulping and bleaching processes are shown in Figures 1 and 2 respectively.

2.3.2 The Sulfite Process

The emphasis in this thesis in on a alkali lignin and sulfate mill wastes, but for comparison a short look at the sulfite process is justified.

FIGURE NO 1. KRAFT PULP PROCESS



In sulfite pulping lignin and other wood solids (except cellulose) are solubilized by cooking wood chips in an acid containing mainly calcium (or NH_4 or Mg, Na) bisulfate, sulfurous acid and sulfer dioxide. After the cooking process cellulose fibres and the cooking acid, now called spent sulfite liquor, are separated. Of the solubilized wood solids more than half is lignin in the form of cooking base chemical salt of ligno-sulfonic acid. These are mixed in the spent liquor principally with wood sugars, with lesser amounts of other products hydrolyzed from hemi cellulose, with wood extractives such as resins and terpenes, and with inorganic pulping chemical residues (Bansal et Wiley 1975). Contrary to sulfate pulping, where black liquor chemicals are recycled, this is not generally done with spent sulfite liquor.

Some information of sources and characteristics of waste water from a typical sulfite pulp operation is given in the following table (Table 1) (Blisser et Gellman 1973).

A flow diagram of a sulfite pulp mill is shown in picture 3.

TABLE 1

Waste sources in a sulfite Mill

Process source	BOD lb/ton	Suspended solids lb/ton	Total solids lb/ton	pH	gal/ton
Blow tower	116	1	247	2.2-2.9	1900
Condensate	66	0.1	47	2.3-3.1	1100
Uncollected liquor	53	21	105	2.2-2.6	7500
Acid plant wastes	-	5	10	1.2	300
Boiler blowdown	0.05	2	22	-	100
Screening	8	8	27	5.4-5.7	6000
Washing and thickening	18	8	131	2.4-3.9	7500
Bleaching	25	15	220	2.9-6.8	15000
Total	286	60	809	29.400	
Total in ppm	730	153	2000		

FIGURE NO 2. BLEACHING WASTES

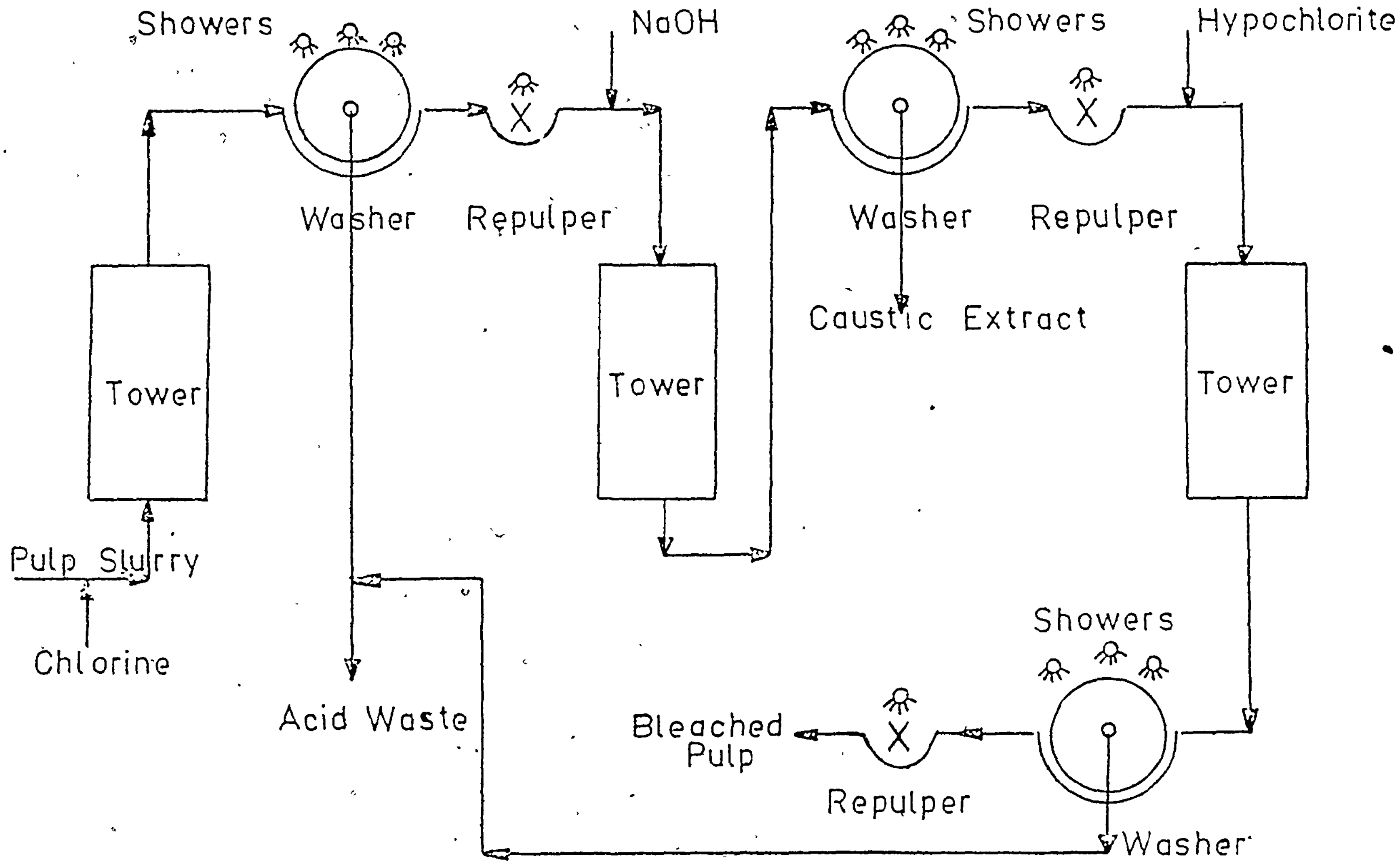
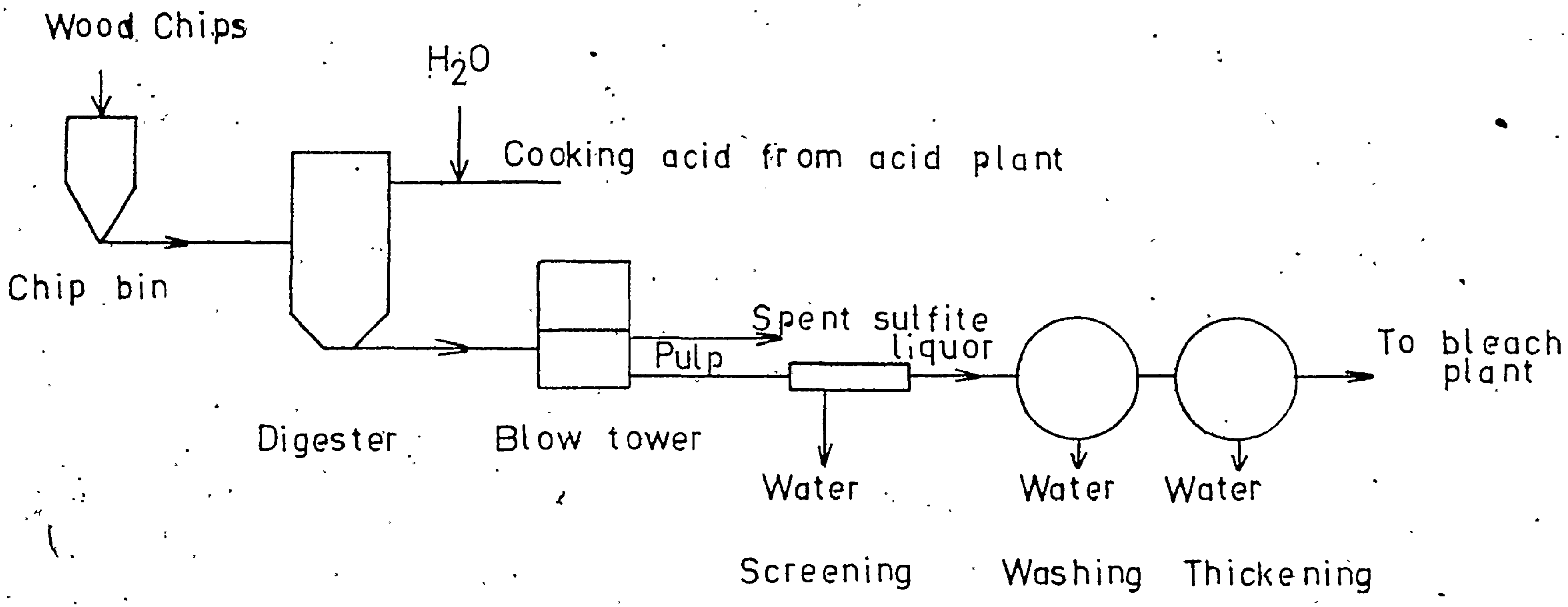


FIGURE NO 3. FLOW DIAGRAM FOR SULFITE PULPING PROCESS



2.4 Lignin

Lignin is defined in the paper industry as that part of plant material which is not saccharified by the action of 72% sulphuric acid or 42% hydrochloric acid after the resins, waxes and tannins have been removed (American Paper and Pulp Asn. 1940). Another definition says that lignin is a system of tridimensional polymers which permeates the membranous polysaccharides and the phases between plant cells. Its presence brings about a physiological death of the tissue. It is a functional component of wood and it occurs in mature wood as a preformed completed substance (Pearl 1967).

Lignin is one of the most abundant natural products. Coniferous woods (soft-woods) contain, in average, about 28% lignin and deciduous woods (hardwoods) about 24%. Lignin contact also varies from one wood species to another and from tree to tree and with the location of the tree.

A great many formulae have been proposed for lignin over the years. The rapid change of these formulae reflects the rate at which information has been accumulated during the last decades. There appear to be different kinds of lignins depending on the family classification of the tree.

The building materials for spruce lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. When a mixture of these in proportions of 14%, 80% and 6%

respectively is dehydrogenated until 1.5-2 hydrogen atoms per unit have been removed, natural spruce lignin has been duplicated. An idea of the complexity of this reaction is illustrated by an experiment done with coniferyl alcohol alone as starting material. When 1.0-1.2 hydrogen atoms per unit were removed the number of products were about 30 (Pearl 1967). One suggested formula for lignin is shown in Figure 4 (Kirk-Ottmer 1967).

Lignin in wood appears to be insoluble unless modified by physical or chemical treatment which changes its state of polymerization or hydrolyzes its bonding to other wood constituents. In general the methods for isolating lignin dissolve either lignin, or the other constituents, particularly cellulose. Since cellulose requires reactive solvents, lignin is probably also affected. Commercial lignins are byproducts of the pulp industry. The sulfite process has byproducts consisting of various lignosulfonates and lignosulfonic acid.

Alkalilignins may be precipitated from black liquor by lowering the pH. Thus isolated lignins contain approximately two thirds of the aromatic components in the black liquor. The non-precipitable aromatic material comprises of lower lignin oligomers, and phenolic monomers and dimers (Rankin 1975). Alkalilignins have a wide polydispersity.

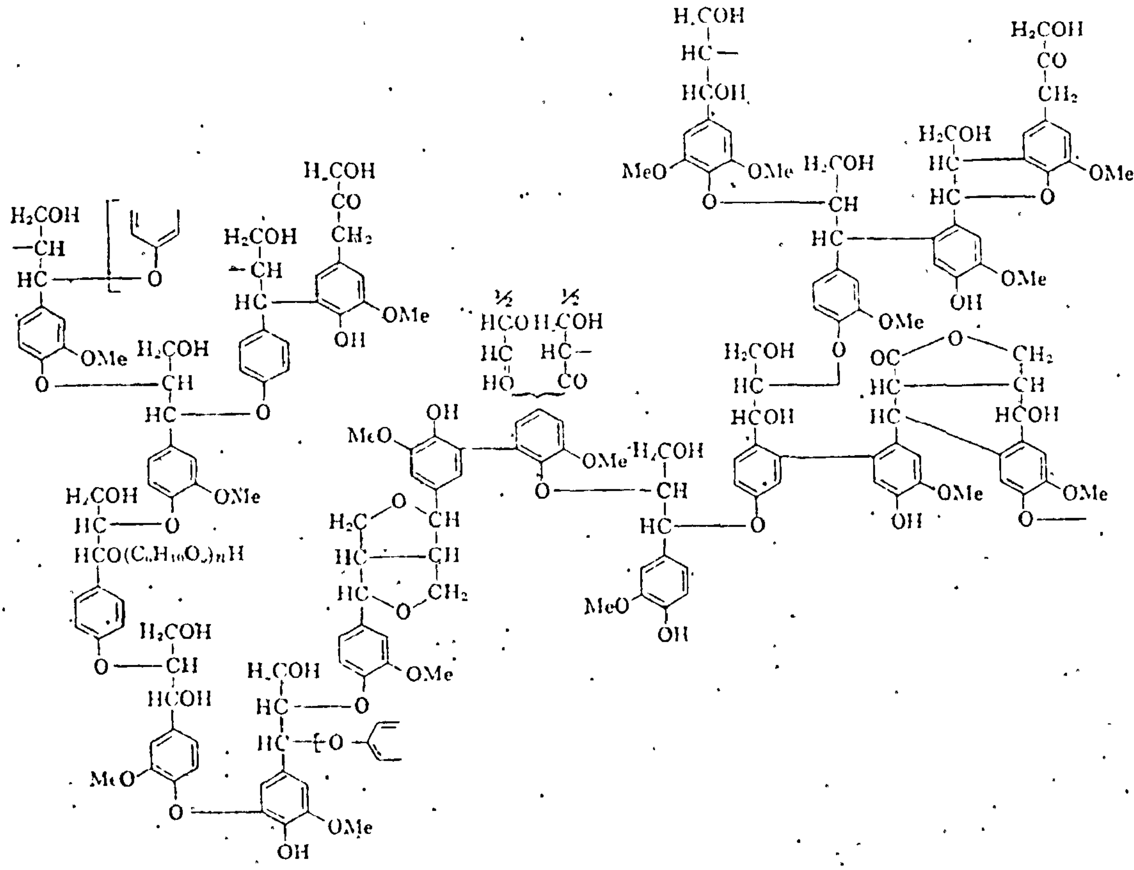


FIGURE 4 LIGNIN

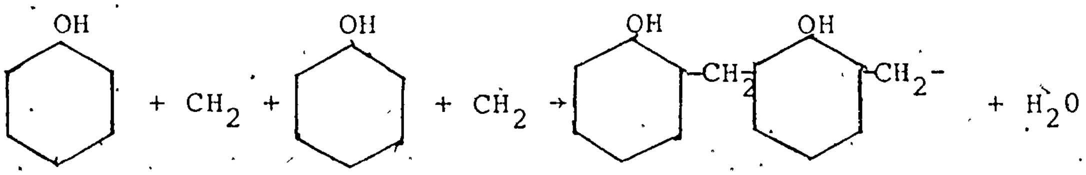
At low and medium pH, lignin is not soluble in water. At higher pH, the dissociation of lignin functional groups to negatively charged ions starts. The ionization continues with increasing pH until at pH 12 lignin is completely soluble. It is properly called alkalilignin only in this state. If acid is added to alkalignin solution the degree of ionization is gradually reduced and lignin precipitates as acid lignin which is shiny due to the solvation by water. At still lower pH lignin becomes partly soluble because of positive charges in lignin molecules due to loss of OH^- groups. This will reduce the amount of solvation water round lignin molecules because the added positive charges make the formation of hydrogen bridges more difficult.

The length of a lignin polymer depends on pH. Experiments made by Rankin (1975) indicate that a pH decrease is associated with an increase of the average molecular weight of alkalilignin. At pH 7 about 90% of the solution colour was exerted by constituents greater than 300 000 in molecular weight, corresponding to a hydrodynamic radius of 200Å (lignin molecules are almost spherical in solution). At pH 10 the same percentage was only 40%. At pH lower than 7 alkalilignin precipitates as acid lignin.

Whalen (1975) has proposed for separation of lignin the use of compounds which are able to replace some of the solvation water molecules around lignin molecules. This also increases the filterability of lignin. Although these compounds are soluble in water they are much less hydrophilic than water molecules themselves. Whalen compounds form a hydrogen bond to the acid lignin molecule through the slightly acidic (positive) hydrogen atom on a carbon atom carrying a requisite electronegative group.

$$\underset{\text{lignin}}{\equiv C = \overset{\partial -}{O}} \;---\; \underset{\text{Whalen compound}}{\overset{\partial +}{H} - CCl_3} \qquad \text{cf} \qquad \underset{\text{lignin}}{\equiv C = \overset{\partial -}{O}} \;----\; \underset{\text{water}}{\overset{\partial +}{HOH}}$$

The net results of the use of Whalen compounds are a change in physical properties of lignin and easier coagulation of lignin colloids or molecules with their associated solvation sphere. Aldehydes react with phenolic groups according to the formula (Schlenk 1965).



It is well known that the phenolic groups in lignin react with formaldehyde forming resins (Pearl 1967).

Acidification of any of the commercial black liquors from alkaline wood pulping processes will yield an alkali-lignins. This precipitates at low pH in a slimy, gelatinous form. Its physical nature makes it difficult to separate from the acidified, aqueous phase by centrifugation, settling and decantation or filtration. Separation of lignin by these techniques retains a substantial amount of mother liquor and thus becomes contaminated by sodium salts and numerous water soluble free organic acids.

Several other ways have been tried to change the undesirable properties of precipitated lignin in order to make their separation easier. The established techniques are based mainly on coagulating acid precipitated acid lignin or alkalilignin by heating black liquor at or near its boiling point at normal or at superatmospheric pressure. Elevated pressure is used to prevent actual boiling. Then lignin is allowed to settle and is recovered by decantation. Coagulation by freezing has been tried to convert lignin to a more easily separated form (Pearl 1967). Direct spray drying has also been proposed (Whalen 1975).

2.4.1 Ultrafiltration of Pulp Mill Wastewaters

Ironside and Sourirajan (1967) applied the reverse osmosis using cellulose acetate membranes to municipal wastewater, detergent and lignin solutions. The results, shown in Table 2, were not encouraging because product fluxes were low at a high pressure.

Wiley, Ammerlaan and Dubey (1967) used spent sulfite liquor and kraft bleach plant effluent at different

Table 2 Some Ultrafiltration Results

Solution	Membrane	Rejection %	Rejection unit	Flux $\frac{gal/ft^2}{day}$ psi	Ref.
lignin	C.A.	99	lignin	16.2/1000	Ironside, Sourirajan 1967
municipal sewage	C.A.	100	bacteria	31.1/1000	- " -
spent sulfite liq. and kraft	C.A.	~90	COD	2-13 /660	Wiley et al 1967
spent sulf.	lignin	80	color	87 /700	Perona et al 1967
- " -	lignin + ZrO_2	93	"	47.5/500	- " -
bleach plant eff.	lignin	90	"	7.5-9/400	
spent sulf. liq.	C.A.	>90		3.2/190	Collins et al 1973
- " -	C.A.	>90		12.4/430	- " -
	lignin			6.4/350	- " -
kraft mill eff.	lignin	93		20 /350	- " -
spent sulf. liq.	C.A.	85	lignin	20.7/300	Bansel and Wiley 1975
NaCℓ	C.A.	>99	color	125/300	- " -
kraft mill	ZrO_2	>99	color	70-135/450	Johnson et al 1974
bleach plant	ZrO_2	96	color	80-100/200	- " -
- " -	ZrO_2			68/400	Moore et al 1972
bleach plant	C.A.	99	color	22/750	Bansel 1975

concentration with a similar membrane as Ironside and Sourirajan. The operating pressure was kept at 600 psi. The rejection of COD was around 90% which is to be expected as their solutions were not pure lignin solutions and contained several species of small molecular weight components. Product fluxes were of the same order for all solutions studied varying from 2 gal/ft^{2}day to 13 gal/ft^{2}day depending on the concentration of feed solution. Kraft mill bleach plant effluent seemed to be more concentration dependent than other solutions.

Perona et al. (1967) formed dynamic membranes with spent sulfite liquors where calcium lignosulfonates constituted about 60% of total dissolved solids. They used both ceramic and carbon tubes as membrane supports. The cross-flow velocity was very high, 46 ft/sec (14 cm/sec). With 1% spent sulfite liquor and 400 psi with the feed flow inside 0.38μ pore diameter carbon tube the permeation rate decreased and colour rejection was apparent immediately after starting the test. After half an hour the observed rejection of colour was 75% and the product flux had decreased to 103 gal/day ft^2. After about 2 hours the observed rejection and product flux leveled off at 80% and 87.5 gal/day ft^2. They remained constant until the experiment was altered after 7 hrs by adding hydrous zirocium oxide to the liquor to a concentration of 10^{-3} M. The observed rejection then rose to 93% and the flux decreased to 47.5 gal/ft^{2}day. Different supports of the membrane gave different fluxes and rejections. Sometimes supports that were supposed to be similar gave different results for unexplained reasons. Runs were made also with sulfite mill bleaching plant wastes. A membrane was first formed on ceramic supports (0.9μ and 1.4μ pore size) with spent sulfite liquor. The system was drained and filled with bleach plant effluent. After 15 hours of operation at 500 psi over 90% rejection was obtained but product flux was low, only from 7.5 to 9 gal/ft^{2}day. Perona et al. concluded that if all variables affecting the performance of these membranes can be controlled, a production facility operating at 60°C and less than 500 psi will result in fluxes around 30 gal/ft^{2}day and rejections of greater than 90%.

Collins et al (1973) separated reducing sugars from spent sulfite liquor. With cellulose acetate membranes they attained over 90% rejection of lignin and their product fluxes ranged from 3.2 to 12.4 gal/ft^{2}day at pressures between 190 psi and 430 psi. With a dynamic lignin membrane the flux was 6.4 gal/ft^{2}day. They also formed a dynamic membrane from kraft bleach plant effluent containing 0.2% solids on a ceramic tube. After 100 hours of operation the flux rate was 20 gal/ft^{2}day, rejection was 93% at 350 psi and the crossflow velocity was 3.9 ft/sec (120 cm/sec).

Bansal and Wiley (1975) also used membrane processes to separate lignosulfonates and reducing sugars in spent sulfite liquor. They observed a negative rejection of reducing sugars, i.e. the composite permeate had a higher concentration of sugars than the feed solution. This happens if an ultrafiltration system operates in an osmosis zone of negative driving force. Although the membrane used was made of cellulose acetate which would be expected to hydrolyze at low pH, this did not happen due to the formation an effective dynamic membrane which protected the cellulose acetate membrane. Product flux was 20.7 gal/ ft^2day with spent sulfite liquor compared to 125 gal/ft^2day with sodium chloride solution, both at 300 psi. This indicates that the character of the membrane had changed. The rejection of lignosulfonates was 85%. Moore et al. (1972) succeeded in producing fluxes around 70 gal/ft^2day at 400 psi with ZrO_2 membranes but perhaps the most promising results are given by Johnson et al (1974). They utilized dual layer membranes, prepared by exposing the support material already coated with hydrous zirconium oxide to a solution containing polyacrylic acid and sulfuric acid at low pH. The feed solutions were kraft mill effluents simulated with diluted black liquor and bleach plant effluent. The flux was between 70 and 135 gal/ft^2day with kraft mill effluent and between 30 and 60 gal/ft^2-day with bleach plant effluent both at 950 psi. Colour reduction, in both cases, was over 99%. They reran these experiments (with the same solutions) using single layer hydrous oxide membranes. The reduction of colour was again over 99% and fluxes were between 80 and 100 gal/ft^{2}day at only 200 psi. The difference in these two types of membranes could be observed by measuring the rejection of smaller ions e.g., the chloride ion. With the single layer membrane at 200 psi, chloride rejection was about 15% whereas with the other membrane it was over 80% at 950 psi.

3. Dynamic Membrane Ultrafiltration Theory

In ultrafiltration with a dynamic membrane at constant operating conditions the number of molecules deposited on the membrane is inversely proportional to the membrane thickness because of the increasing flow resistance and the decreasing solvent flux through the membrane. The number of molecules removed from the membrane by the action of shearing forces which are proportional to the square root of the cross-flow velocity is assumed to be constant because the changes of the cross-flow velocity due to changes of the membrane thickness are relative small. Thus, the change of the membrane thickness is:

$$\frac{dL}{dt} = \frac{k_1}{L} - k_2 \qquad (13)$$

where $\frac{dL}{dt}$ = change of membrane thickness

L = membrane thickness

k_1 = constant

k_2 = constant

Equation 13 has a solution $(t=0,\ L=0)$

$$t = \frac{-L}{k_2} - \frac{k_1}{k_2^2}\ln(k_1 - k_2L) + \frac{k_1}{k_2^2}\ln k_1 \qquad (14)$$

The final thickness is reached when $dL/dt = 0$. Thus

$$L_f = \frac{k_1}{k_2} \qquad (15)$$

where L_f = the final thickness

Equation 14 can be expanded by using two first terms of Taylor's series

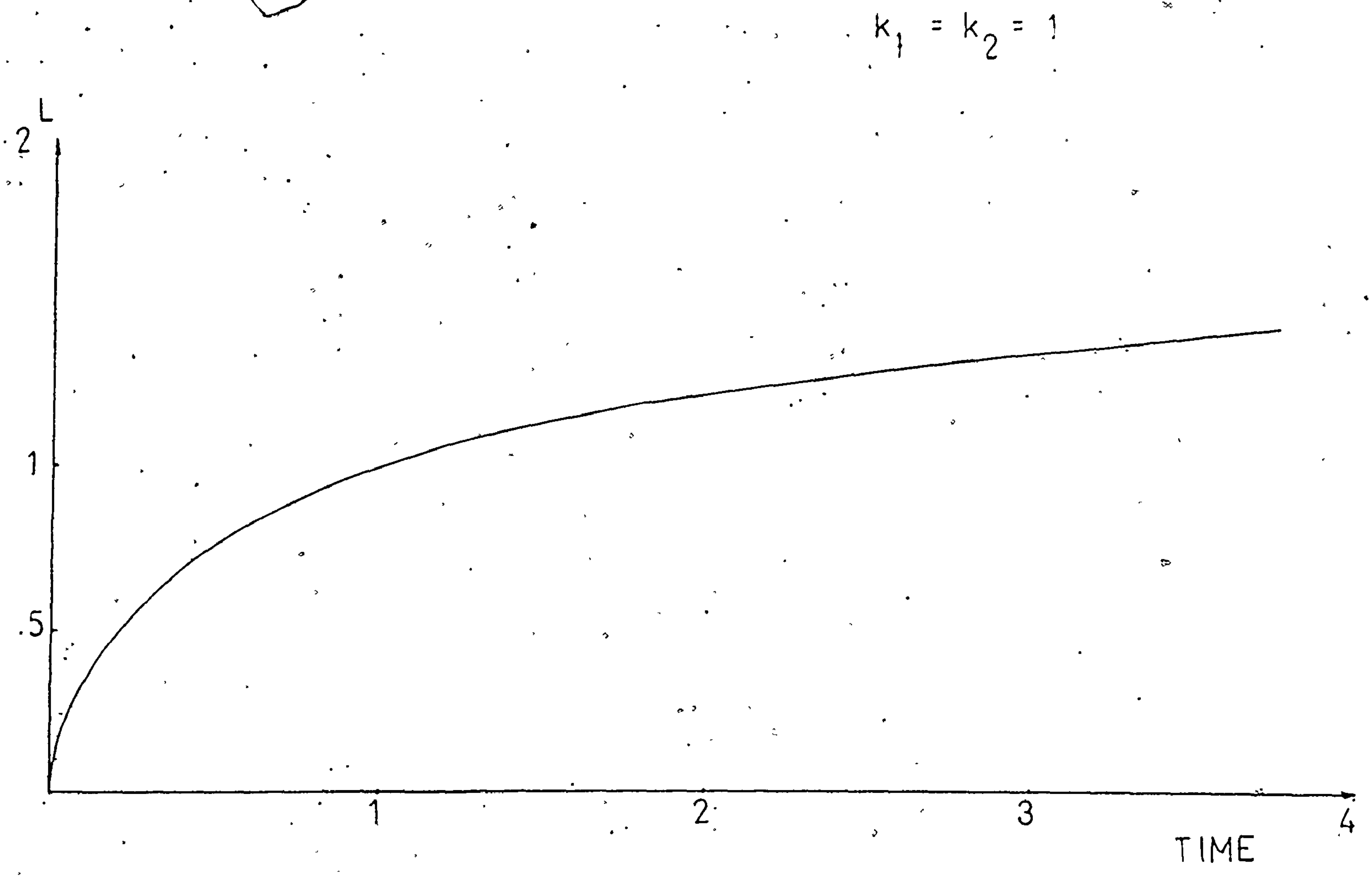
$$t = \frac{L}{-k_2} - \frac{k_1}{k_2^2}\left[\ln k_1 - \frac{2k_2L}{2k_1 - k_2L}\right] + \frac{k_1 \ln k_1}{k_2^2} \qquad (16)$$

or

$$t = \frac{-L^2}{k_2} + \frac{2k_1L}{k_2(2k_1 - k_2L)} \qquad (17)$$

Equation 17 is presented graphically in Figure 5, using values $k_1 = k_2 = 1$.

FIGURE NO 5. EQUATION 17



4. EXPERIMENTAL

4.1 Apparatus

The schematics of the system used in this thesis is shown in Figures 6 and 7. The feed solution is circulated from a 30.5ℓ stainless steel storage tank by a Y81 triplex positive displacement pump to the ultrafiltration unit with a rate of 10.5ℓ per minute. The unit consists of a stainless steel cylinder with openings for incoming and outgoing liquids. The support tube, located coaxially inside the cylinder, has both ends closed, except for a small tube in one end through which the product flux was collected and recycled back to the storage tank. The main flow was also recycled to the storage tank through an automatic pressure regulator. The overall system also consisted of a set of lines and valves for reversing the flow. Spring type pressure gauges were attached to both sides of the ultrafiltration unit.

The temperature was controlled by a mercury switch, immersed in the storage tank, and connected to a relay which operated a valve in the cooling water line. Tap water circulated inside copper cooling lines around the storage tank and the ultrafiltration cylinder.

Stainless steel, "316", was used originally throughout the apparatus itself with the exception of brass valves

FIGURE NO 6. ULTRAFILTRATION APPARATUS SCHEMATIC

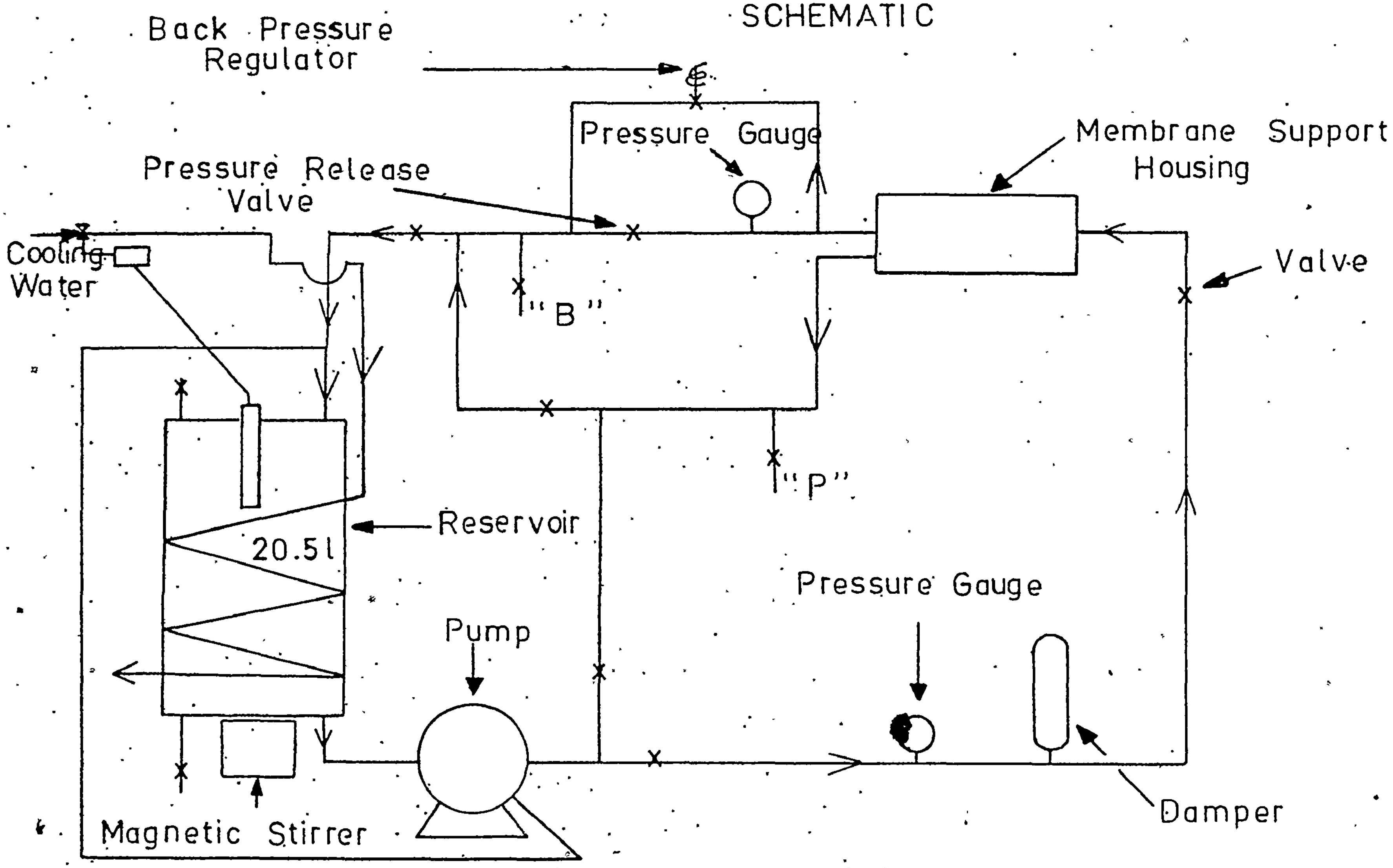
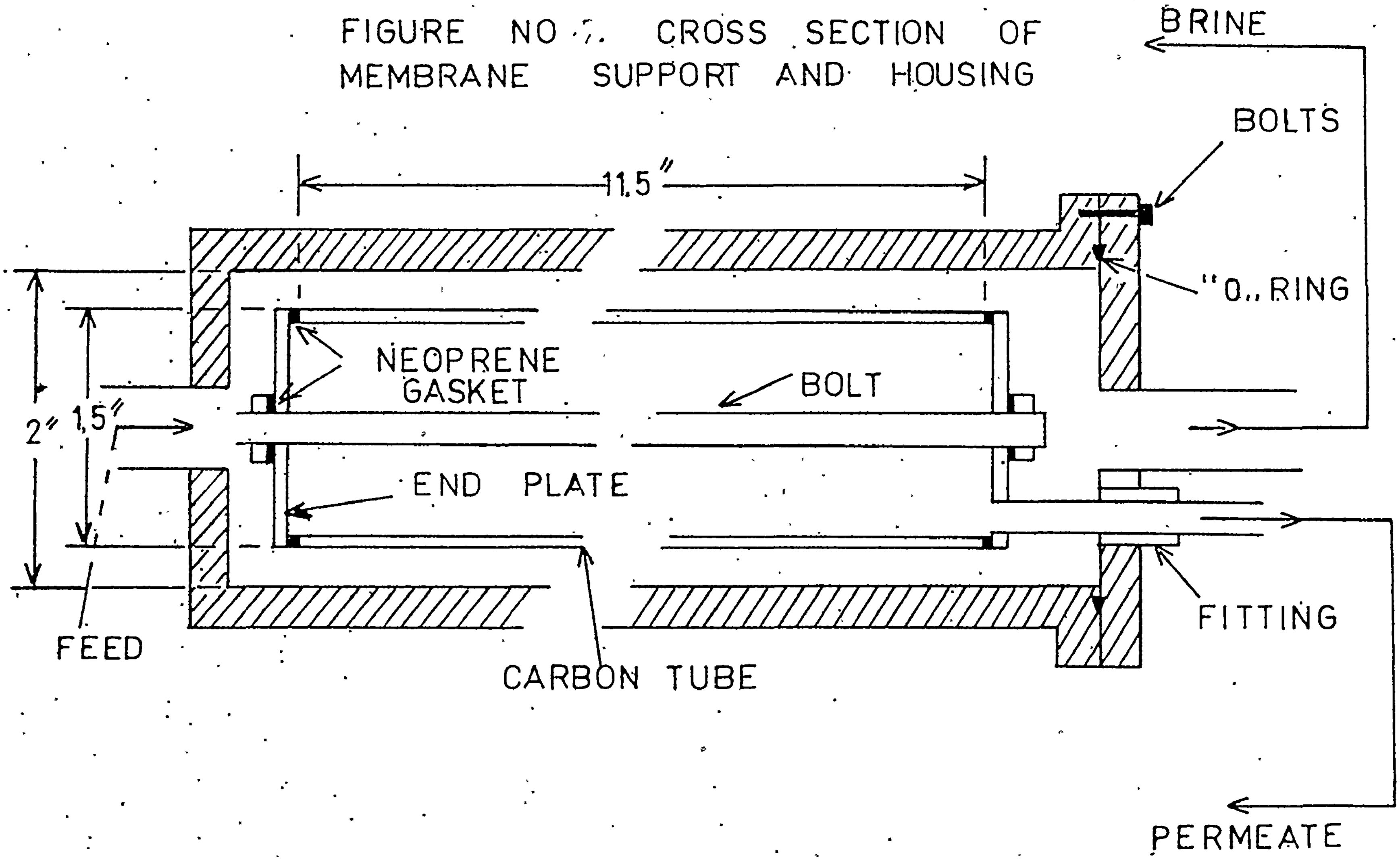


FIGURE NO 7. CROSS SECTION OF MEMBRANE SUPPORT AND HOUSING



and fittings. Later when the return flow to the storage tank was changed the top of the tank to the bottom (to avoid foam problems) some parts on the low pressure side were changed to teflon tubing. The storage tank was stirred magnetically.

The inside diameter of the ultrafiltration cylinder was 2" but was reduced to 1 9/16" by using two sleeves inside each other. Owing to the sleeves the cross-flow velocity was increased from 19.8 cm/sec to 158 cm/sec. Corresponding Reynolds numbers were (as calculated in Appendix 4) 2550 and 2780.

Support tubes for the membranes were supplied by Pure Carbon Co. These were carbon tubes with median pore size of 6.9μ and 0.9μ. Other properties are listed in Table 3. The tubes were 28 to 29 cm long and 3.79 cm in diameter two stainless steel rings were used to strengthen them thus leaving an available surface area of 310 cm^2 to 335 cm^2 or 0.334 ft^2 to 0.361 ft^2. The tubes were bolted to the product outlet pipe in one end of the cylinder and sealed on both sides with steel plates and rubber gaskets.

The surface of the 6.9μ nominal pore size tube was full of larger pores with a diameter up to 100 to 200μ. However, the majority of the pores were of the nominal size when observed through a 120 times magnifying microscope. None of the larger pores seemed to go deeper than their

Table 3 Properties of Carbon Ultrafiltration Support Tubes

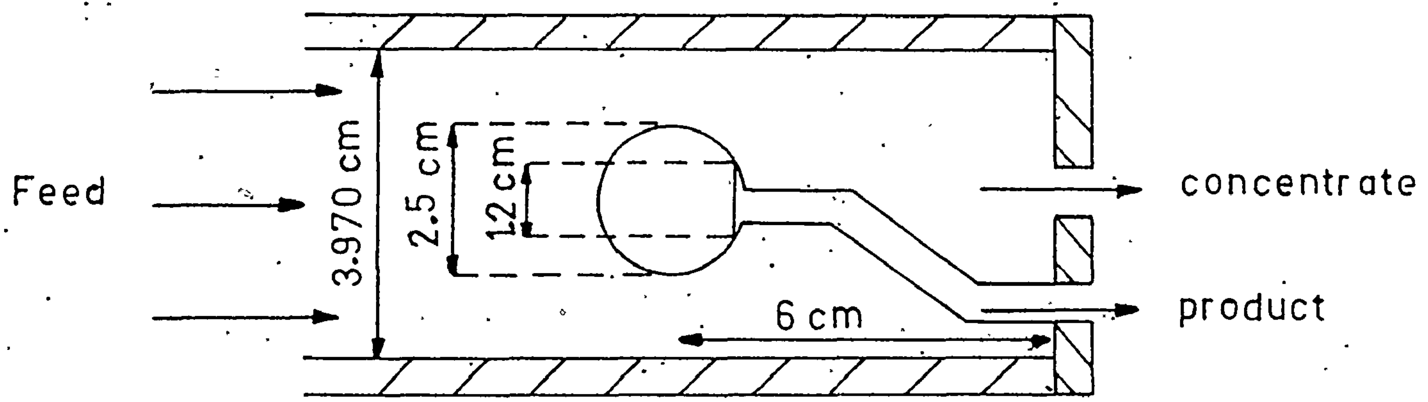
Tube	E-29	EC-23
Median pore diameter (μ)	6.9	0.9
Density (g/cm^3)	1.35	1.65
Pore volume (cm^3/g)	0.231	0.121
Pore volume (%)	18	20
Ark (%) Ash	0.2	6
Flexual strength (psi)	3500	6500
Scheroscope hardness	58	65-75
Resistance (ohm /cm)	0.003	0.005

diameter from the surface. About 30% of the surface did not have any pores at all. After 500 hrs of use the same tube was rougher on the surface having a greater proportion of larger pores. Lignin had accumulated in these pores and also on the surface of the tube. The 0.9μ nominal pore size tube had a similar surface structure as the one with the 6.9μ nominal pore size except in a scale of about 1/8th.

The entire apparatus was enclosed in a box of sheet-metal and panelling for noise control. Because of difficulties of obtaining a ceramic support tube, a spherical one was used. It was attached to the out-flow end of the ultrafiltration cylinder as shown in Figure 8. Its surface area was 18.5 cm^2 the maximum cross-flow velocity was 23.5 cm/sec

FIGURE NO 8. CERAMIC SUPPORT AND HOUSING

(replacing the arrangement of Figure 7)



corresponding a Reynolds number 3500. An estimated average pore size was about 15μ.

The lignin used for this study was a softwood alkalilignin , Indulin AT, supplied by Westvaco Co. It was an acid precipitated pine kraft lignin , amorphous powder containing 99% organic material. Its water content was 3%, pH 6.0, average molecular weight according to manufacturer 1600 and specific gravity 1.3.

Combined sulfate mill samples were obtained for these experiments from Abitibi in Smooth Rock, Ontario. Sulfite samples came from C.I.L.'s mill in Hawkesbury, Ontario. Details of these samples are described in Appendix 10.

4.2 Procedure

The feed solutions containing lignin for ultrafiltration were prepared by dissolving lignin in 4 liters of pH 12 sodium hydroxide solution. This solution was poured in the storage tank and diluted to 30.5ℓ. The lignin concentration was, in most cases set at 1000 mg/ℓ. The solution was adjusted to the operating pH by using sulfuric acid or sodium hydroxide.

The pressurized solution was circulated through a pressure regulator to an atmospheric pressure. When the effect of the feed solution temperature was studied, the solution was heated with a hot plate underneath the storage tank.

Samples were taken only of the feed and the permeate because the small permeate fluxes were not presumed to alter the concentration of the feed significantly. The permeate flowrate was measured at the time of the sampling by collecting the return flow of the permeate from the disconnected tubing in a graduate cylinder. Sample sizes ranged from about 15-25 mℓ.

4.3 Analytical

The samples from ultrafiltration were analyzed for lignin concentration using a Spectronic 20 spectrometer at a 465 nm setting. The absorbance was converted to concentrations through calibration curves measured by diluting the feed solutions as recommended by Rankin (1975).

The conductivity was measured with a Radiometer CDM-2 conductivity meter.

Sulfite, fluoride, copper and manganese were tested with Hach Chemical Company DR-EL/2 metrods. Aluminum and potassium were measured with a Varian Techron AA6 atomic absorption spectrophotometer. The TOC (total organic carbon), IC (inorganic carbon) and OC (organic carbon) were analyzed by a Beckman model 915 total carbon analyzer. Standard methods were used for analysis of phenol, linear alkylsulfonate, total solids, suspended solids, volatile suspended solids and biological oxygen demand (B.O.D.). Zeta-potentials were measured by timing particles in a Zeta-Meter$^{(R)}$.

5. RESULTS AND DISCUSSION

A complete schedule of ultrafiltration runs is presented in Appendix 11. The purpose of the first four runs was to establish a suitable backwashing technique. The rest of the runs were to establish the effects of the operating parameters and compare the results of the pure lignin solution runs to the pulp mill effluent runs.

5.1.1 Backwash

Four ultrafiltration runs were made at pHs between 3 and 11 lasting from less than one hour to 3 hours. The support tubes were washed with distilled water at different pHs after the runs. Typically after about 3 minutes of backwashing from inside the support tube towards the outside at pH 11, the backwash water did not show a measurable quantity of lignin. Nevertheless, when the ultrafiltration cylinder was opened and the support tube was taken out, a slimy membrane still remained on the surface of the support tube. Possibly, the inside-out backwashing opens some channels first, through which the main flow continues to flow out leaving other pores plugged. Higher backwash pressures could not be used due to tube cracking.

The support tubes could be cleaned also by washing them for a long period of time from "outside in" with a high pH solution. But it was decided to open the cylinder after each run and to clean the tube separately by keeping it for at least 45 minutes in a sodium hydroxide solution at pH 12. This method assures the removal of all visible parts of the membrane. At the same time the tube could be inspected for cracks.

Although the maximum tap water flux through the carbon tube E-29 was about 130 gal/ft^2 day at 150 psi, this could never be observed with a lignin solution because of the fast formation of a flow resisting lignin membrane.

The excellent reproducibility of the product flux in sequential runs is shown in Figure 9. Figure 10 compares product fluxes at standard conditions (pH9, 150 psi, 1000 mg/ℓ, 30°C) during and at the end of the experiments. The broken line is with another, newer, E-29 support tube at the same conditions when it has not yet reached its long term properties. The results for the first tube are within experimental error.

5.1.2 The Temperature

Runs were made at temperatures 25, 40, 50 and 70°C at pH 7, 150 psi and with the feed solution concentration 1000 mg/ℓ lignin. The results are shown in Figures 11 and 12.

Between 25°C and 40°C there is essentially no change in the product flux and concentration. The slightly lower product flux and concentration at 40°C, after 38 hrs of operating time, could be due to relatively greater decomposition of lignin. Smaller molecules would build a tighter

FIGURE NO 9. REPRODUCIBILITY OF THE PRODUCT FLUX IN CONSEQUENT RUNS

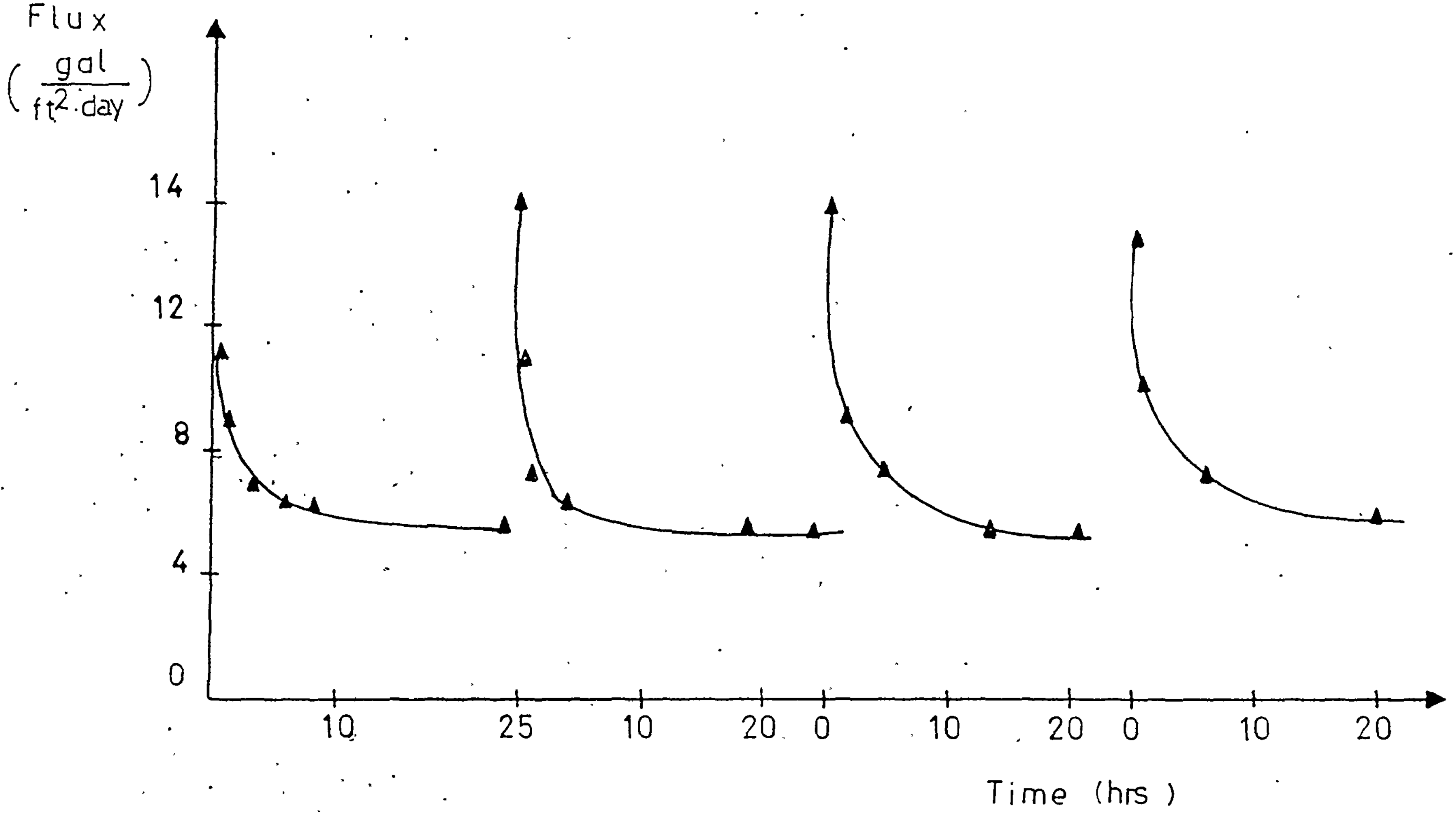


FIGURE NO 10. REPRODUCIBILITY OF THE PRODUCT FLUX IN THE BEGINNING DURING AND IN THE END OF THE EXPERIMENTS

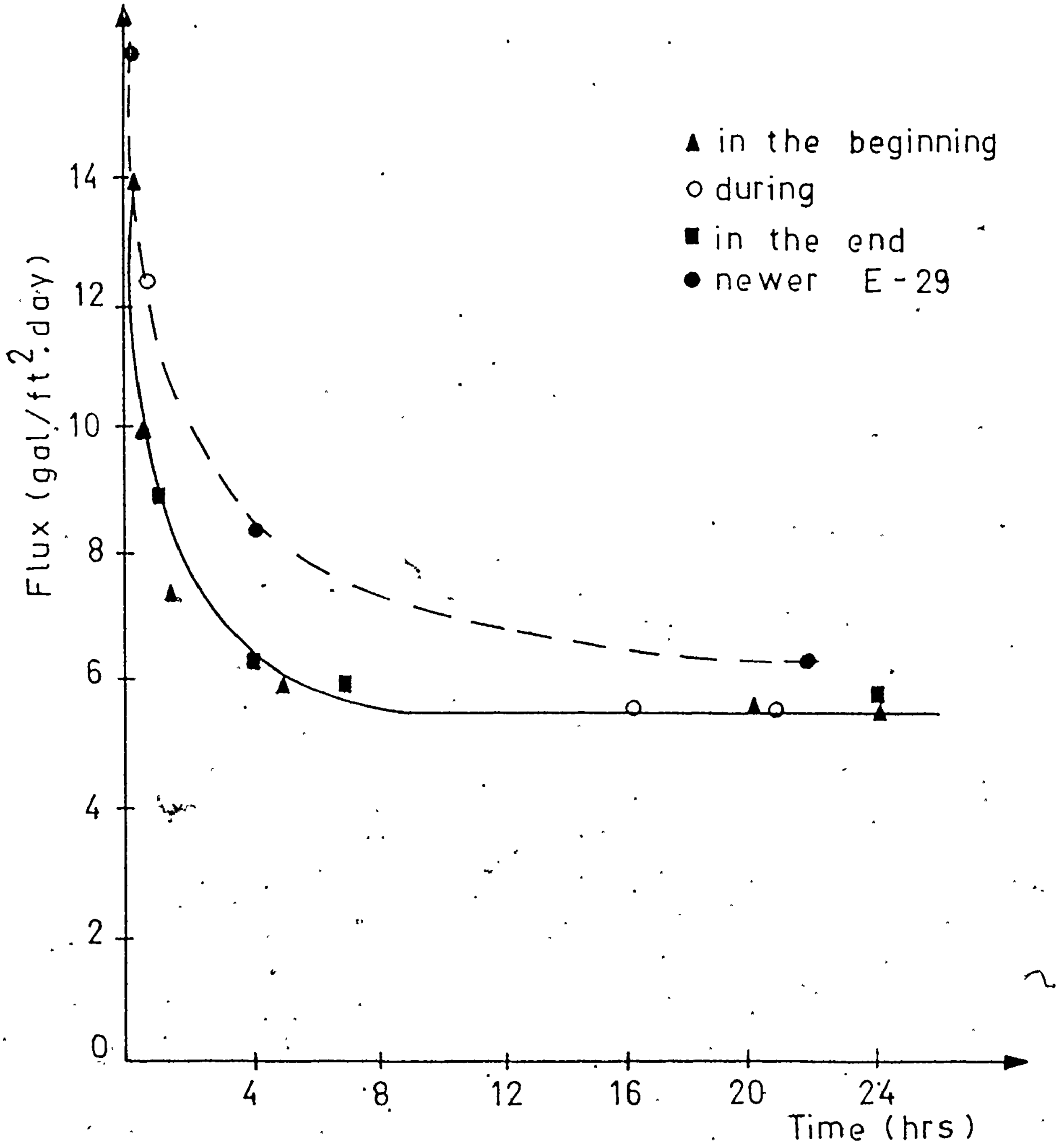


FIGURE NO 11. THE PRODUCT FLUX AS A FUNCTION OF THE TEMPERATURE AFTER 10, 21 AND 38 hrs

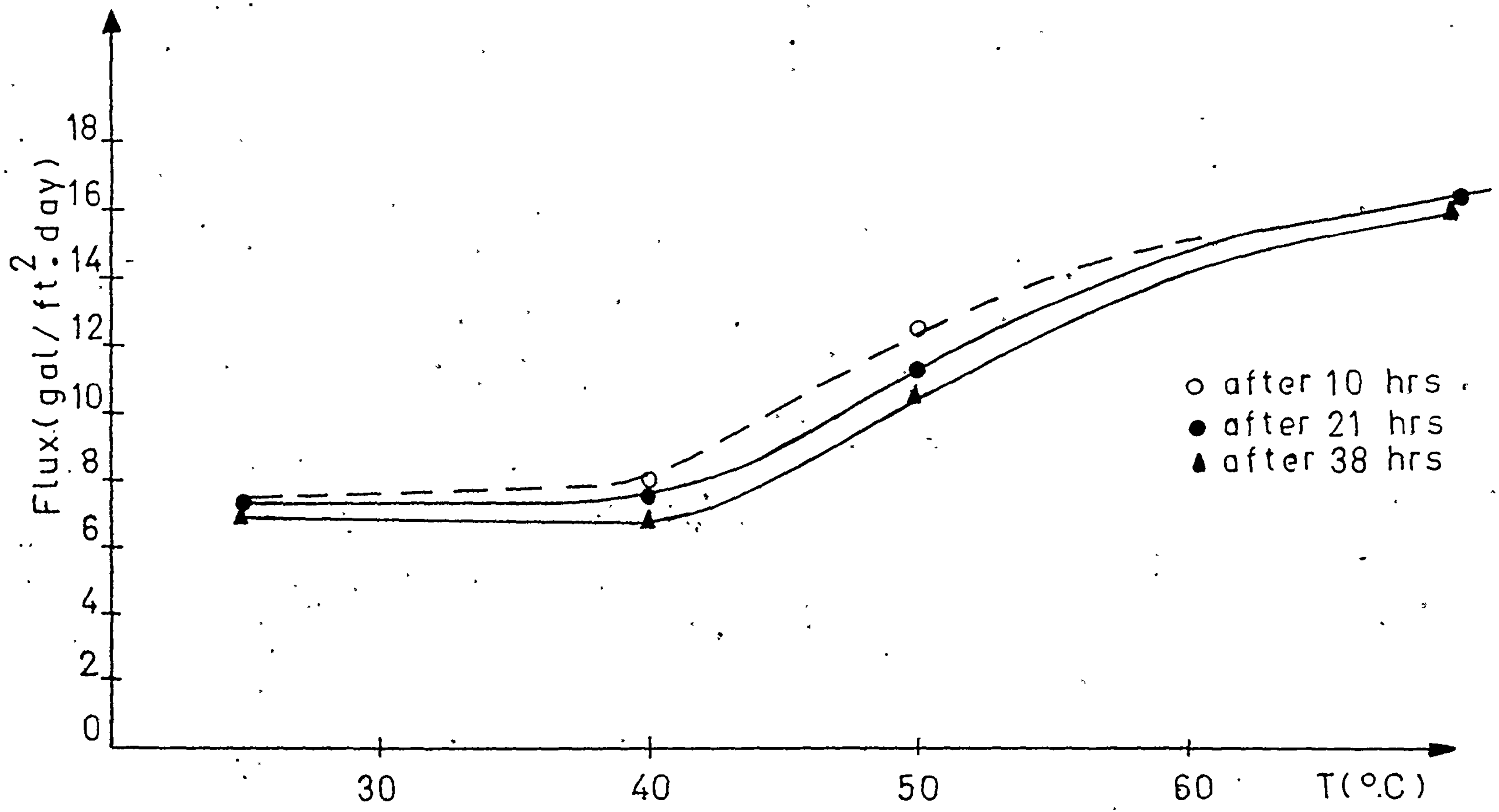
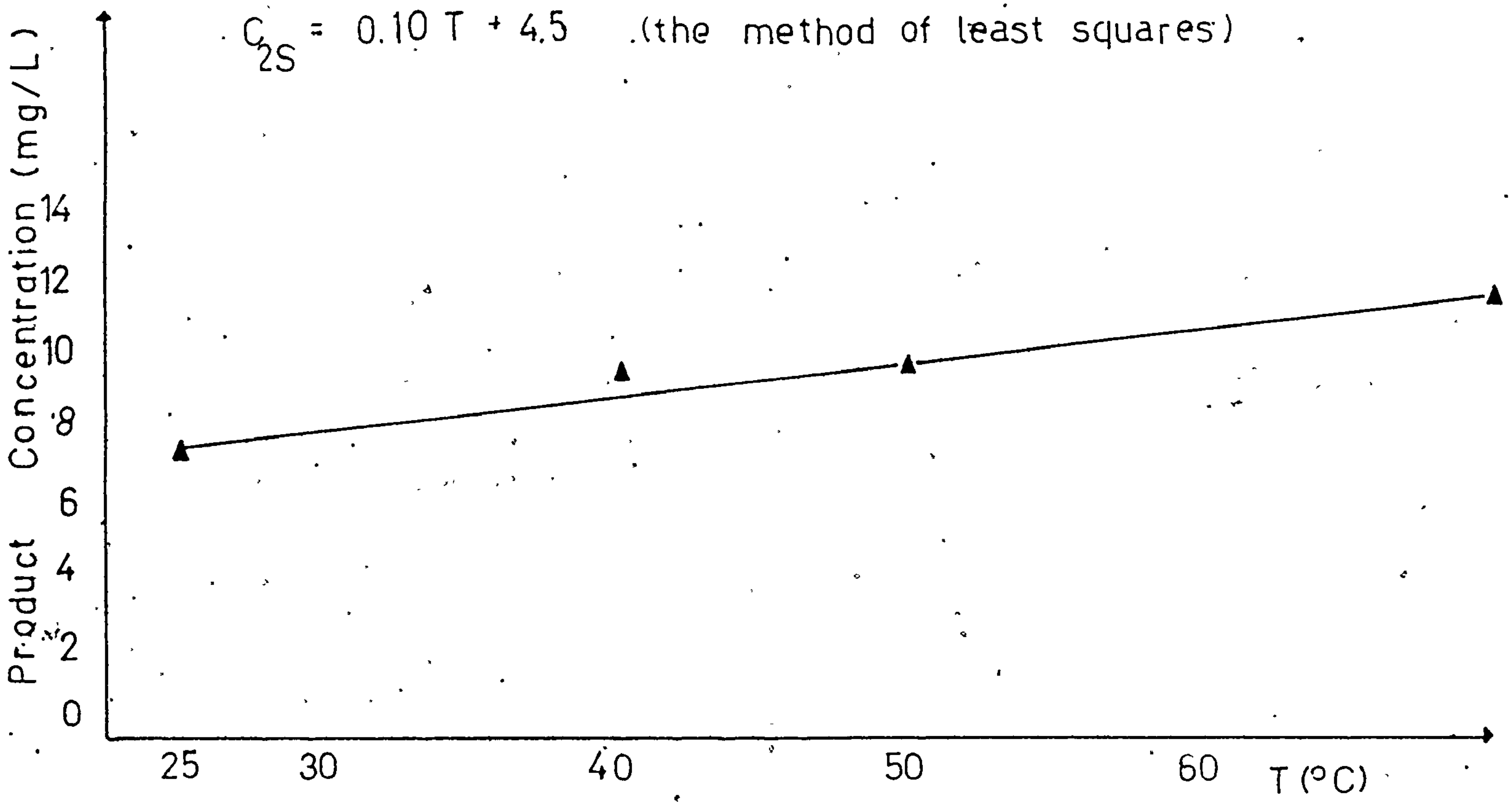


FIGURE NO 12. PRODUCT CONCENTRATION VS. TEMPERATURE AFTER 21 HOURS



membrane with a higher flow resistance. The higher rejection at this point indicates only the rejection of lignin molecules. An experimental error is another very probable reason for the small variations of the product flux and concentration.

Whatever the reason for the above behaviour, the effect of it is overcome at temperatures above 50°C. The final flux after 38 hrs running time at 70°C is twice that at 40°C. The concentration of lignin in the product flux is higher at higher temperatures too.

The osmotic pressure is dependent on the temperature (cf. equation 1) but the osmotic pressure at concentrations used is negligible as seen in more detail in Appendix 3.

A lower flux seems to result from an increase in the temperature according to equation 5. However, combining the non-temperature dependent terms, the diffusivity constant of water can be written as (Wilke and Chang 1955).

$$D_w = k_2 \; T/\mu \qquad (18)$$

where k_2 = constant. Because the viscosity is inversely proportional to the temperature equation 18 becomes

$$D_w = k_3 \; T^n \qquad (19)$$

where k_3 = constant

$$n > 1$$

Thus equation 5 changes to

$$F_W = k_3 \frac{T^{n-1} V_m}{R \; \delta_m} \; (P - \pi) \qquad (20)$$

The same temperature dependency can be derived from equation 12 by placing the temperature dependency of the viscosity into it.

The results do not follow curves that can be described by equation 20. A probable reason is that the membrane thickness is a variable with its own, maybe with complicated temperature dependency. The tendency of lignin to coagulate at elevated temperatures (Farber et al., 1955) could thicken the membrane and thus cause the deviation of the exponential growth of the product flux as should be expected according to equation 20.

In the solute flux equation

$$F_s = -D_s \frac{dC}{dx} + C_s u_m \qquad (6)$$

the temperature term is in the diffusivity. Neglecting the second term in equation 6 and assuming the same temperature dependency for the diffusivity as above gives

$$F_s = k_4 T^n (\Delta C) \qquad (21)$$

where k_4 = constant.

The concentration of solute in the product flux is

$$C_{2s} = \frac{F_s}{F_s + F_w} \qquad (22)$$

Because F_s is small compared to F_w

$$C_{2s} \simeq \frac{F_s}{F_w} \qquad (23)$$

Placing equations 20 and 21 in 23

$$C_{2s} = \frac{k_4 \; T^n \; (\Delta C)}{k_3 T^{n-1} \dfrac{V_m (\Delta P - \Delta\pi)}{R \; \delta_m}} = k_5 \; \frac{\delta_m \; T \; (\Delta C)}{(\Delta p \; - \; \Delta\pi)} \tag{24}$$

Equation 24 suggests a linear relation between the product concentration and temperature. This is in accordance with the results until a longer operating time changes it.

The product flux does not follow an Arrhenius type equation either

$$F_w = k_6 \; e^{-k_7/T} \tag{25}$$

where k_6 and k_7 are constants, or

$$F_w = \frac{-k_7}{T} + \ln k_6 \tag{26}$$

This can be seen in Figure 13 where 1/T is plotted as a function of F_w. In such a figure, data fitting on the Arrhenius equation will form a straight line.

5.1.3 The Pressure

The results of ultrafiltration runs at different pressures are shown in Figures 14 and 15. The pressure was varied between 25 and 300 psi. Runs were made at pH 9 and pH 7.

The flow through an ultrafiltration membrane was described by equation 10.

$$F_w = \frac{\Delta \, p}{R_m} \tag{10}$$

FIGURE NO 13. PRODUCT FLUXES IN THE $\mathrm{LnF_W}$ AND 1/T COORDINATES

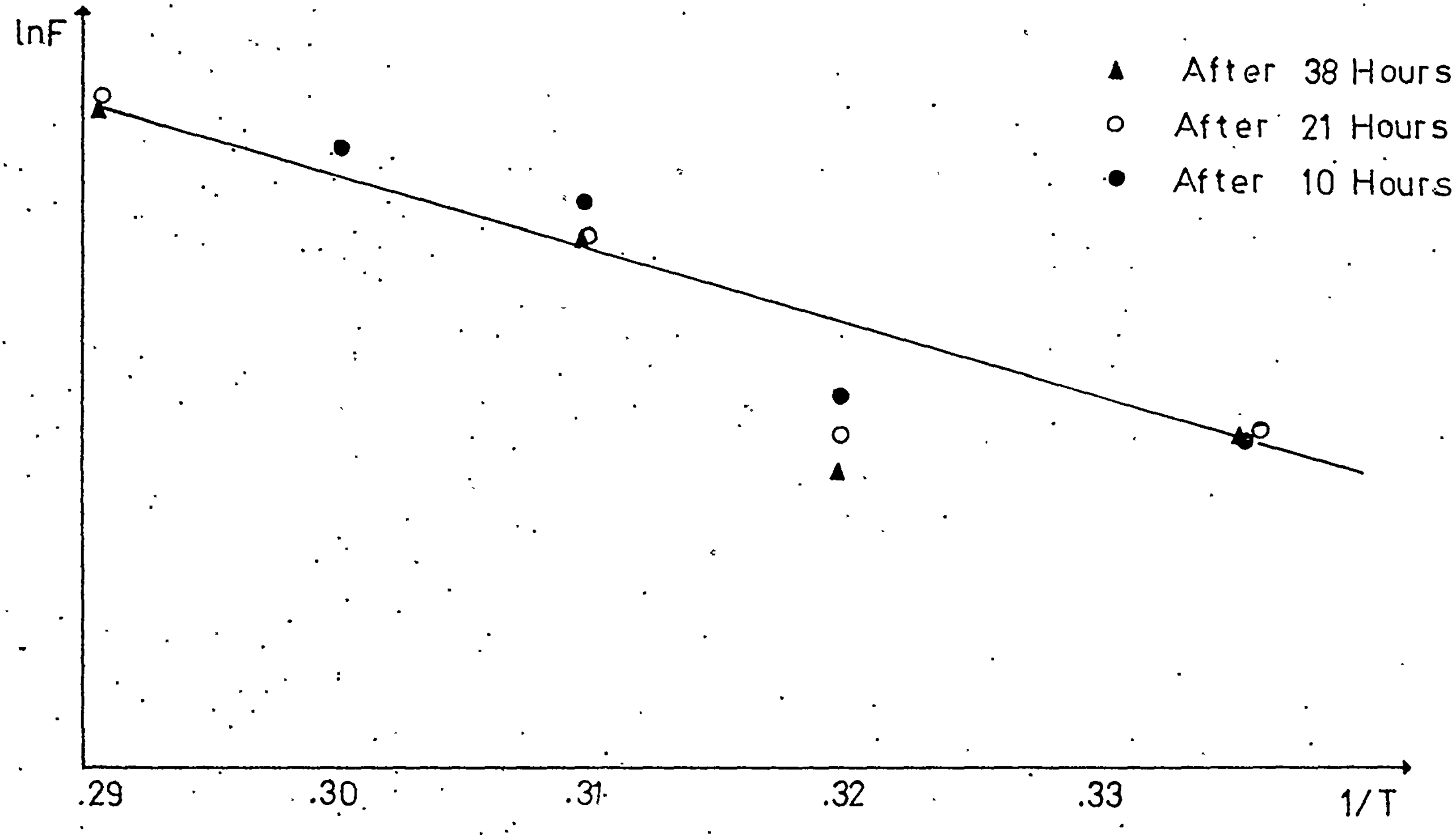


FIGURE NO 14. THE EFFECT OF THE PRESSURE ON THE PRODUCT FLUX AT pH 7 AND 9 AFTER 24hrs

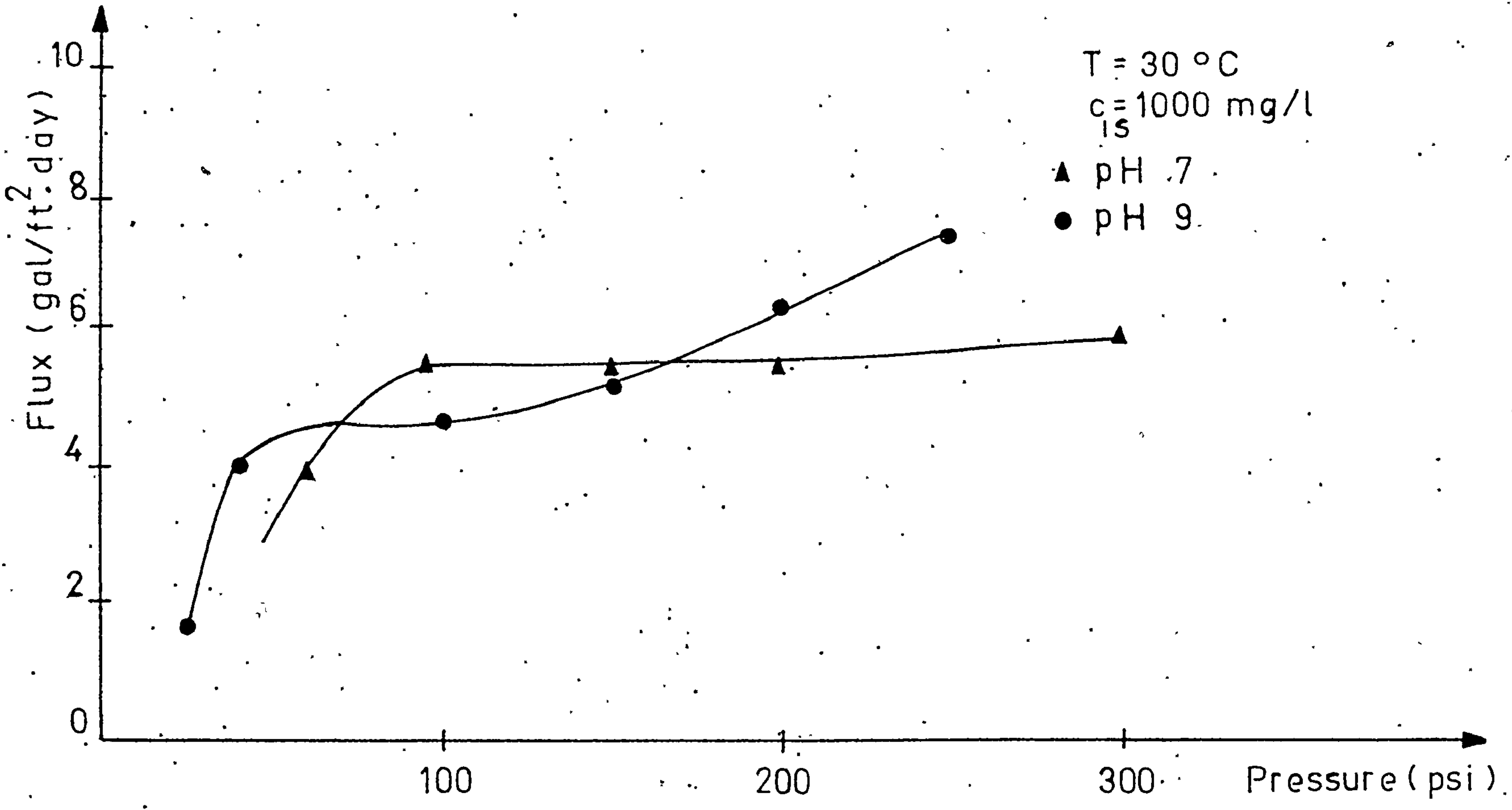
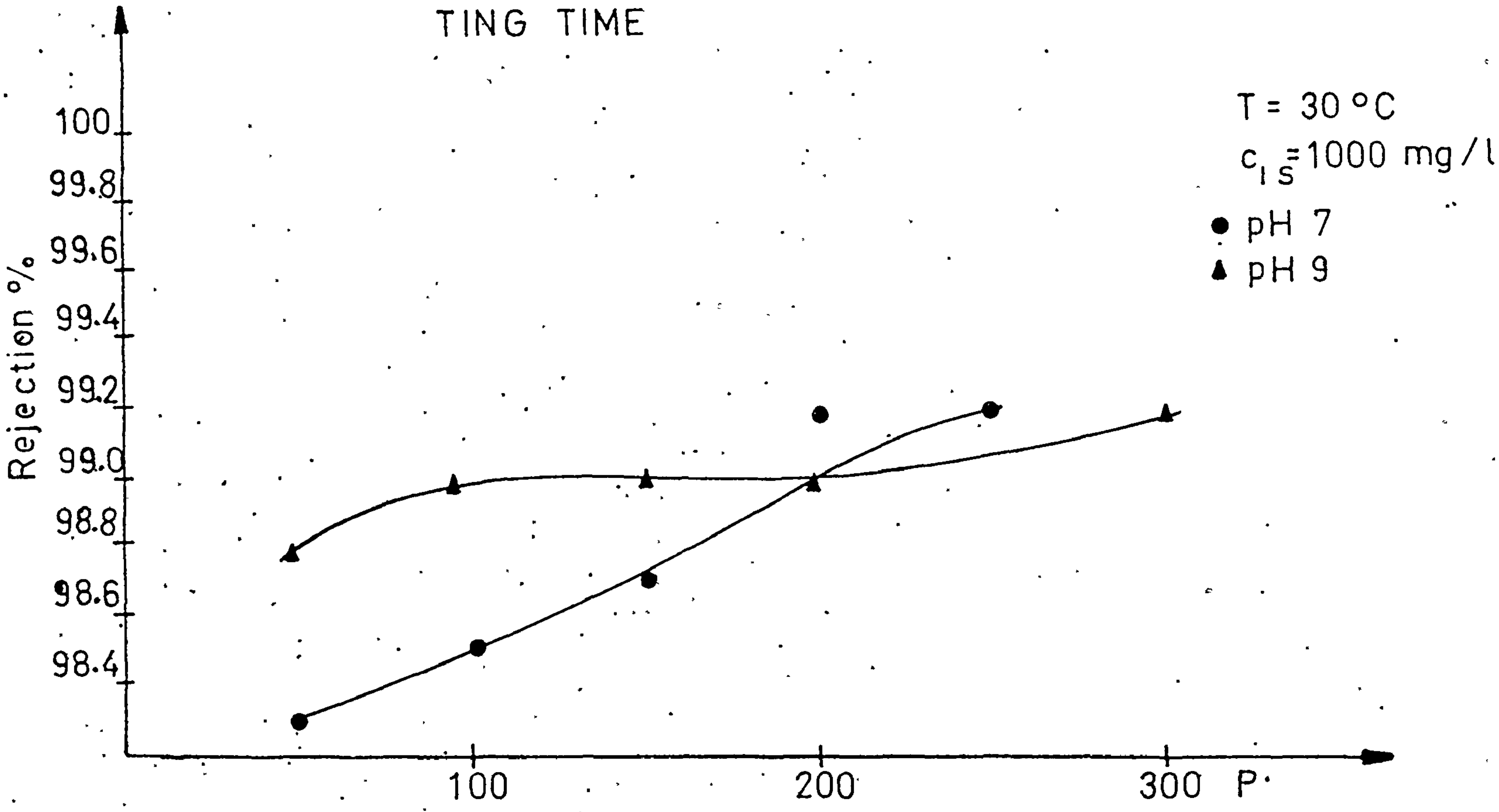


FIGURE NO 15. THE EFFECT OF THE PRESSURE ON THE REJECTION OF LIGNIN AFTER 24 hrs OF OPERATING TIME



Using values from Appendix 5

$$F_w = 0.04 . \Delta P \tag{27}$$

No one value of the slope in equation 27 could describe the behaviour of the product flux at either pH used at the experiments. But the product flux as a function of the pressure curve could be approximated by using two different slopes and gradually changing the domination from one to the other. This would describe the tightening of the membrane under pressure. The equation could be of the form

$$F_1 = \frac{A^n}{(\Delta p + a)^n} k_8 \Delta p \tag{29}$$

where $n > 1$

$k_8 =$ constant

$A =$ constant

$$F_2 = \frac{\Delta p^m}{(\Delta p + A)^m} k_9 \Delta p + \frac{\Delta p^m}{(\Delta p + A)^m} F_o \tag{30}$$

where $m < 1$

$k_9 =$ constant

$F_o = F_2$ at $\Delta p = 0$ in equation 32.

A is the crossing point pressure of lines F_1 and F_2 without the weighting factor.

$$F_1 = k_8 \Delta p \tag{31}$$

$$F_2 = k_9 \Delta p + F_o \tag{32}$$

$$A = \Delta p = \frac{F_o}{k_8 - k_9} \tag{33}$$

The constants k_8 and k_9 can be written in the same form as in equation 12

$$k_8 = \frac{\varepsilon_1 a_1^2 \zeta_\ell}{8\tau_1^2 \mu \delta m_1} \tag{34}$$

$$k_9 = \frac{\varepsilon_2 a_2^2 \zeta \ell}{8\tau_2^2 \mu \delta m_2} \tag{35}$$

Most of the factors in equation 12 are dependent on the pressure and they have their extreme values in equations 34 and 35. Placing equations 29 and 30 into 28 gives

$$F_w = \frac{A^n}{(\Delta p + A)^n} k_8 \Delta p + \frac{\Delta p^m}{(\Delta p + A)^m} (k_9 \Delta p + F_o) \tag{36}$$

Figure 16 has been calculated using values: $n = \frac{1}{m} = 2$

$k_8 = 0.072$

$k_9 = 0.005$

$F_o = 5.0$ gal/ft^2 day

A closer fit to the observed points is possible by adjusting the constants. Porter and Michaels (1971) explained the horizontal part in the flux vs. pressure curve by assuming an equilibrium between the diffusive back transport of the solute and the convective transport of the solute to the membrane

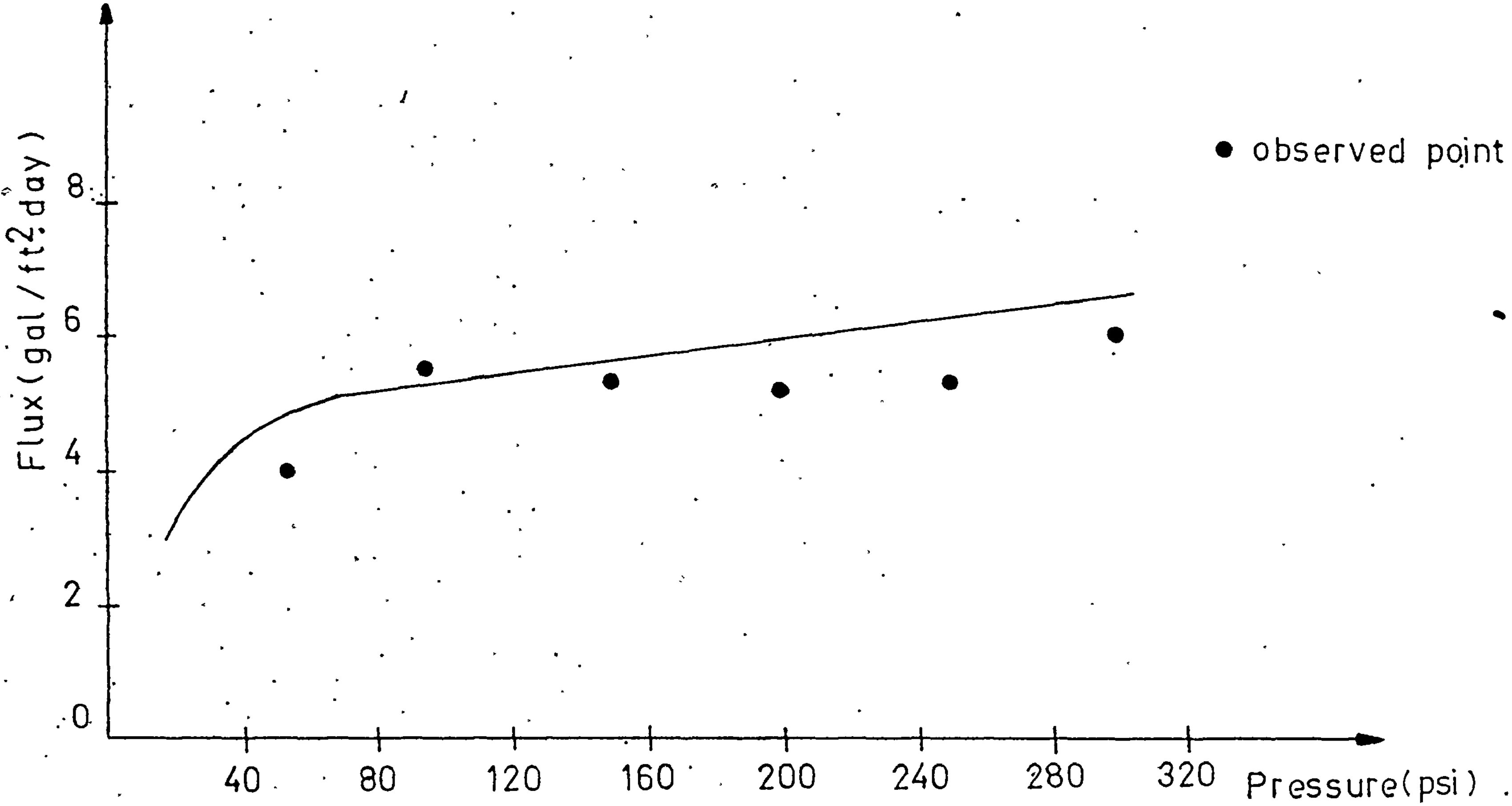
$$F_w C_s - \frac{D_s dc_s}{dx} = 0 \tag{37}$$

where x = distance

or

$$F_w = k_{10} \ln \frac{C_{3s}}{C_{1s}} \tag{38}$$

FIGURE NO 16. EQUATION 36 COMPARED TO ULTRAFILTRATION RESULTS AT pH 9 AFTER 24 hrs



where C_{3s} = solute concentration on the membrane. At conditions in equation 38 the flux can be independent of the pressure, if attempted to increase the flux by using a higher pressure causes tightening of the membrane. This increases the flow resistance in equation 10. The lowest point where this happens is called the critical pressure corresponding approximately the pressure A in equation 36.

The critical pressure depends on the pH. It is at pH 7 approximately 50 psi and at pH9 90 psi.

The rejection of lignin increased with increasing Δp at both pH values. It increased at pH7 from 98.5% to 99.2% when the pressure grew from 50 psi to 250 psi. At pH 9 the change in the rejection at the same time was from 98.8% to 99.1%. This is well in correspondence with the membrane tightening at higher flow resistance theory.

A high pressure does not help in ultrafiltration at pH9. An optimum pressure would be the lowest one where the required rejection is reached. At pH7 a higher pressure improves the membrane performance.

5.1.4 The pH

The ultrafiltration results at pH's between 2 and 11 are shown in Figures 17 and 18.

The product flux and the product concentration decrease with an increasing pH until pH6, stay constant until about pH9, and increase again after that.

At high pH lignin is almost completely soluble and the average molecular weight is smallest as shown in

FIGURE NO 17. THE PRODUCT FLUX AS A FUNCTION OF THE pH

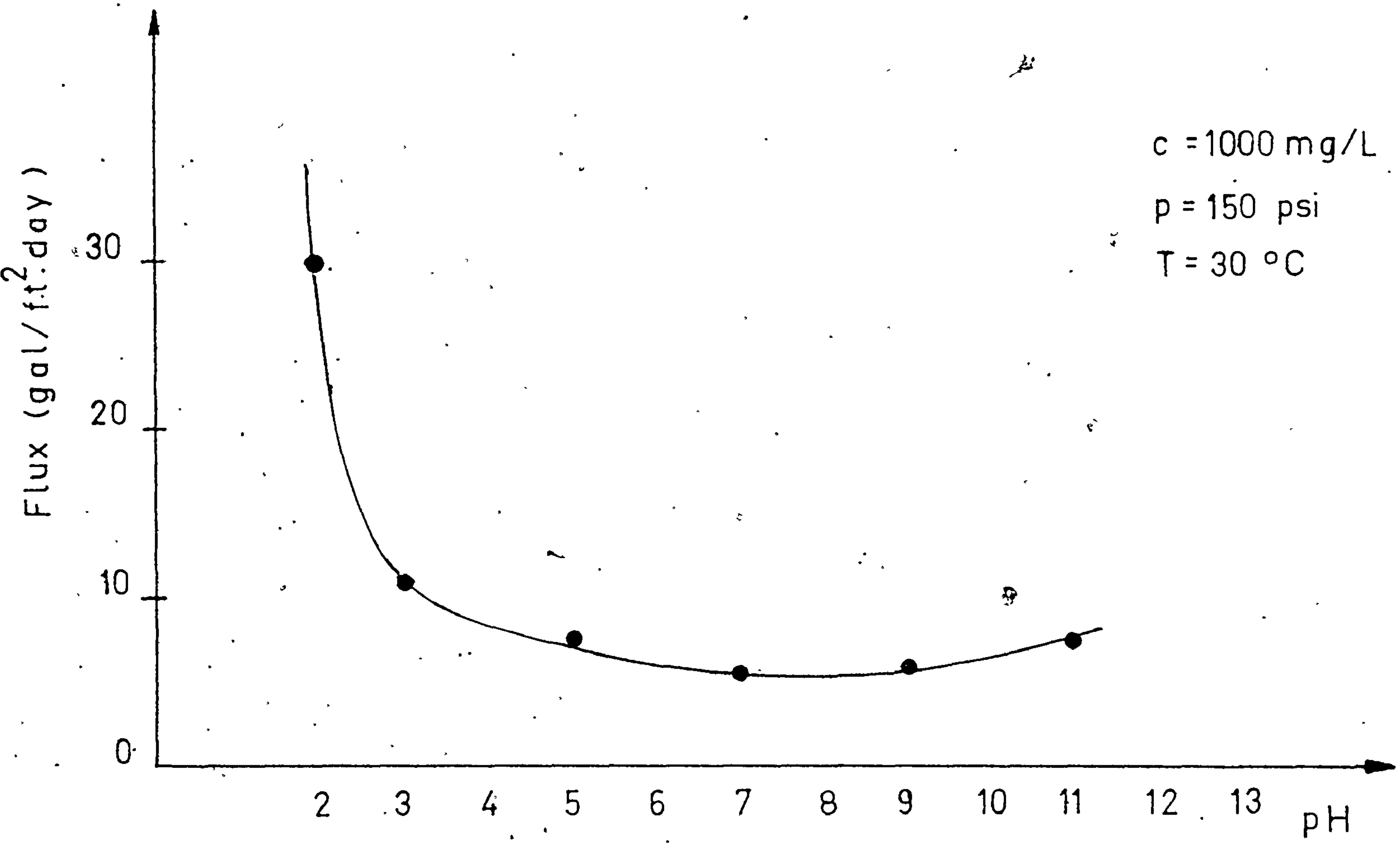
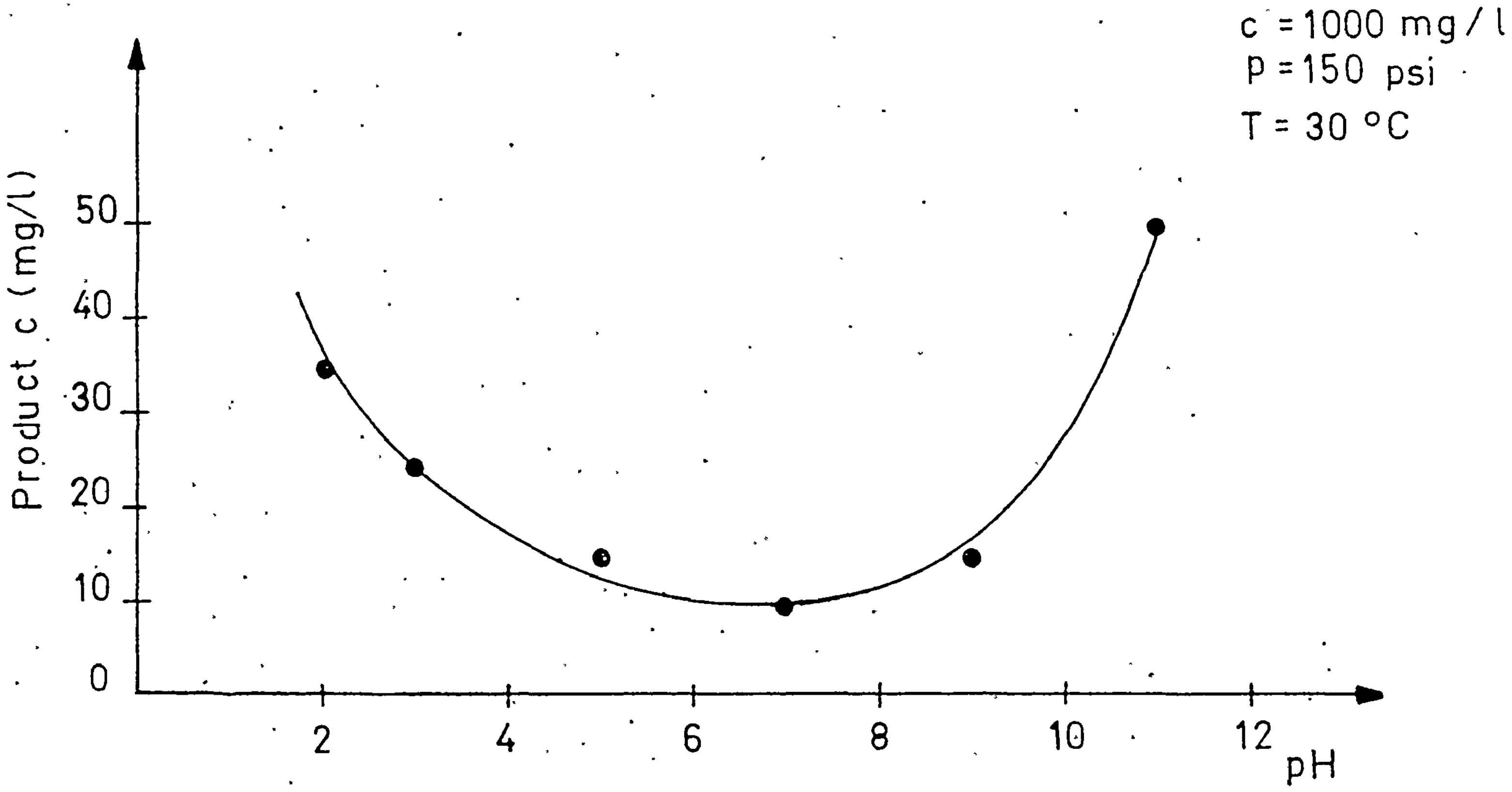


FIGURE NO 18. THE PRODUCT CONCENTRATION AS A FUNCTION OF THE pH



Appendix 7. A greater part of the solute molecules can then penetrate through the membrane because of the smaller size of some lignin molecules and because of the even smaller hydrolysis products. The dependency of the rejection on the molecular size and valency is discussed in more detail in Appendix 9.

At the middle pH range where lignin starts to precipitate (cf. Appendix 7 and 8), the membrane is thicker because lignin precipitates on the support tube until horizontal forces are stronger than forces of adhension retaining the membrane on the support surface. The addhesion forces are relatively strongest at this pH range because lignin is not ionized at all. Furthermore, there are fewer hydrolysis products to decrease the rejection.

At a low pH, where lignin loses its solvation water and its zeta-potential approaches zero (cf. appendix 8), the membrane is more granular and has less flow resistance. This increases the product flux. But at the same time the solution contains more acid hydrolysis products to decrease the rejection.

The best range for ultrafiltration would be at pH 2.5 or lower taking only the product flux into consideration. The best practical range, taking both the flux and the rejection into consideration appears to be from pH5 to pH7.

5.1.5 The Cross-Flow Velocity

Ultrafiltration runs at cross-flow velocities 158 cm/sec which was used for most other runs also and 19.8 cm/sec are compared in Figures 19 and 20.

The membrane forms slower at the lower cross-flow velocity. The product concentration is lower all the time at the higher cross-flow velocity. The product flux is also lower at the higher cross-flow velocity all the time. However, the rejection and the flux varies only little at velocities tested, indicating that the cross-flow velocity has only a minor effect on them.

These results are different from those reported by other investigators. For example Ammerlaan et al (1969) reported an increasing product flux with an increasing cross-flow velocity below the minimum linear velocity (cf. page 17). Above the minimum linear velocity the product flux is either independent of or increases with the cross-flow velocity (Perona et al 1967). The reason for the different results is probably that the Reynolds number changed very little in our experiments. Without geometrical changes in the ultrafiltration cylinder the Reynolds number is directly proportional to the cross-flow velocity. Possibly the other experiments have been performed by adjusting only the pumping rate and thus at different Reynolds numbers.

FIGURE NO 19. THE EFFECT OF CROS.-FLOW VELOCITY ON THE PRODUCT FLUX

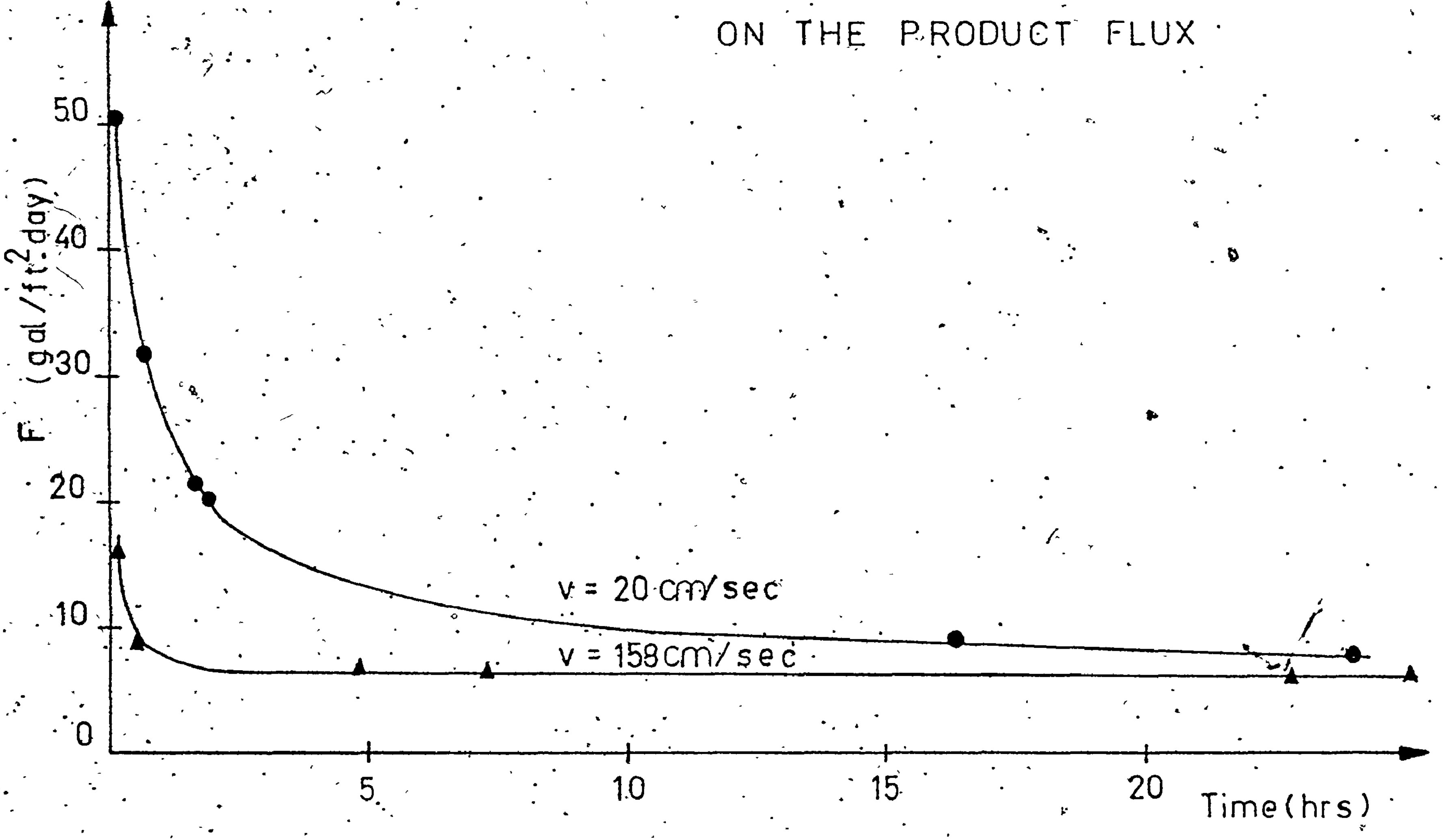
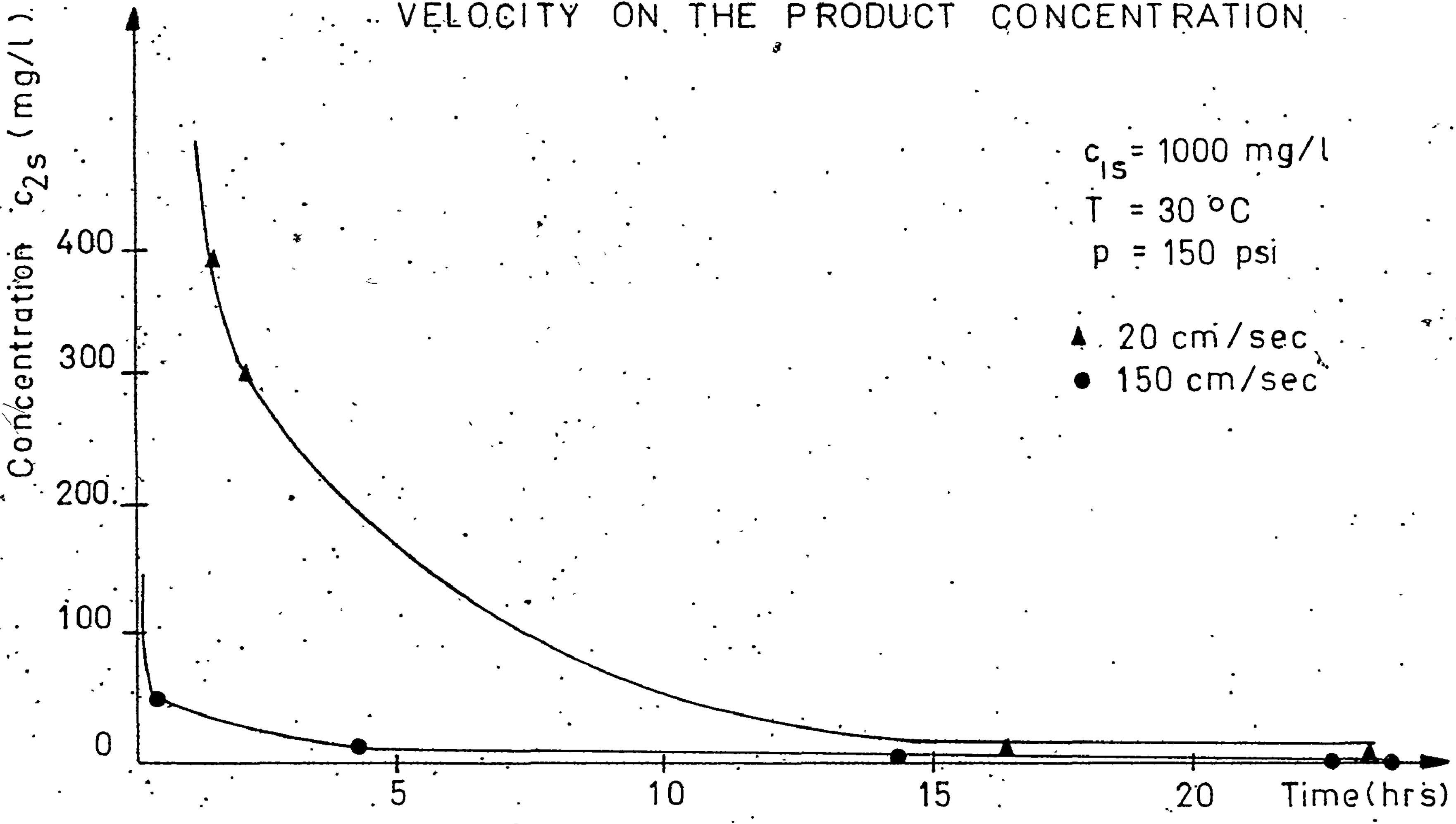


FIGURE NO 20. THE EFFECT OF THE CROSS-FLOW VELOCITY ON THE PRODUCT CONCENTRATION



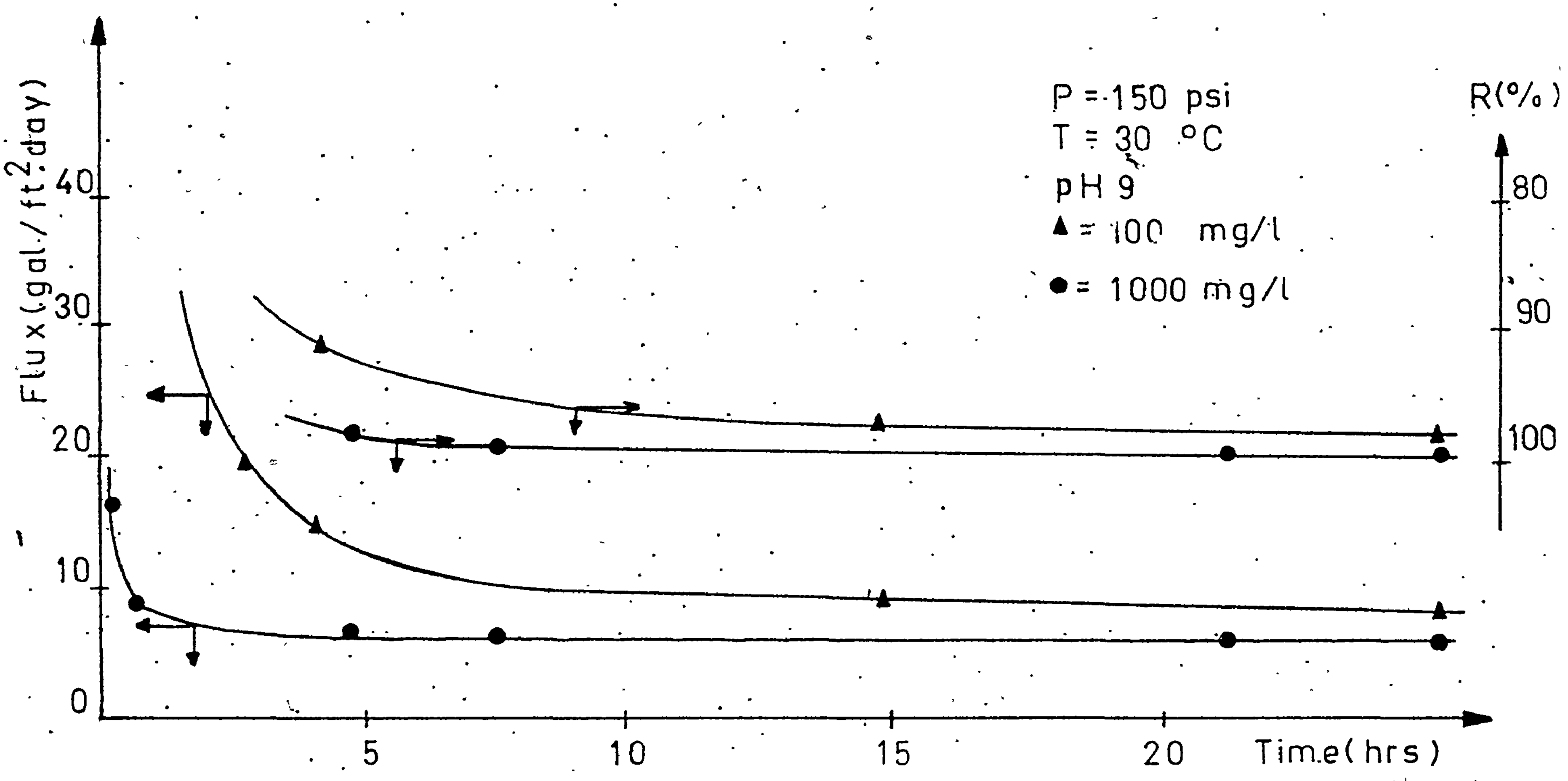
At larger changes of the cross-flow velocity the membrane thickness changes because of varying shearing forces. Although no exact measurements were made, it was observed visually that the lignin layer was thicker at the lower cross-flow velocity. The slower formation of the membrane at slower cross-flow velocities can be explained by the smaller mass transfer coefficient. The flow through the membrane is of the same order at both cross-flow velocities, after the very initial stage, causing a similar amount of concentration polarization. This corresponds in equation 6 to the second term which is usually small anyways compared to the first term.

5.1.6 The Feed Solution Concentration

The effect of the feed solution concentration on the product flux and on the rejection was studied as function of time in concentrations 100 and 1000 mg/ℓ of lignin. The results are shown in Figure 21. In one ultrafiltration run the lignin concentration was increased during operating from 1000 mg/ℓ to 50g/ℓ.. This is shown in Figure 22.

The membrane formed slower at the 100 mg/ℓ concentration. The rejection is higher and the product flux is lower at the 1000 mg/ℓ concentration throughout the test, but after 24 hrs of operating the rejection and the flux are almost the same in both conditions. The final flux after 24 hrs was 3 gal/ft^2 day at the concentration 50 g/ℓ compared to 6 gal/ft^2 day and 8 gal/ft^2 at concentrations 100 mg/ℓ and

FIGURE NO 21. THE EFFECT OF THE CONCENTRATION ON THE PRODUCT FLUX AND REJECTION



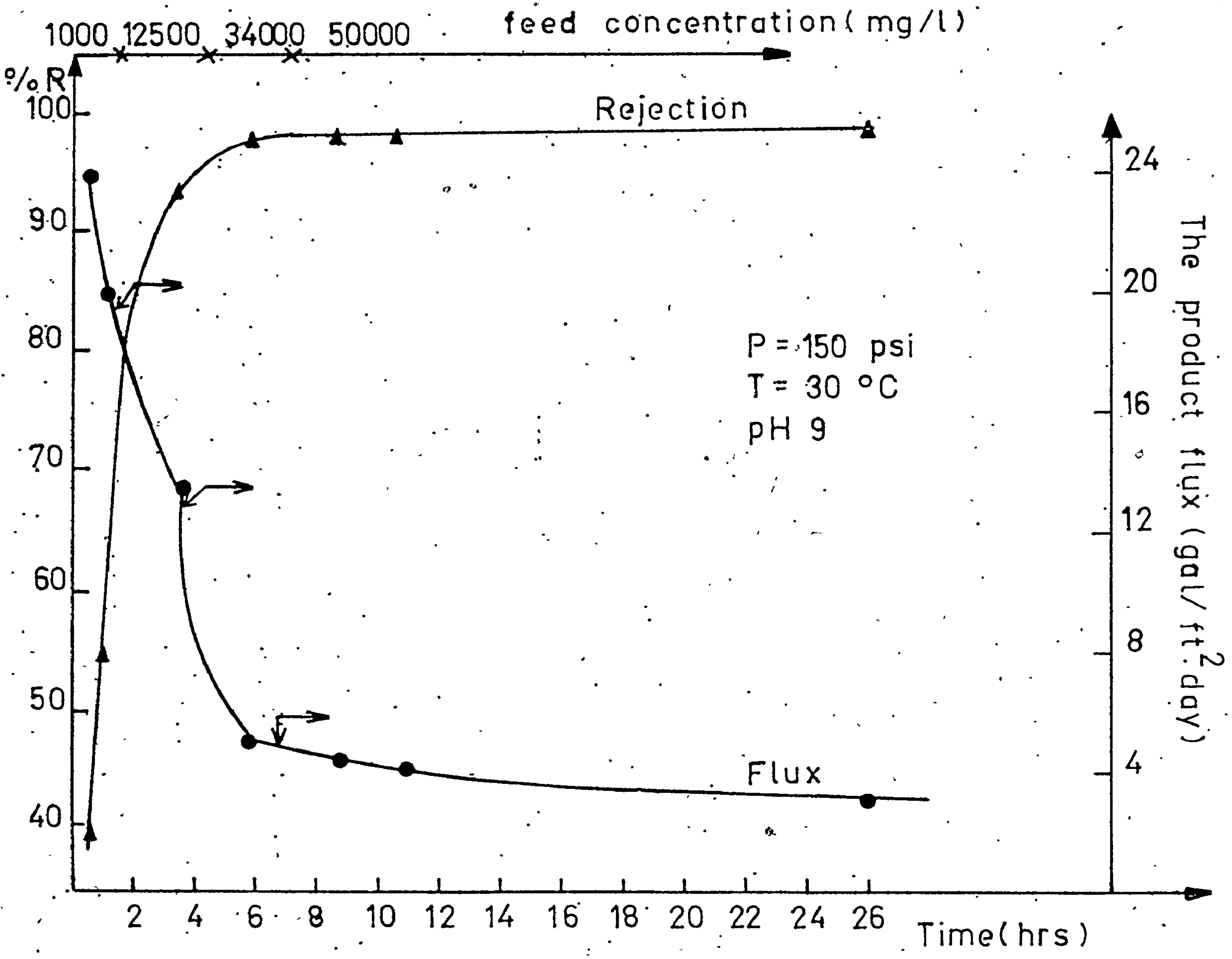


FIGURE NO 22. THE EFFECT OF HIGH CONCENTRATIONS ON THE PRODUCT FLUX AND REJECTION

1000 mg/ℓ correspondingly. The final rejection was over 98% in all runs.

The slower formation of the membrane at the lower concentration can be explained by a basic material balance. The less building material is brought to the construction site, the slower the membrane forms. It is interesting to note that membranes seem to be at the same state of formation at the same values of equation

$$Q = C_{1s} \, v \, t \qquad (42)$$

where Q = indicator of the state of formation of the membrane. This is shown in Table 4 where product fluxes are compared at same Q-values. Equation 42 neglects variations of the flow through the membrane. The cross-flow velocity, v, is in equation 42, because at higher cross-flow velocities, possibly smaller colloids can coagulate and the eddy diffusivity is higher.

Another indicator of the membrane growth was equation 17. Calculating the constant k_1 from

$$k_1 = k_2 \cdot 0.3 \qquad (43)$$

(cf equation 15 and Appendix 6)

and using inverted product fluxes (ft^2.day/gal) instead of membrane thicknesses the following values are obtained at pH9, 150 psi, 30°C (t=hrs) C_{1s} = 1000 mg/ℓ

$$k_1 = 0.008 \qquad k_2 = 0.0027$$

According to equations 1 and 5 the product flux is dependent on the concentration if the osmotic pressure is

Table 4

	v	c	t	flux
Q	cm/sec	mg/ℓ	hrs	gal/ft^{2}day
316 x 10^3	158	1000	2	7
316 x 10^3	20	1000	15.8	9
316 x 10^3	158	100	20	8.5
142 x 10^3	158	1000	1	9
142 x 10^3	20	1000	7.9	10.1
142 x 10^3	158	100	10	10.5

significant. A lignin solution at concentration 50 g/ℓ has on osmotic pressure of only 2.5 psi at pH9, compared to about 300 psi with kraft mill effluent (Bansel 1975). Thus the highest possible concentration for ultrafiltration of kraftmill effluent e.g., at 150 psi, is 25 g/ℓ.

A quite different membrane could be expected if lignin is first precipitated by acidification and then decanted and ultrafiltered because of changed average molecular weight. The precipitation procedure is explained in Appendix 7. The original concentration 1000 mg/ℓ was reduced to 50 mg/ℓ by precipitation. The results of an ultrafiltration run with this solution is shown in Figure 23.

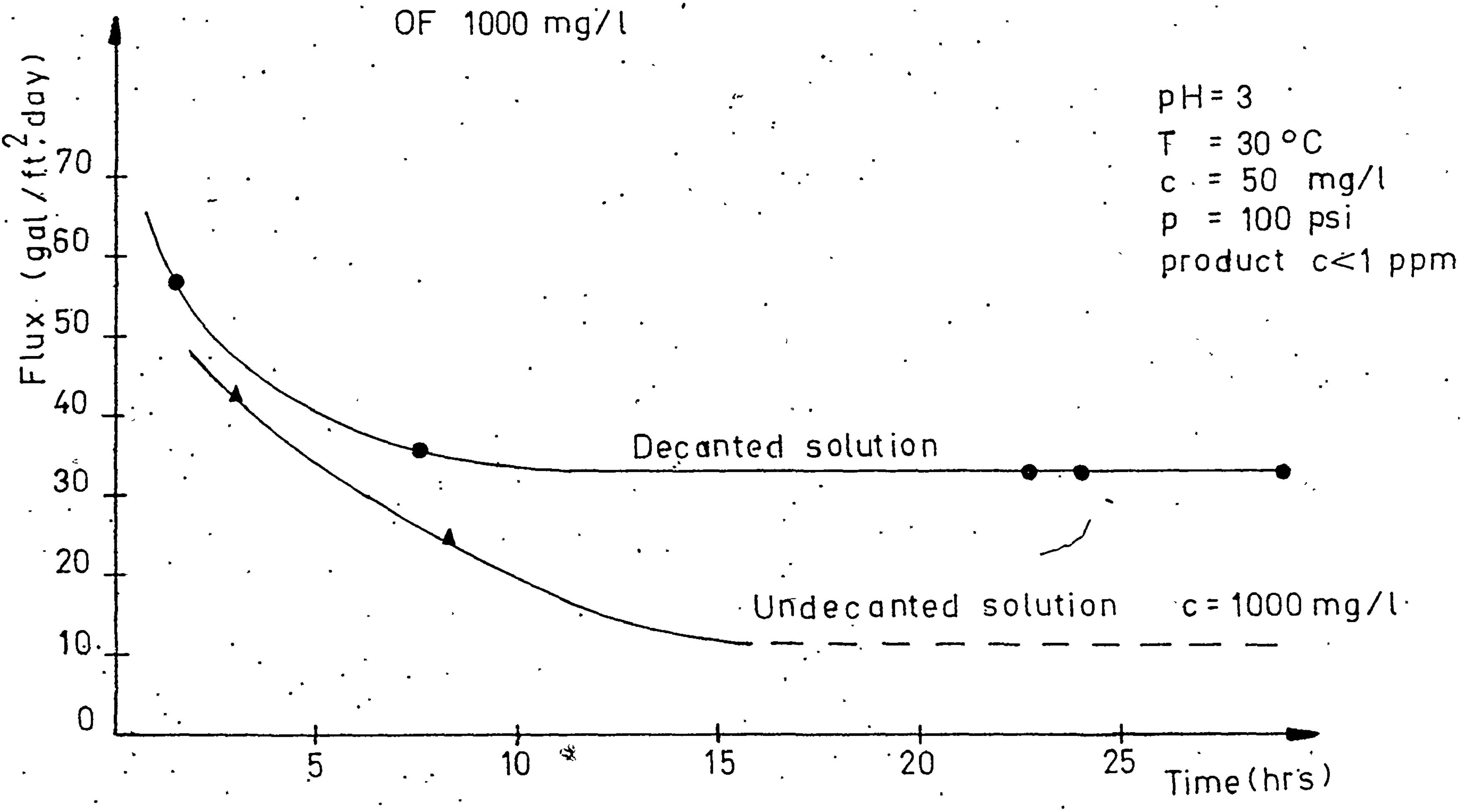
The final product concentration was less than 5 mg/ℓ The final flux was about 3 times the usual flux at the same pH. In this case the membrane probably was not only a lignin membrane any more but decomposition products were a significant part of its constituents. This can change completely the properties of a membrane as discussed earlier.

5.1.7 The Support Tube Pore Size

Ultrafiltration runs with carbon membrane support tubes with average pore sized 0.9μ and 6.9μ are shown in Figures 24 and 25. Both tubes were used for the first time in these runs.

The product flux decreased more rapidly in case of the larger pore size tube. The flux started from a lower value and was lower in the smaller pore size tube all the

FIGURE NO 23. ULTRAFILTRATION OF A DECANTED LIGNIN SOLUTION WITH AN ORIGINAL CONCENTRATION OF 1000 mg/l



time. The starting fluxes were about 600 gal/ft^2 day and 200 gal/ft^2 day for the tubes. After 24 hrs of operating time they had decreased to 11 and 8.5 gal/ft^2 day correspondingly.

The product quality is much poorer with the larger pore size tube and approaches its final value slower. A possible reason is that the new tube with 6.9μ average pore size contains also many pores too wide to support a membrane. It is possible that even 6.9μ is too large (cf. Perona et al 1967). Pores without a membrane leak the feed solution to the other side of the support. Because of the lower resistance of the flow through non-membrane pores, channeling occurs and there is less flow through the membrane. When solids from the feed gradually plug these holes, a rejecting membrane builds up.

The pores of the support tube tend to plug irreversibly as shown in Figure 26. After several ultrafiltration runs and backwashes the performance of the 6.9μ pore size tube resembles more and more that of the 0.9μ pore size tube. Finally the former can have a lower flux and better rejection than a new 0.9μ pore size tube.

5.1.8 The Support Tube Material

Two consecutive ultrafiltration runs with a carborundum membrane support are shown in Figure 27.

The product flux with the new carborundum support tube starts from over 1500 gal/ft^2-day (compared to 600 gal/

FIGURE NO 24. THE EFFECT OF PORE SIZE ON THE FLUX

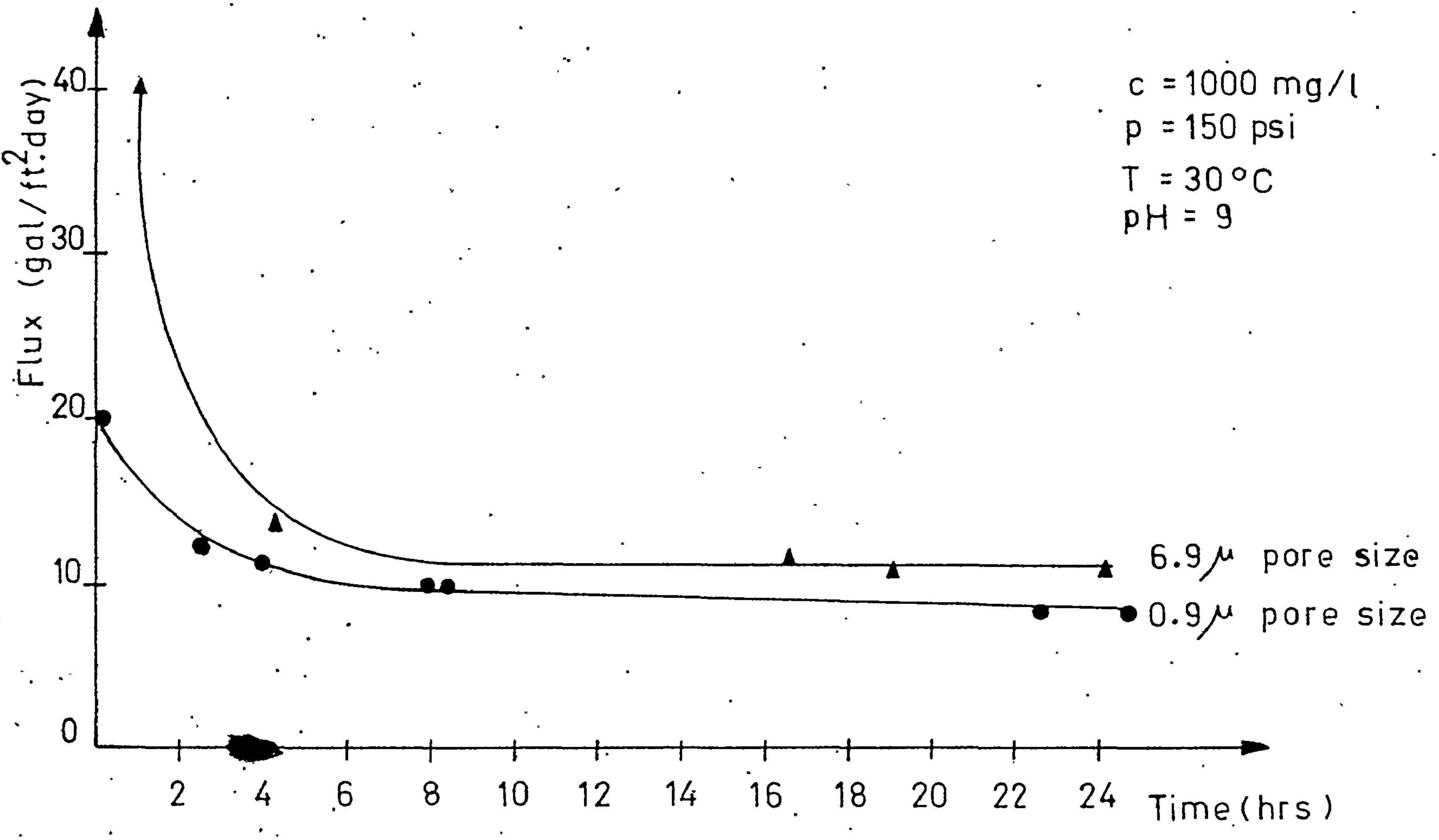
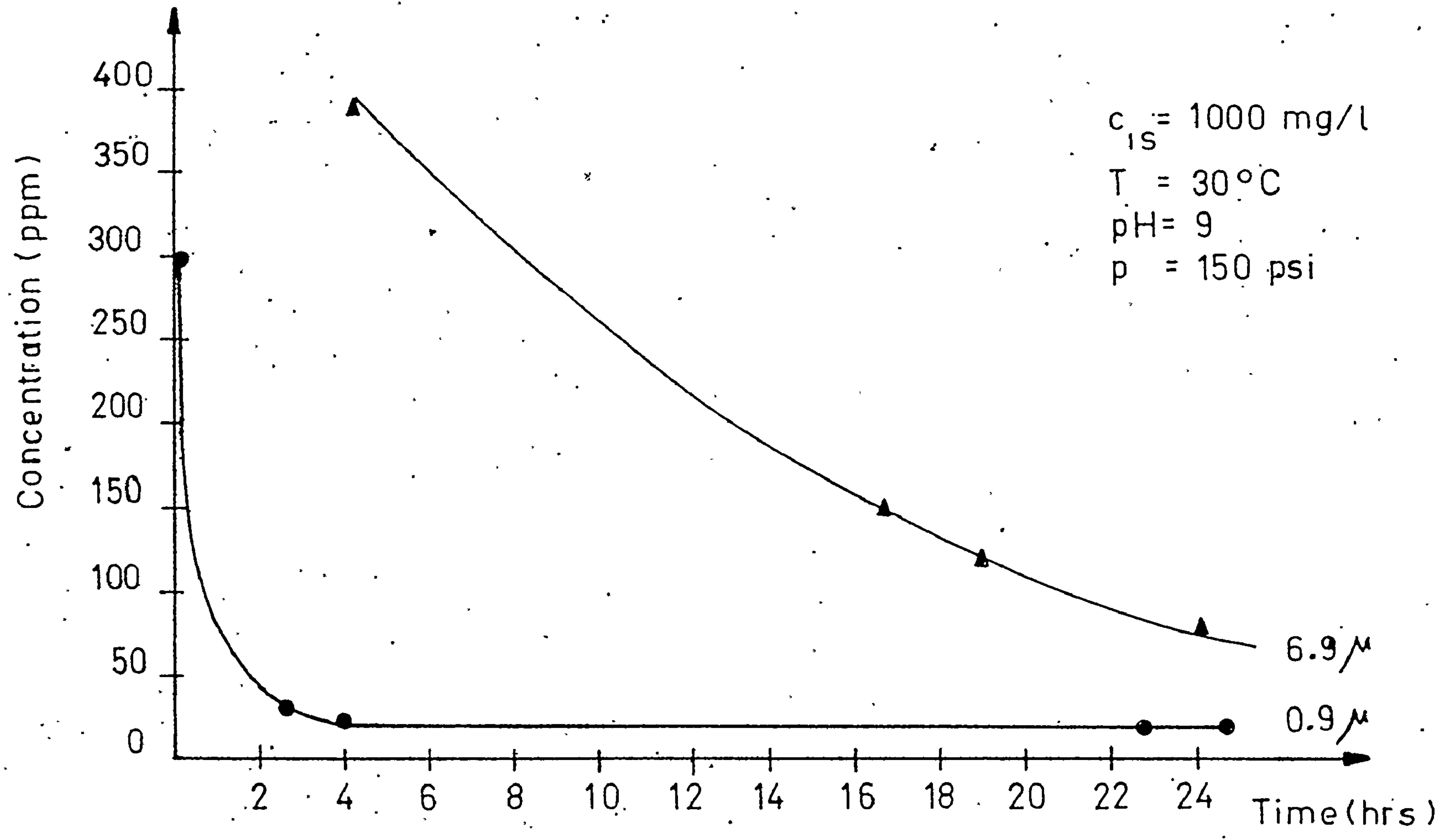


FIGURE NO 25. THE EFFECT OF PORE SIZE ON THE PRODUCT CONCENTRATION



ft^2·day with the 6.9μ pore size tube). It diminished rapidly without fully recovering during a backwash. The flux was, in the end of the second run, of the same order as that with used carbon support tubes. The rejection increased gradually and by the end of the second run approached the rejection obtained with carbon support tubes at similar flux rates (97%).

The material of the support tube; therefore, makes normally little difference in ultrafiltration. The rejection is caused by the membrane and the supporting structure does not have any effect on the membrane performance, unless, the support surface influences the formation of a dynamic membrane. An example of this will be seen in the chapter dealing with the pretreatment of the support tubes.

5.1.9 Chemical Additives

An ultrafiltration run was made after adding 1000 mg/ℓ formaldehyde to a feed solution containing 1000 mg/ℓ lignin at pH 9 (150 psi, 30°C). Another run was made at similar conditions but at pH2. The product flux as a function of time is shown in Figure 28.

The product flux was the same with and without formaldehyde at pH9. But a pH2 a 50% increase in the flux rate was observed with formaldehyde. The product concentration of lignin was about the same with and without formaldehyde.

FIGURE NO 26: THE FLUX THROUGH A NEW SUPPORT TUBE VERSUS A USED SUPPORT TUBES

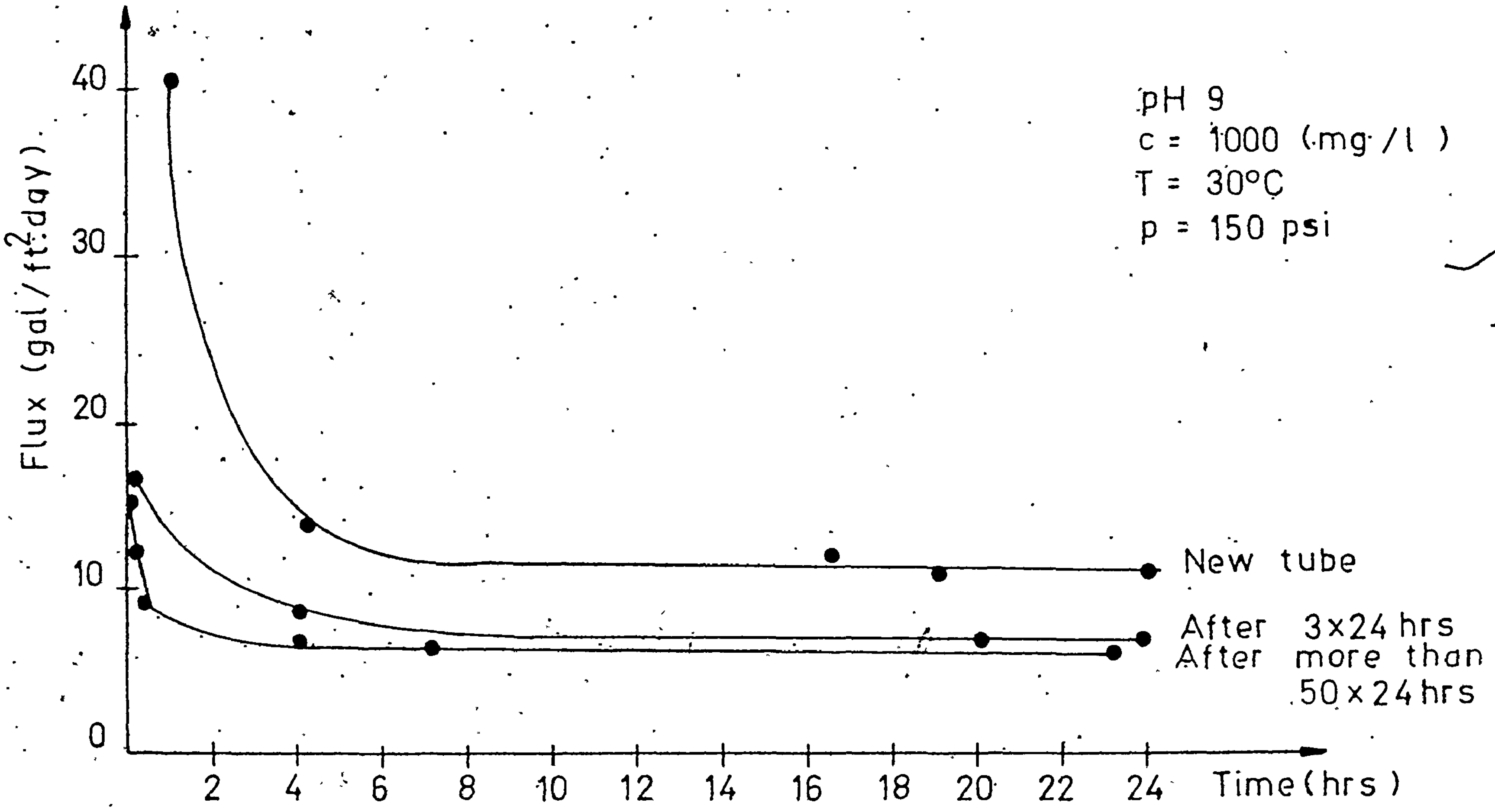
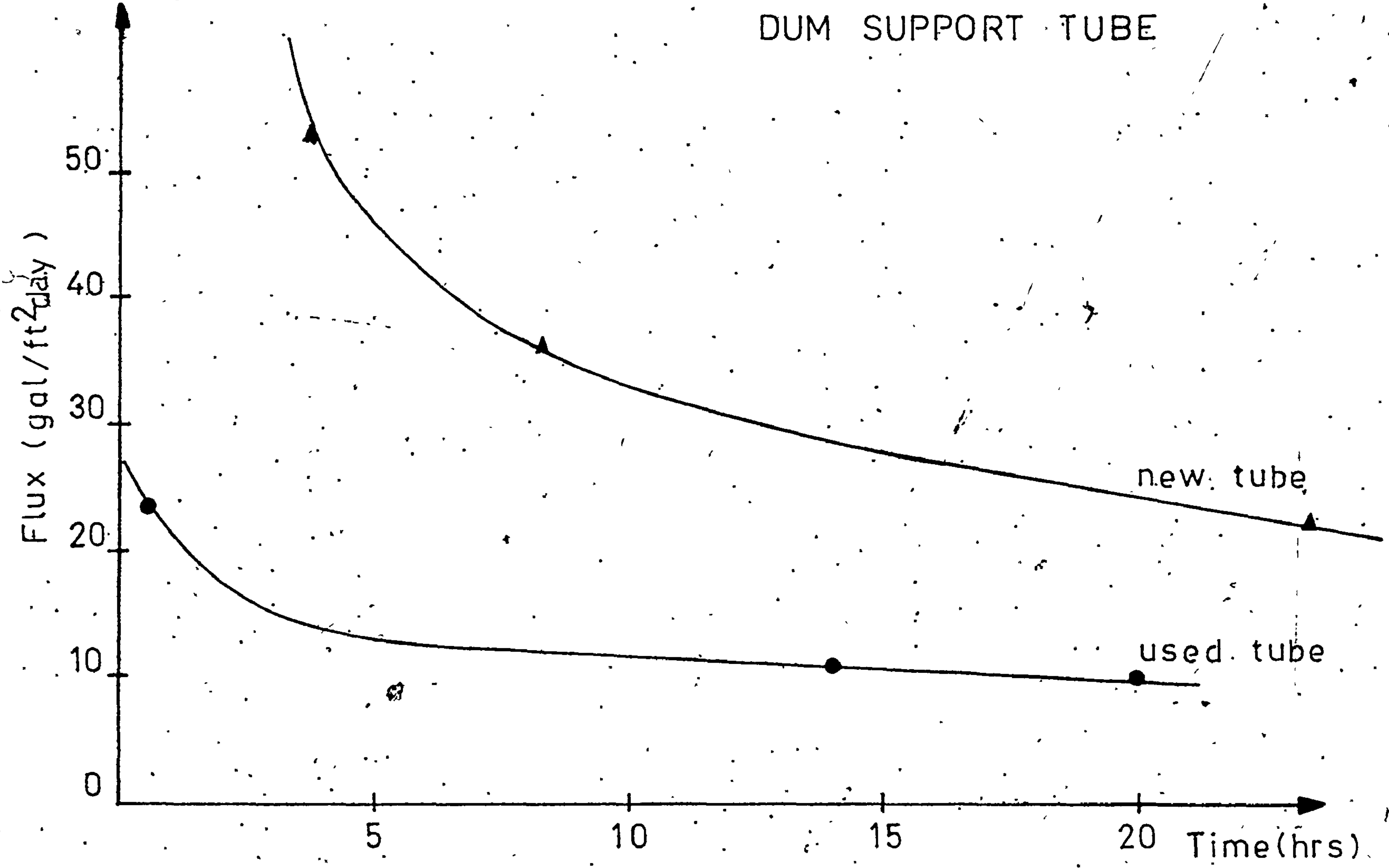


FIGURE NO 27. ULTRAFILTRATION WITH CARBORUNDUM SUPPORT TUBE



Chloroform was chosen to represent the group of compounds proposed by Whalen (1975) as additives for filtration of lignin. Both lignin and chloroform concentrations were 1000 mg/ℓ (150 psi, 30°C, pH2.5-3). No improvement in the flux or in the rejection could be observed. The final flux was 11.1 gal/ft^2 day and the product lignin concentration was 25 mg/ℓ. This is the same as without chloroform.

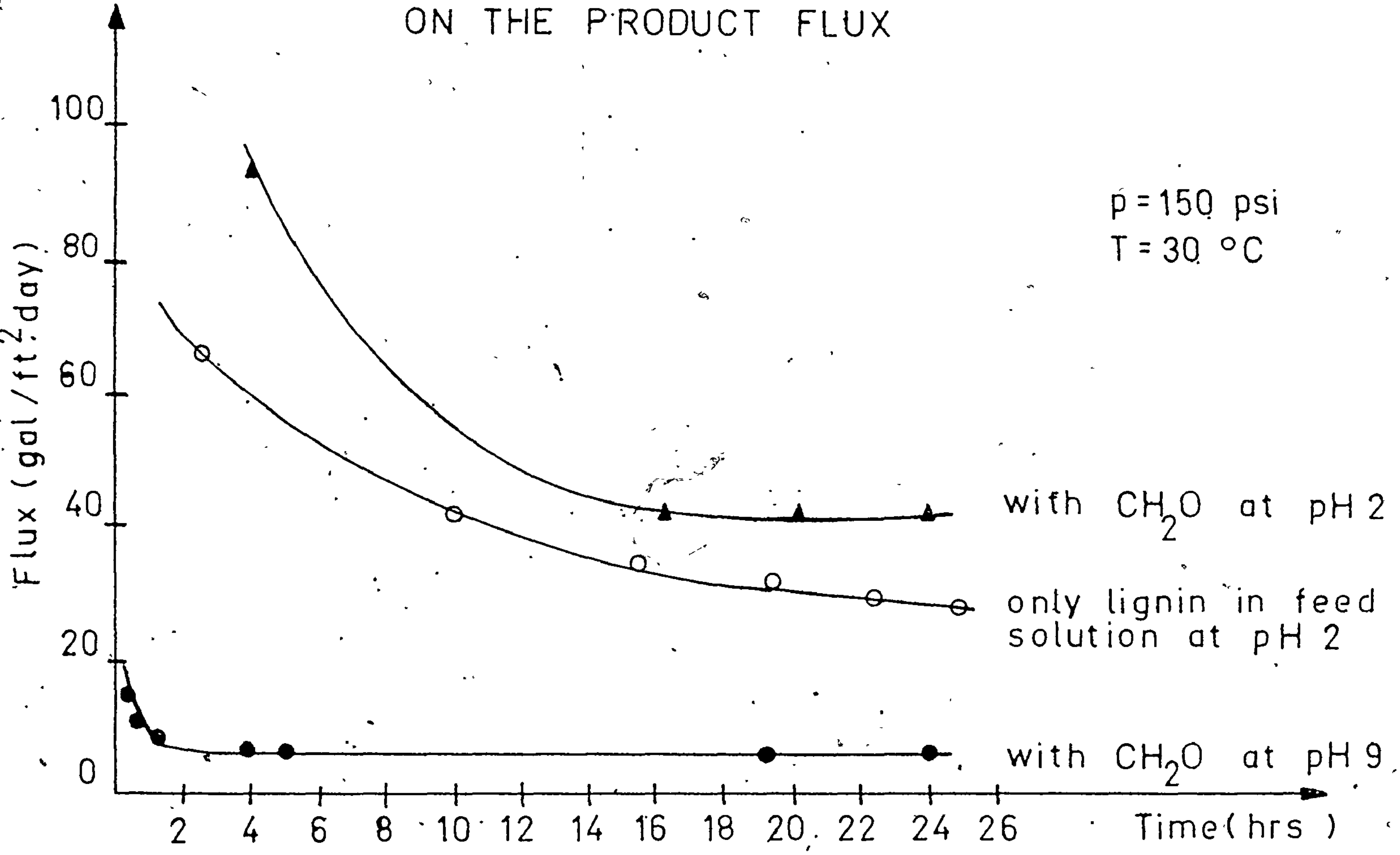
Acetic acid, which is not a Walen compound, did not increase the flux rate or the rejection either at the above conditions.

5.1.10 The Acid Pretreatment

A carbon support tube was sealed in a HCℓ solution at pH 1.5 for 40 minutes after the regular washing procedure used between ultrafiltration runs. The results of an ultrafiltration run after such a pretreatment are shown in Figure 29.

Such a pretreatment appeared to double the product flux. The product concentration was the same as without the treatment. The effect of the pretreatment was to be only slowly reversible because the flux was still at the end of the next run at the same conditions without additional pretreatment. After a few months the acid pretreatment was repeated to the same tube. This time the product flux was only about 50% higher than without pretreatment. There are two possible reasons for the effectiveness of the acid pretreatment.

FIGURE NO 28. THE EFFECT OF FORMALDEHYDE ON THE PRODUCT FLUX



Firstly, the acid left in the pores and especially on the surface of the support tube reacts with lignin by the exchange of hydrogen ions to the sodium ions of lignin. This brings about precipitation of lignin or membrane formation by neutralized or precipitated lignin colloids. The lack of reproducibility implies change in the character of the support tube.

Secondly, the acid treatment dissolves some of the lignin in the pores, not removed by an alkaline backwash (the solubility of lignin is discussed in Appendix 7). Thus the tube gets the same properties as after only a few runs. The poor reproducibility could be due to relatively larger portions of neither alkali nor acid soluble particles plugging the pores after the first acid treatment.

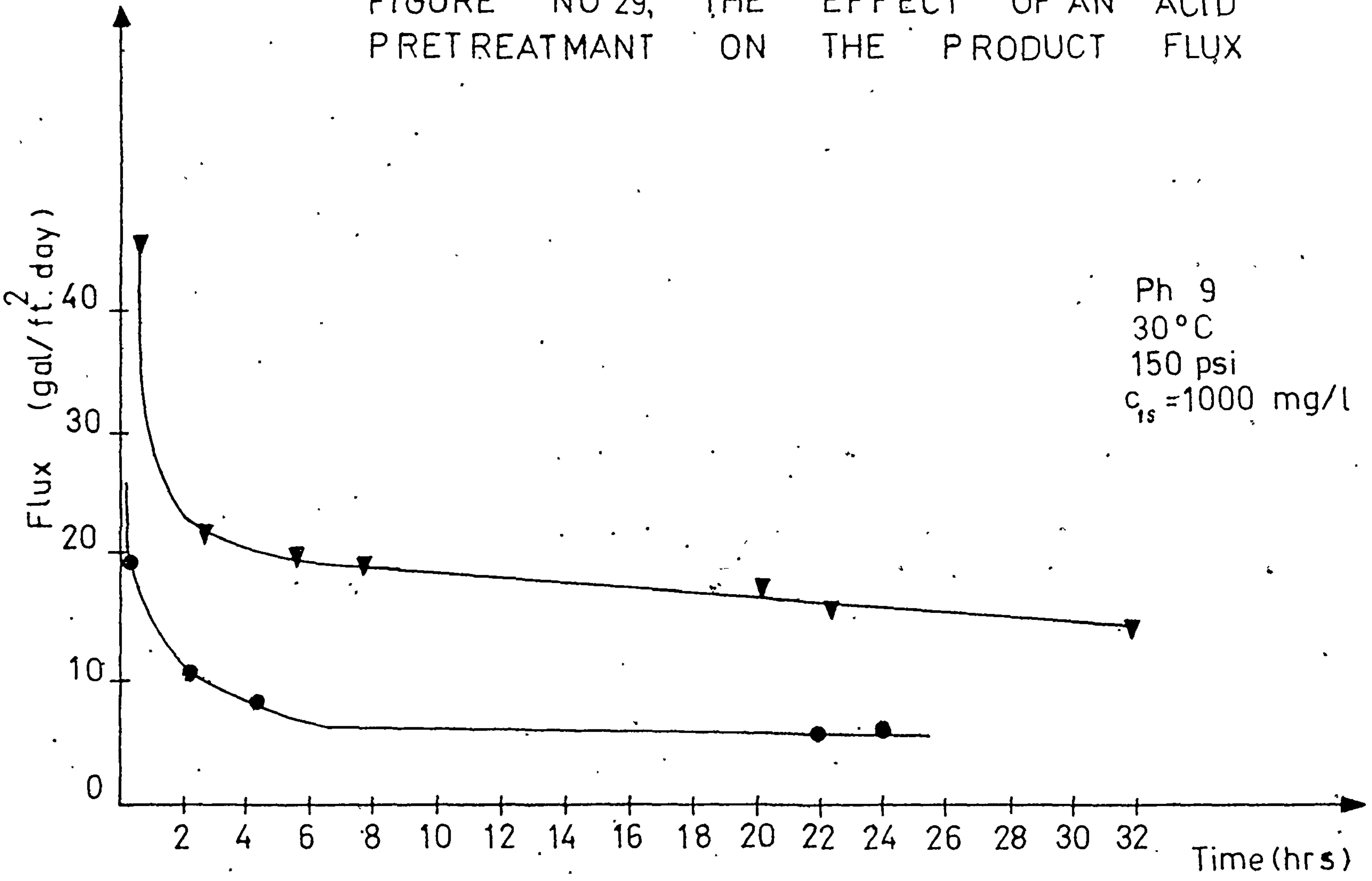
Both explanations appear to be possible. Both mechanisms might contribute to the acid treatment at the same time.

5.2 Ultrafiltration of Pulp Mill Effluent Samples

5.2.1 The Combined Kraft Mill Effluent Sample

The properties of the combined kraft mill effluent sample are given in Appendix 11. The sample was ultrafiltered at its normal pH 6.9 and acidified to pH 3. The results of these runs are shown in Figure 30 and Table 5. In the end of the second run the feed solution was acidified to pH 1.9 and 1000 mg/ℓ formaldehyde was added to it. This experiment was continued for four hours.

FIGURE NO 29, THE EFFECT OF AN ACID PRETREATMANT ON THE PRODUCT FLUX



The product flux dropped rapidly in both ultrafiltration runs to values 6 and 9 gal/ft^2·day after 24 hours of operating time at pHs 3 and 6.9 correspondingly. The lower flux was obtained at the lower pH contradicting results from experiments with pure lignin. The final effluent concentration was about three times as high at pH 3 as at pH 6.9. The acidification and addition of formaldehyde increased the flux only to 9 gal/ft^2-day.

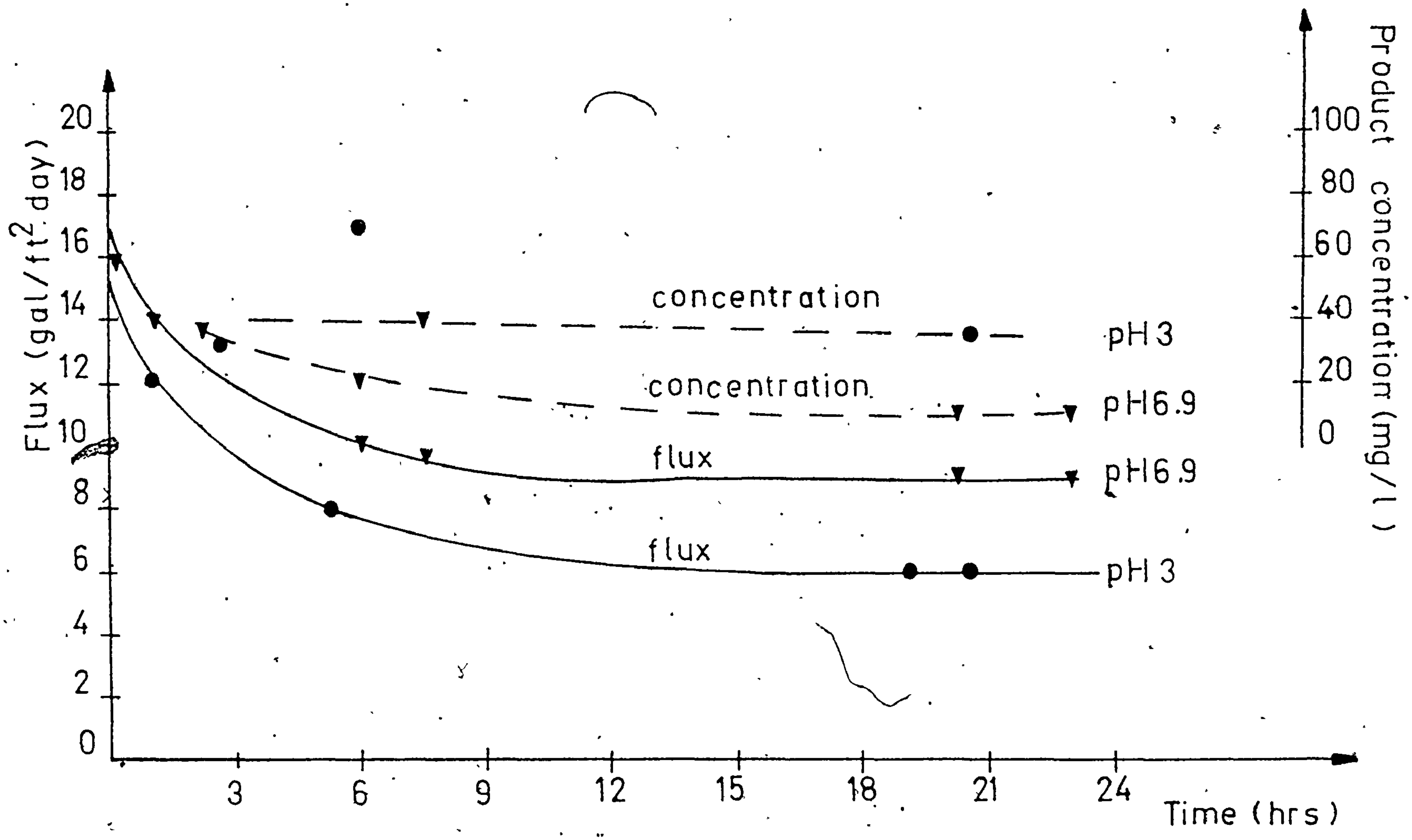
Table 5 Ultrafiltration of Kraft Mill Effluent

	Feed	Ultrafiltrate		
		pH 3	pH 6.9	
TC	187	35	46	
IC	44	2	2	
TOC	143	33	44	
BOD_5	180	160	80	(both at pH 6.9)
lignin by colour	450	38	10	
Rejection		93%	98%	

Suspended solids of feed at pH 6.9 = 60 mg/ℓ
at pH 2.5 = 110 mg/ℓ

The tendency to have a higher product concentration at a lower pH was observed in pure lignin solutions also, but it was not as apparent as in case of the kraft mill effluent. Probably the acidification of the kraft mill

FIGURE NO 30. ULTRAFILTRATION OF THE COMBINED KRAFT MILL SAMPLE



effluent hydrolyzed a part of the non-biodegradable organics making them biodegradable as seen by comparing BOD values in Table 5. Some lignin coagulates at pH 3 as can be seen from the suspended solids values of the feed solutions and is not able to pass through the membrane as TOC values indicate. Hydrolysis products that go through the membrane easily because of their smaller size are probably biodegradable and highly absorptive at the wavelength used for lignin determination (cf. Table 5).

The lower product flux at the lower pH can be explained by assuming that some of the hydrolyzing products are incorporated into the membrane and have an opposite effect to formaldehyde on the product flux.

A further difference between the kraft mill effluent and a pure lignin solution was that, although the kraft mill effluent lost about 10% of its colour when acidified to pH 3, it did not form flocs or visible precipitates in 1.5 hrs. Obviously lignin is easier to precipitate from a pure lignin solution (cf. Appendix 7).

The ultrafiltration of combined kraft mill effluents through a self-rejecting dynamic membrane seems to have some advantages compared to cellulose acetate membranes as is shown in Table 6. The highest flux with about 99% rejection of colour using cellulose acetate membranes for ultrafiltration of bleach plant effluents is reported to be about 22 gal/ft^2-day at 75^0 psi (Bansel 1975). Assuming only a linear increase in cost with increasing pressure, the cost of filtering through a cellulose acetate membrane would be about 50% higher than through a lignin dynamic membrane. The comparison is in reality even more advantageous for the dynamic membrane because the cost increase is linear taking only energy requirements into consideration but exponential when all factors are included. The easy replacement, the low cost of the membrane and the probably longer life time make the lignin membranes even more favourable compared to the possibly hydrolyzing cellulose acetate membranes.

Table 6 Comparison of Membranes

	Lignin membrane	Cellulose Acetate membrane	Zirconium Oxide membrane
Product flux			
at 150 psi	9		
200 psi			80
750psi		22	
Rejection	% 99	99	99
Advantages	- Easy replacement - Low cost of membrane - Long life time - Low pressure	- Commercially available - Best known properties	- High flux - Easily cleaned and replaced - Low pressure

Zirconium oxide membranes (Johnson et al., 1974) appear to have a superior performance compared to dynamic lignin membranes when treating kraft mill effluents (Table 6). Johnson's product flux of 80 gal/ft^2·day at 200 psi with 99% rejection, is over 100% better than lignin membranes show with pure lignin solutions at any operating conditions and 800% higher than observed with the kraft mill effluent. Both membranes can be operated at relatively low pressures and are easily replaced on site, but only the material of a lignin membrane is free of costs. The life expectancy of neither membrane is known but it is probably long because zirconium oxide is not degradable and although lignin hydrolyses slowly the lignin membrane can renew itself continuously. The recovery cost of zirconium oxide is not known. This is one factor that might decide in the future the feasibility of the use of zirconium oxide membranes.

All the three types of membranes have their own advantages but for ultrafiltration of kraft mill effluents the zirconium oxide membranes seem, at this moment, to be the most promising.

5.2.2 Sulfite Mill Samples

Some properties of the spent sulfite liquor and the bleach plant effluent samples are given in Appendix 11. The samples were ultrafiltered only at their original pH. The results are shown in Figure 31 and Table 7.

The product flux was 3.5 gal/ft^{2}day after 24 hrs with the bleach plant effluent and 7 gal/ft^{2}day with the spent sulfite liquor. The rejection of colour was only 50% and 80% correspondingly. After the ultrafiltration the support tube was coated by a black tar like substance. It appeared to contain some cellulose fibres as it did not dissolve, at room temperature, between pH 1.5 and 12.

These product fluxes are of the same order as those observed by Wiley (1967) with cellulose acetate membranes using spent sulfite liquor. Wiley got product fluxes between 7 and 17 gal/ft^{2}day at 600 psi with a COD rejection of about 99%. The pressure used with the lignin membrane was only 1/6th of that with cellulose acetate membranes making lignin membranes superior if only fluxes are considered. However the rejection of cellulose acetate membranes is so much better that they would be a probable choice, if only these two types of membranes were considered for the ultrafiltration of sulfite mill wastes.

FIGURE NO 31. ULTRAFILTRATION OF SPENT SULPHITE LIQUOR AND BLEACH PLANT EFFLUENT

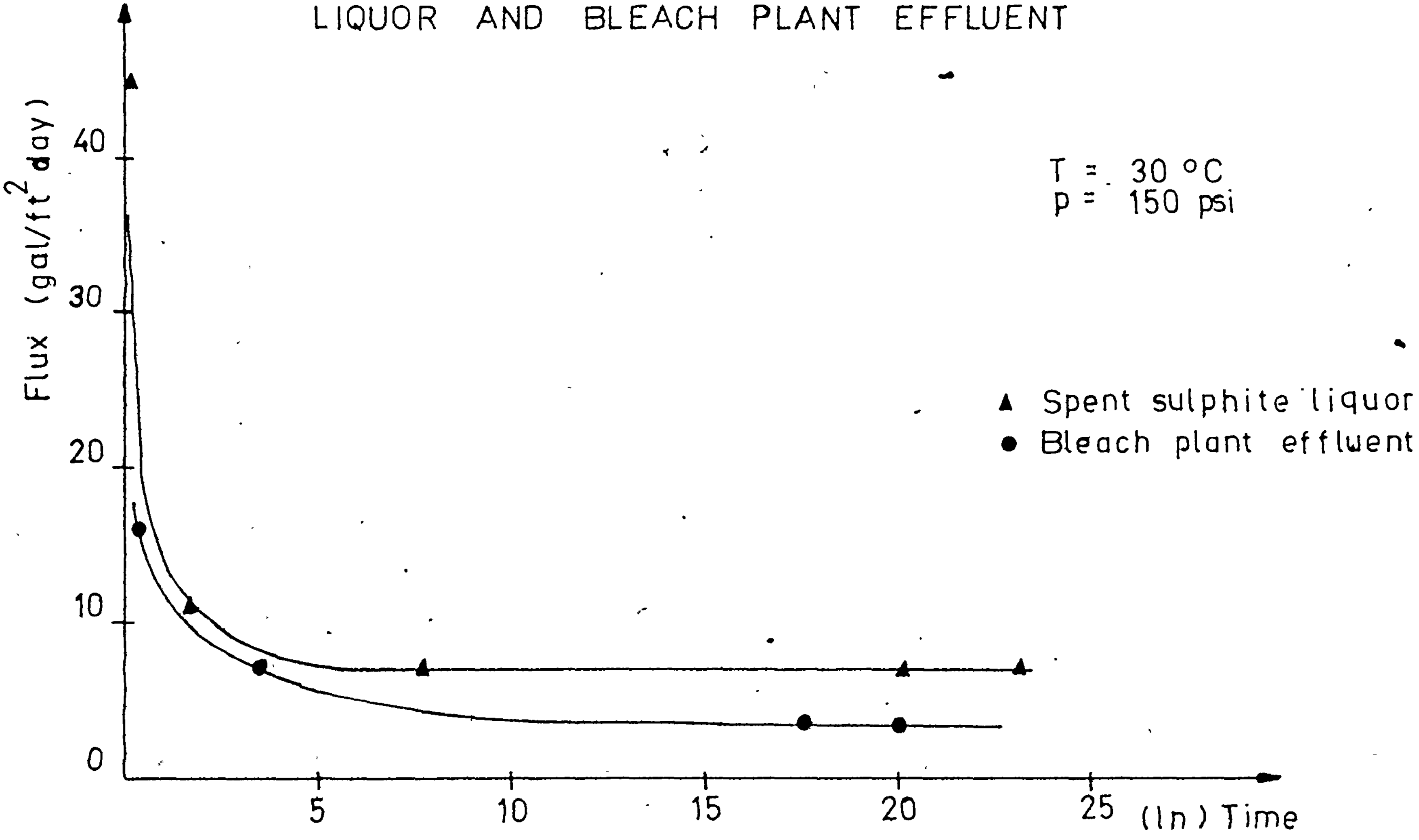


Table 7 Ultrafiltration of Sulfite Mill Samples

	Bleach plant effluent	Bleach plant effluent ultrafiltrate	Cooking liquor	Cooking liquor ultrafiltrate
TOC	800	220	3500	2000
TC	880	220	3500	2000
IC	2	2	2	2
BOD_5	310	170	900	590
SS	210	0	120	0
COD	1450	900	8000	6500
COD/TOC	1.8	4.1	2.4	3.3
BOD/TOC	0.39	0.77	0.26	0.30

- Smaller organic compounds have a higher COD/TOC ratio. Thus molecules in the filtrate are in average smaller than in the feed solution.

- Higher BOD/TOC ratio in the filtrate shows that more non-biodegradable (as f.ex. lignin) than biodegradable substances are rejected.

As in case of sulfate mill effluents, the zirconium oxide membranes seem to be the most promising also in the ultrafiltration of sulfite mill wastes. Although Perona et al., (1967) were able to obtain high fluxes with a dynamic lignin membrane, only the addition of zirconium oxide increased the rejection to over 90%.

6. CONCLUSIONS

In ultrafiltration through a dynamic lignin membrane:

1. The product flux increases with an increasing temperature, but it does not follow a simple equation. The product concentration is linearly proportional to the temperature until chemical changes of the recycling feed solution complicate the relation.

2. The product flux depends very little on the operating pressure above a critical pressure. The product concentration decreases with an increasing pressure.

3. The product flux depends on the pH. It is lowest at the middle pH range. The hydrolysis of lignin decreases the rejection near both ends of the pH scale.

4. The effects of the cross-flow velocity and the feed solution concentration on the product flux and rejection are small after the initial formation of the membrane. The membrane forms slower at a lower cross-flow velocity or a lower concentration.

5. The support tube material does not normally affect the membrane performance.

6. A different support tube pore size causes only initially different product fluxes and rejections.

7. The addition of formaldehyde to the feed solution can increase the product flux at low pH without decreasing the

rejection. At alkaline pH, formaldehyde does not increase the product flux. Whalen compounds or acetic acid do not improve the membrane performance.

8. Soaking the carbon support tubes in strong hydrochloric acid increases the product flux by 100%. This increase in the product flux gradually declines unless the treatment is repeated. Subsequent acid treatments, however, result in less significant improvements.

9. The ultrafiltration of combined kraft mill effluents through a dynamic lignin membrane is preferred over a cellulose acetate membrane. The zirconium oxide membrane, however, seem to show the most promising performance.

10. Both the zirconium oxide and cellulose acetate membranes have better performances in case of sulfite mill effluents than dynamic lignin membranes.

7. RECOMMENDATIONS

Many aspects of this thesis or field could be studied further. Some of these are

a) The measurement of the effect of some inorganic salts or polymers on membrane performance.

b) The electrokinetic formation and backwash of membranes.

c) The effect of very high cross-flow velocities, say 10 times the ones used in these experiments.

d) The flux and rejection of zirconium oxide membranes.

Appendix 1

Evaluation of Membrane Performance

Transport equations 3 and 7 were

$$F_W = W_p \ (\Delta P - \Delta\pi) \tag{3}$$

$$F_S = B \ (C_{1s} - C_{2s}) \tag{7}$$

Concentration of product water is determined by relative salt and water fluxes

$$C_{2s} = \frac{F_s \ C_{w2}}{F_W} = \frac{B(C_{1s} - C_{2s})C_{W2}}{W_p(\Delta p - \Delta\pi)} \tag{42}$$

where C_{W2} is the concentration of water in product stream and is approximately 1 g/cm^3. Combining equations 8 and 42 and neglecting C_{W2} gives:

$$C_{2s} \ W_p \ (\Delta P - \Delta\pi) = B \ C_{1s} - B \ C_{2s} \tag{43}$$

$$C_{2s} \ (B + W_p \ (\Delta P - \pi)) = B \ C_{1s} \tag{44}$$

$$1 - \frac{C_{2s}}{C_{1s}} = 1 - \frac{B}{B + W_p(\Delta p - \pi)} \tag{45}$$

$$R = \frac{W_p \ (\Delta p - \pi)}{B + W_p \ (\Delta p - \pi)} \tag{46}$$

$$\frac{W_p}{B} = \frac{R}{(1-R)(\Delta p - \pi)} \tag{47}$$

Substituting to 47: $W_p = \dfrac{F_W}{\Delta p - \Delta\pi}$

gives:

$$\frac{W_p^2}{B} = \frac{R\ F_W}{(1-R)(\Delta p - \Delta\pi)} \qquad (48)$$

Obviously it is desirable to maximize both W_p and the ratio W_p/B. However, it is usually true that if modifications are made to increase W_p, the quantity of W_p/B decreases. Londsdale (1973) proposes the product of $W_p \times W_p/B$ as an empirical formula of merit. It combines to a single value both water flux and salt rejection. The value is independent of salt concentration of feed solution and operating pressure. On the other hand the value depends on the type of salt or compound used in experiments. Also the figure W_p^2/B is very sensitive to apparently small changes in rejection as the rejection approaches 100%. Thus this figure of merit for 99.9% rejection would be twice that for 99.8%. At the following Table 8 W_p^2/B has been calculated at some operating conditions. Because Lonsdale's figure of merit is relatively new and not generally accepted, comparable values for lignin are not published in literature but were calculated from results given in publications. Example: Run at pH 9, T = 30°C p = 150 psi

$$R = 1 - \frac{15}{1000} = 0.985$$

$$F_W = \frac{6\ \text{ml}}{\text{min}\ 340\ \text{cm}^2} = 2.94 \times 10^{-4}\ \frac{\text{g}}{\text{sec.cm}^2}$$

Table 8 Membrane Performance Numbers at Different pH

pH	W_p^2/B	g / cm^2 sec atm
11	8.4×10^{-4}	at T = 30°C
9	18.4 x "	p = 150 psi (10.5 atm)
7	26 x "	
5	24 x "	
3	12 x "	
2	35 x "	

from Perona et al., (1967)

	W_p^2/B [g/cm sec atm]
PVC-membrane $D_p = 0.45$ + secondary membrane	38×10^{-4}
c-a-membrane + secondary membrane	2×10^{-4}
dynamic lignin membrane on carbon tube $D_p = 0.41$	4×10^{-4}
" " " on ceramic tube $D_p = 0.91$	1×10^{-4}

$$\frac{W_p^2}{B} = \frac{R\ F_W}{(1-R)\Delta p} = \frac{0.985 \times 2.94 \times 10^{-4}}{0.015 \times 10.5}\ \frac{g}{\text{atm sec cm}^2}$$

$$= 18.4 \times 10^{-4}\ \frac{g}{\text{cm}^2\text{-sec-atm}}$$

At high pH the relatively poor rejection brings about lower W_p^2/B values. It does not change much at middle range of pH but at pH 3 it is small before increasing flux more than compensates for the poorer rejection at pH 2. Values calculated from results given by Perona et al., (1967) are smaller with the exception of PVC-membrane.

Higher temperature increases the value of W_p^2/B by increasing F_W without impairing R too much. A grouping of $W_p^{3.5}/B$ has been proposed (Lonsdale 1973) to be independent of the temperature, but W_p^2/B would give a more constant value according to our experiments. These groupings are presented in Table 9.

The effect of pressure was eliminated in equation 48 by permeability term $F_W/(\Delta p - \Delta\pi)$. This assumes a linear relation between product flux and operating pressure as can be expected with non-compressible stationary membranes. With dynamic membranes the situation is different. An increased pressure causes an increased radial flow which brings about thickening of the membrane with increased flow resistance. Also tightening of the membrane increases flow resistance as discussed earlier. Thus with dynamic

Table 9 Membrane Performance Numbers at Different Temperatures

T[°C]	R[%]	W_p g/cm^2 sec-atm	W_p/B	$W_p^{3.5}/B$	W_p^2/B	$W_p^{1.5}/B$
25	99.2	2.7 10^{-5}	11.8	132×10^{-15}	3.1×10^{-4}	19.1×10^{-3}
40	99.3	2.6	13.5	131	3.3	21.2
50	99.0	4.12	9.43	282	3.7	18.7
70	98.8	5.18	7.84	570	4.3	18.4

Table 10 Membrane Performance Numbers at Different Pressures

p[psi]	[atm]	$F_w/\Delta P-\Delta\pi$	R	W_p^2/B	$W_p^{1.5}/B$	W_p/B
50	4.22	0.5×10^{-4}	97.8	23×10^{-4}	32×10^{-2}	45
95	6.68	0.48×10^{-4}	99	48×10^{-4}	69×10^{-2}	100
150	10.54	0.31×10^{-4}	99	31×10^{-4}	55×10^{-2}	100
200	14.06	0.23×10^{-4}	99	23×10^{-4}	48×10^{-2}	100
300	21.09	0.17×10^{-4}	99.2	21×10^{-4}	51×10^{-2}	123

compressible membranes a lower permeability and lower W_p^2/B is to be expected with increasing pressure. This tendency is clearly shown in Table 10, where W_p^2/B is tabulated at pressures between 50 and 300 psi (30°C, 1000 mg/ℓ lignin). The only exception is at 50 psi where permeability is at its highest value but poor rejection lowers Lonsdale's figure of merit. Groupings $W_p^{1.5}/B$ and W_p/B are not much better in this case either.

Trying to combine parameters rejection and flux to one number to express membrane performance does not seem to succeed with lignin dynamic membranes. Deviations occur at different operating conditions. Also near the spectroscopic detection limit of lignin determination of rejection is not accurate enough to support the use only one combined figure of merit. For above reasons the use of permeability is also not recommended, but product flux, rejection and operating conditions should be known for correct evaluation of membrane performance.

Appendix 2

Concentration Polarization

Concentration polarization can be calculated from equation 49 (Sherwood et al 1965)

$$\frac{C_{3s}}{C_{1s}} = \exp \frac{8.96\ F_W\ (N_{Sc})^{3/4}}{C_W\ v} \sqrt{\frac{2}{f}} \tag{49}$$

where C_{3s} = solute concentration on the membrane surface

N_{S_c} = Scandt number

f = friction factor

$$N_{S_c} = \frac{\nu}{D_s} = 3000 \tag{50}$$

where ν = kinematic viscosity = $0.009\ \frac{cm^2}{sec}$

$D_s = 0.3\ .\ 10^{-5}\ \frac{cm^2}{sec}$ (Pennington et al 1947)

Using $f = 0.01$ (Cooper et al 1933)

and $F_W = \frac{6\ m\ell}{min.\ 340\ cm^2} = 0.3 \times 10^3\ \frac{g}{cm^2\ sec}$

$$\frac{C_{3s}}{C_{1s}} = \exp\ 8.96 \times 0.3 \times \frac{10^{-3} g}{cm^2\ sec}\ \frac{cm^3}{1\ g}\ \frac{sec}{150\ cm}\ (3000)^{3/4} \sqrt{\frac{2}{0.01}} = 1.105$$

Table 11. Concentration Polarization at Different Fluxes

F_w $\frac{\text{ml}}{340\ \text{cm min}}$	F_w $\frac{\text{g}}{\text{cm}^2\ \text{sec}}$	F_w $\frac{\text{gal}}{\text{ft}^2\text{day}}$	C_{35}/C_{15}
6	0.3×10^{-3}	5.3	1.105
15	0.75×10^{-3}	13.4	1.290
30	1.5×10^{-3}	26.7	1.650
50	2.5×10^{-3}	44.5	2.330
100	5×10^{-3}	89.0	5.45
200	10×10^{-3}	178	29.5

Table 12 Concentration Polarization at Different Cross-Flow Velocities

v cm/sec	R_e of equipment	f	C_{35}/C_{15}
5	90	0.25	1.835
10	180	0.14	1.500
20	360	0.05	1.408
30	540	0.035	1.312
70	1260	0.018	1.175
100	1800	0.015	1.130
120	2160	0.014	1.150
150	2700	0.01	1.105
200	3600	0.01	1.085

The concentration polarization at different solvent fluxes and cross-flow velocity values are listed in tables 11 and 12. The effect of the cross-flow velocity is not as significant as F_W on concentration polarization because a change in v is counterbalanced by a change of f which depend on v.

Taking extreme values from the previous tables ($v = 5$ cm/sec, $F_W = 178$ gal/ft^{2}day, $C_{1S} = 10$ g/ℓ) gives a concentration of 540 g/ℓ on the membrane surface. This corresponds to an osmotic pressure of 1.9 atm or 27 psi using equation $\underline{1}$. Only at higher feed solution concentrations would the osmotic pressure reach any significance.

Appendix 3

Osmotic Pressure of Lignin Solutions

The average molecular weight of indulin AT at pH 9 is about 7000 (Rankin 1975). Using equation 1 in form

$$\pi = 0.082\ cT \qquad \text{and placing } C = 1000\ \text{mg}/\ell = \frac{1.000}{7000}\ \frac{\text{mol}}{\ell}$$

$$T = 300^{\circ}K$$

$$\pi = 0.082\ .\ \frac{1.000.300}{7000}\ \text{atm} = 3.5 \times 10^{-2}\ \text{atm} = 0.05\ \text{psi}$$

The following table (Table 13) compares osmotic pressures of lignin solutions calculated as shown above and sodium chloride solutions at pH 9 and 300°K. Values for sodium chloride are given by Weber (Weber 1972).

The low osmotic pressure of lignin solutions are due to its high molecular weight. At lower pH, the osmotic pressure would be even lower, because of the increase in the molecular weight of lignin. At less than pH 7, the osmotic pressure reduces sharply because lignin precipitates and solids don't contribute to the osmotic pressure. Even at pH 12.5, where the average molecular weight of indulin is 6000 (Rankin 1975), the osmotic pressure at a concentration 1000 mg/ℓ is still only about 0.06 psi.

Although the osmotic pressure of lignin is low, there is much inorganic and organic material in paper mill wastes,

Table 13 Theoretical Osmotic Pressure of Lignin and NaCℓ Solution, pH 9 300°K

C mg/ℓ	π psi lignin	 NaCℓ
50	0.0025	0.7
100	0.0050	1.4
500	0.025	5.7
1000	0.050	11.4
5000	0.25	57
10000	0.5	114
50000	2.5	over 200
100000	5.0	

which may make osmotic pressure a limiting factor. For example, the kraft mill bleach plant effluent can have an osmotic pressure of 600 psi at 10% total concentration (Bansel 1975). Thus the limiting concentration at 150 psi would be about 2%. On the other hand, ultrafiltration membranes do not reject all kinds of ions (cf. appendix 9) and the effective osmotic pressure is less than the sum of the osmotic pressures of all species.

Appendix 4

Calculation of Reynolds Number in the Ultrafiltration Cylinder

$$N_{Re} = \frac{(d_{in} - d_{out})\ \zeta v}{\mu} \qquad (51)$$

where d_{in} = inside diameter of the cylinder

d_{out} = outside diameter of the support tube

μ = viscosity

ζ = density

v = cross-flow velocity

v_1 = 19.8 cm/sec

v_2 = 158 cm/sec

μ = 1

ζ = 1

$d_{in\ 1}$ = 50.80 mm

$d_{in\ 2}$ = 39.69 mm

d_{out} = 37.92 mm

$N_{Re\ 1}$ = 2550

$N_{Re\ 2}$ = 2780

Appendix 5

Calculated Membrane Resistance

Flow through ultrafiltration membranes was described with equations 10 and 12

$$F_W = \frac{\Delta p}{R_m} \tag{10}$$

$$F_W = \frac{\Sigma\ a^2\ \zeta_\ell}{8(\tau)^2\ \mu\ \delta}\ \Delta P \tag{12}$$

where a is the pore radius. It can be estimated to be of the same order of magnitude as the lignin membrane. The average molecular weight of indulin at pH 9 is about 7000 with a radius of 30Å (calculated from information by Rankin 1975). The cut-off molecular weight for 98% rejection would be about 3000 corresponding to a radius of about 20Å.

Porosity Σ is usually equated to membrane water content C_W. When $C_W = 0.2\ g/cm^3$, $\Sigma = 0.2$. Using 0.3μ from appendix 6 as membrane thickness and $\Delta p = 150$ psi $\mu = 0.009\ \frac{cm^2}{sec}$, $\zeta_\ell = 1\ g/\ell$, $F_W = 6\ gal/ft^2day$, the tortuosity factor τ can be calculated:

$$\tau = \sqrt{\frac{\Sigma\ a^2\ \zeta_\ell\ \Delta P}{8\ F_W\ \mu\ \delta_m}} = 1.3 \tag{52}$$

Using above values in equation 10

$$F_W = \frac{1}{R_m}\ \Delta P = 0.04\ \frac{gal}{ft^2 day\ psi}\ \Delta\ P\ psi \tag{10}$$

Appendix 6

Estimation of Membrane Thickness

When a membrane starts to build up in protected pores it can form a rather coarse structure. But after a while molecules or colloids have to build a more stable, denser structure on open parts of the support. Thus lignin membranes are at least to some degree anisotropic. This is supported by the fact that rejection of lignin membranes increases during formation period and the effective thickness, which will be calculated later, is much less than the apparent thickness.

The effective thickness of ultrafiltration or reverse osmosis membranes is typically in the order of 0.1 to 1.0μ. This "skin" thickness has never a precisely defined value. It also varies from place to place. However, it can be estimated from equation 5

$$F_W = \frac{D_w C_W \ V_m}{RT \ \delta_m} (\Delta P - \Delta\pi) \qquad (5)$$

$$\partial_m = \frac{D_w C_W \ V_m}{F_W \ RT} (\Delta P - \Delta\pi) \qquad (53)$$

Water concentration in the membrane, C_W, varies usually between 0.1g/cm^3 and 0.65g/cm^3 being typically 0.25g/cm^3 for polymer membranes (Lonsdale 1973). Assuming that the effective thickness is established when lignin fills 75% of the volume of membrane, $C_W = 0.25 g/cm^3$. Diffusion coefficient for self-diffusion of water at 30°C is 2.5×10^{-5} cm/sec (Landolt-Bornstein 1969). The effective diffusion coefficient is much smaller. A typical value for a membrane with $0.25 g/cm^3$ C_W is 0.5×10^{-5} cm/sec (Lonsdale 1973). Using final flux from runs at pH 9, 30°C, 1000mg/ℓ lignin and 150 psi:

$$\partial_m = 0.5 \times 10^{-5} \frac{cm^2}{sec} \times 0.2 \frac{g}{cm^3} \times 18 \frac{cm^3}{mol}$$

$$\times \frac{10.5 \text{ atm } cm^2 \text{ sec}}{6 \times 3.75 \times 10^{-5} g} \times \frac{{}^{o}K \text{ mol}}{82 \text{ } cm^3\text{-atm}}$$

$$\times \frac{1}{303^{\circ}K} = 0.34 \times 10^{-6} \text{ cm}$$

$$= 0.34\mu \simeq 0.3\ \mu$$

As can be seen from equation 53 increasing pressure reduces the effective thickness if the coefficient for flux-pressure dependence is less than 1. This is the case with lignin membranes. The increased compression is likely to reduce the open space in the membrane and decrease C_W.

Higher temperature would increase the effective thickness of membrane because temperature dependancy of the diffusion coefficient of water is of higher power than one at temperature range studied. This more than compensates for the temperature term in the denominator in equation 53 E.g., at same conditions as above with the exception of T - 120°C and assuming the same temperature dependency for D_w as for self-diffusion of pure water (Landolt-Bornstein 1969)

$$D_{120} = \frac{0.5 \times 10^{-5} \times 10}{2.5} \frac{cm^2}{sec} = 2 \times 10^{-5}\ cm^2/sec \qquad (54)$$

and substituting in eq. 53:

$$\partial_m \approx 1\mu$$

At pH 2, when operating conditions are kept the same as in the first calculation, the effective thickness is

$$\delta_m = \frac{\delta_{m_1} F_{W(pH9)}}{F_{W(pH2)}} = \frac{0.34 \times 6}{30}\ \mu = 0.07\mu \qquad (55)$$

This value would be in reality larger because of changes in physical appearance of lignin meaning a higher C_W value. Taking this into consideration δ_m would be maybe 0.1μ.

More precise calculations would be meaningless because of uncertainty of D_w and C_W values. These estimates indicate that the effective thickness of a dynamically formed lignin membrane or a carbon support tube is of the same order as that of other membranes used for reverse osmosis.

Appendix 7

Lignin Solutions and pH

The absorbance of six lignin solutions having a concentration of 100 mg/ℓ and pH ranging from 3.2 to 12 was measured at 4650Å. The absorbance depended very much on pH as seen in Figure 32. The maximum absorbance is at high pH and the curve has a minimum at pH between 5 and 6. At lower pH the absorbance increases again. The higher pH part of the curve was observed already by Rankin (1975).

During two week storage at room temperature, the solution pH moved closer to the middle range. At the same time absorbtion changed following absorbtion vs pH curve above the minimum of the curve. But at low pH the final absorbance was higher than that measured earlier at same pH. This could be due to chemical changes making lignin more soluble to acidic solutions.

Suspended solids in lignin solutions at different values of pH were measured by the 0.45μ and 1μ pore size filters. The results are shown in Figure 33. Both filters gave similar type of curves indicating the existence of solids also at high pH. At pH 2 only 1% and 0.1% of lignin could not be separated by filtration with 1μ and 0.45μ filters respectively. These results are not quite exact indicators of solubility due to the formation of a secondary membrane

FIGURE NO 32. THE EFFECT OF THE pH ON ABSORBANCE AT 465 nm

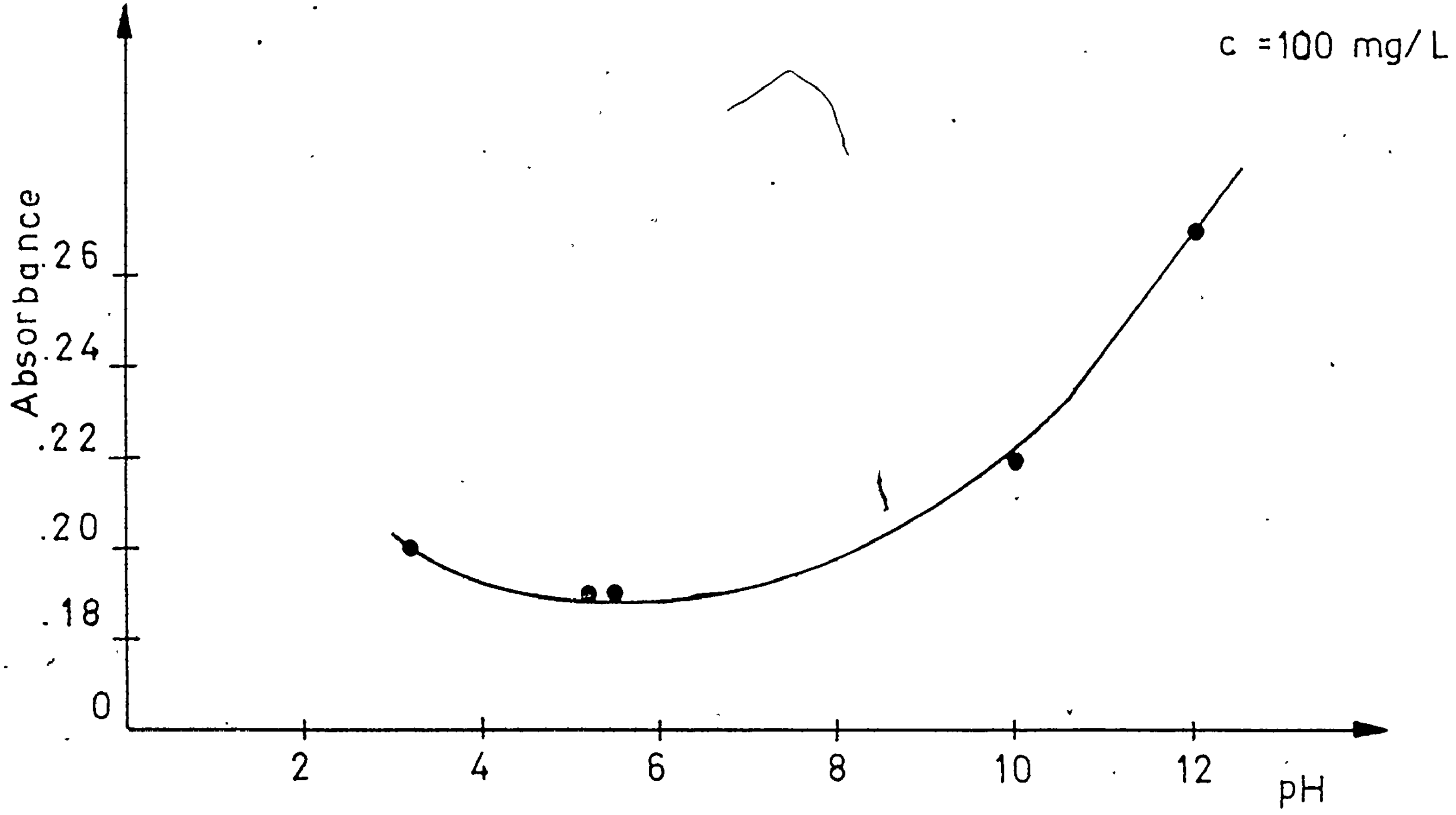
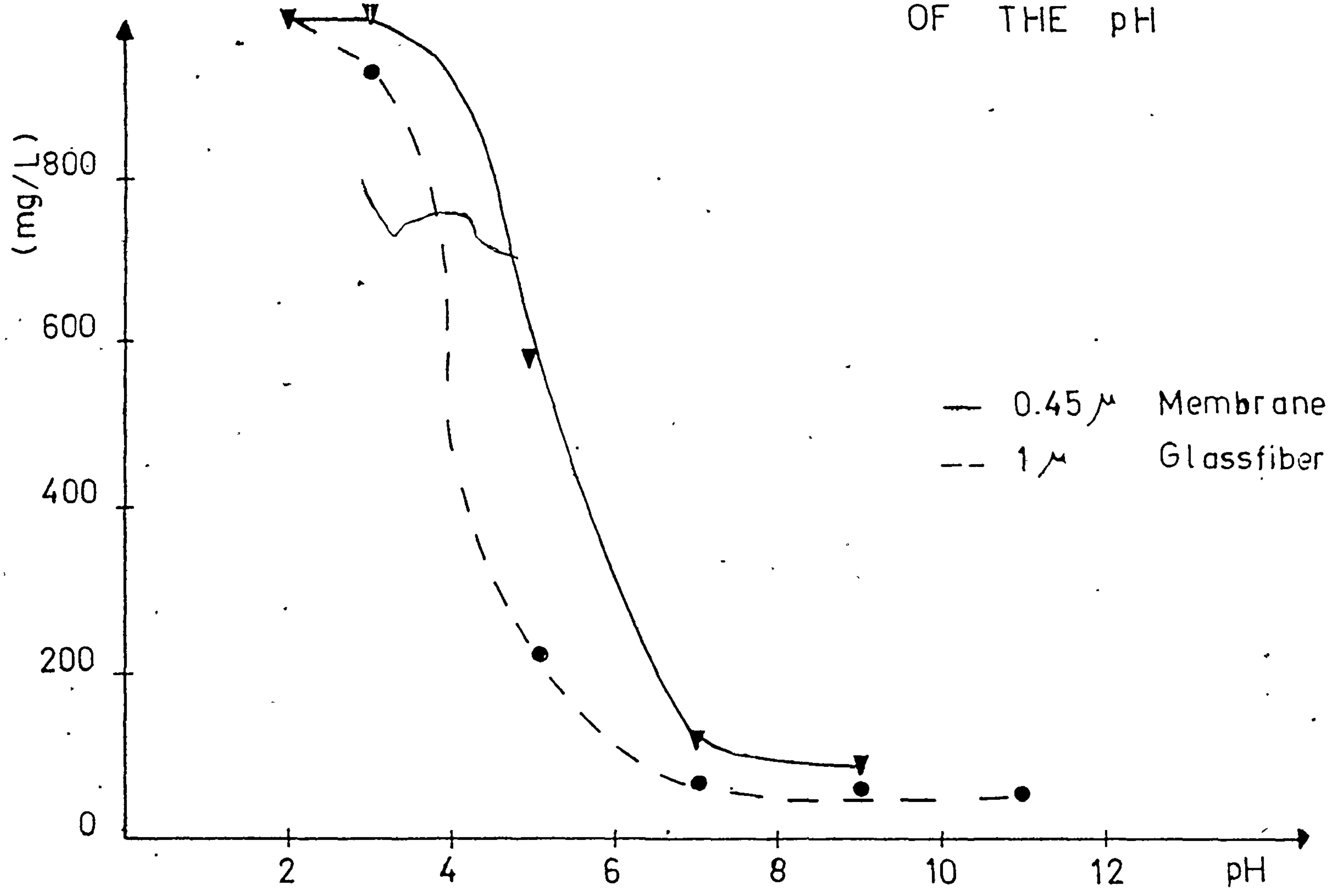


FIGURE NO 33. SUSPECDED SOLIDS AS A FUNCTION OF THE pH

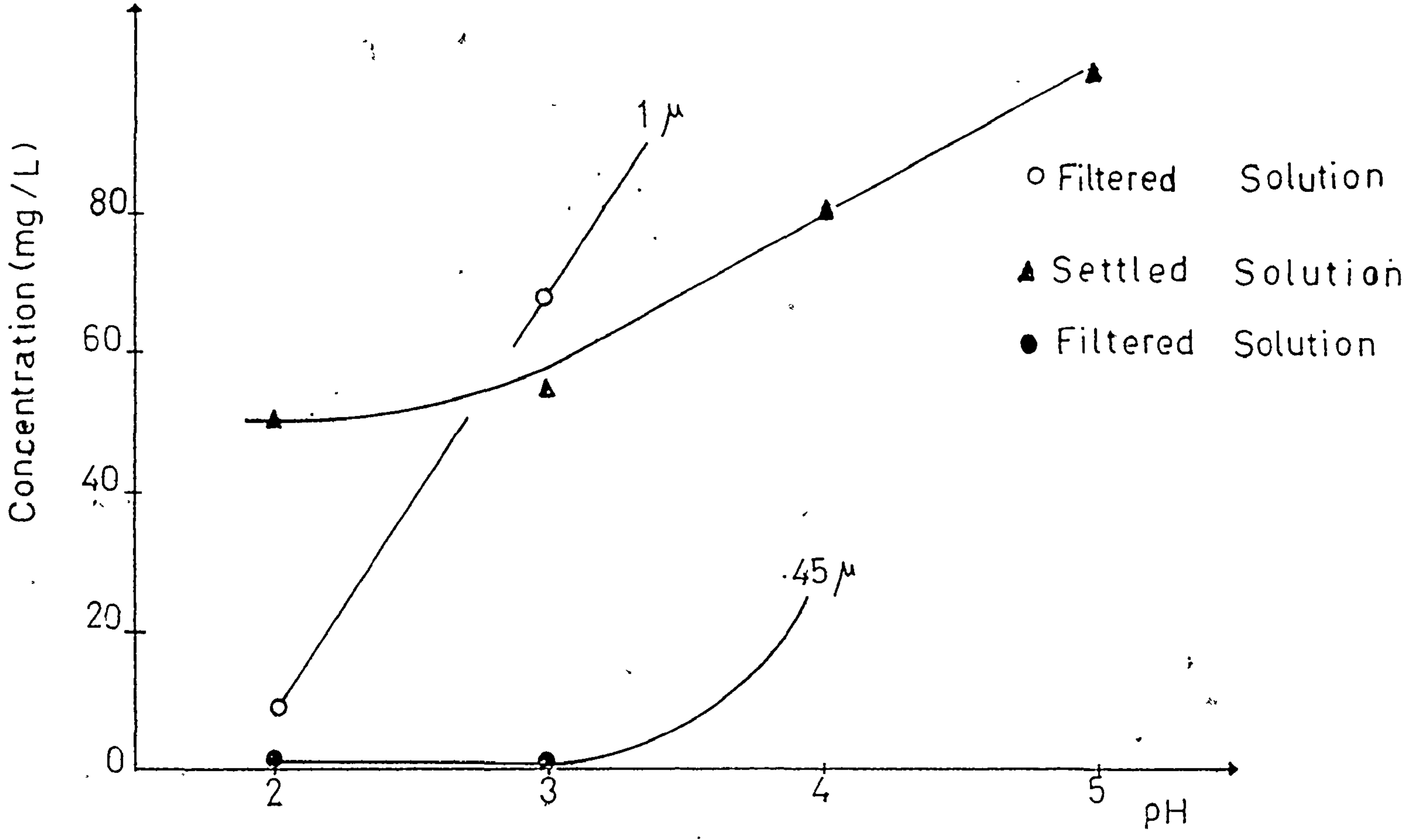


on the surface of the filter. This secondary membrane prevents some of the molecule size lignin passing through the membrane, exactly as in ultrafiltration. The larger pore size filter let more lignin pass through to the filtrate but, most likely, a secondary membrane formed on it as well.

Formation of a lignin rejecting membrane in filtration was shown by indirectly suspended solids and lignin measurements. A 1000 mg/ℓ lignin solution was allowed to settle for 2.5 hrs at pH 2, 3, 4 and 5 and the residual lignin was measured by absorbance as seen in Figure 34. The results show that there is about 50 mg/ℓ of soluble lignin left at pH 2 compared to 9 mg/ℓ after filtering with an 1μ filter without settling. The concentration of soluble lignin was similar although slightly lower than those found by Pilgugina et al. (1964). Pilgugina measured free acids formed from hydrolysis of lignin and they don't necessarily show absorbance at the wavelength used.

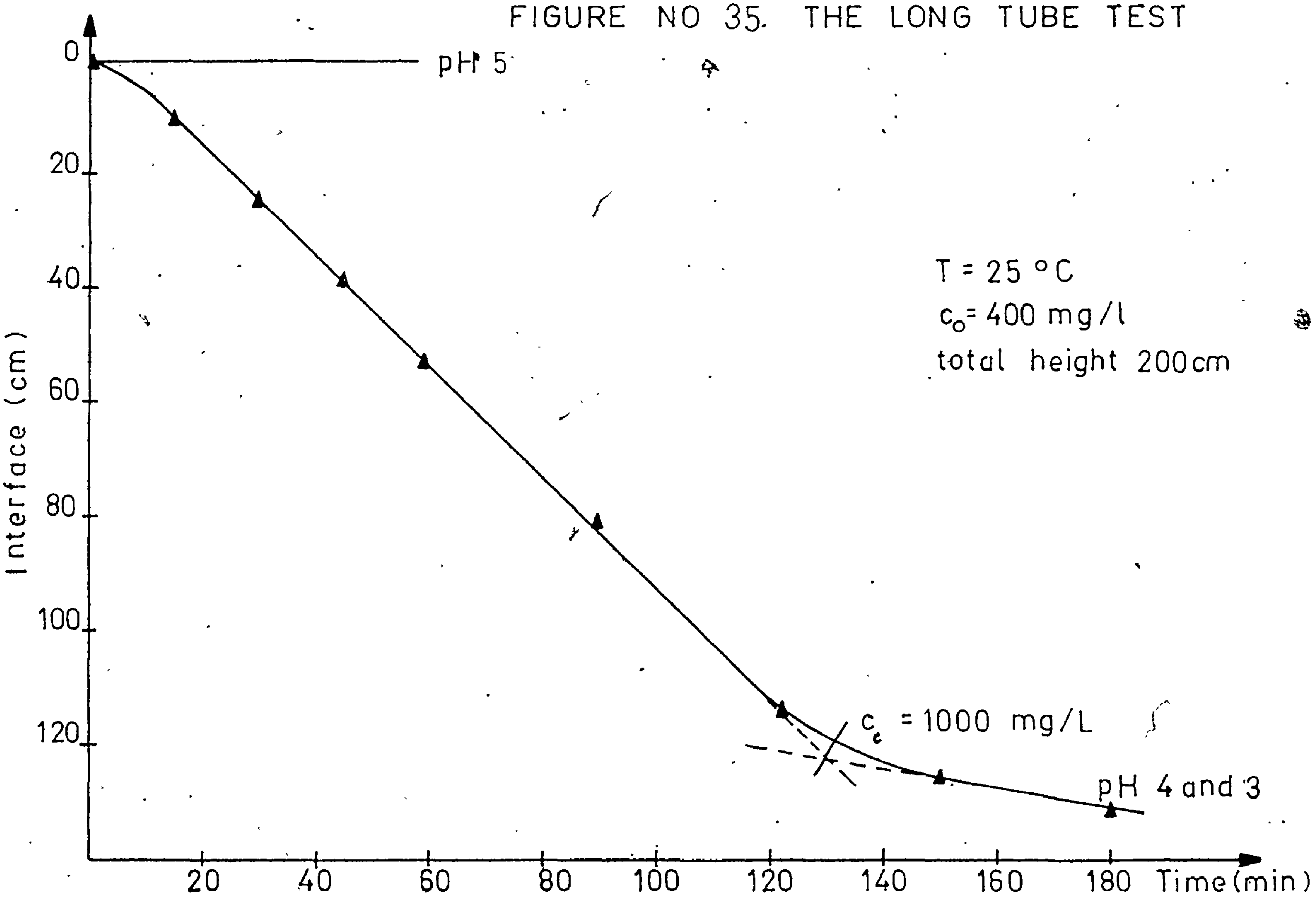
When indulin was dissolved at pH 12 and then acidified to pH 2, 3, 4 and 5 and allowed to settle in small 100 mℓ graduate cylinders, no settling could be seen in pH 5 solution in 1.5 hours. The pH 4 solution had formed an interface but hadn't started to settle yet. At pH 3 and 2 lignin settled at the same velocity.

FIGURE NO 34. CONCENTRATIONS AFTER SETTLING AND FILTERING



A similar series of tests were made in 14 cm diameter cylinders and they confirmed the above results (Figure 35). At pH above 4 lignin didn't settle at all in three hours. At pH less than 4 lignin flocs settled at the same velocity forming a zone settling interface. This settled about 50 cm during the first hour corresponding to an overflow rate of 320 gal/ft^{2}day.

FIGURE NO 35. THE LONG TUBE TEST



Appendix 8

The Zeta-Potential

The stability of colloids depends on adsorption of ions or polymers from the surrounding liquid. There are three methods by which colloids can be stabilized:

i) By adsorbing on the colloid a negatively charged ion or polyelectrolyte

ii) By adsorbing on the colloid a hydrophilic colloid

iii) By adsorbing on the colloid a non-ionic polymer.

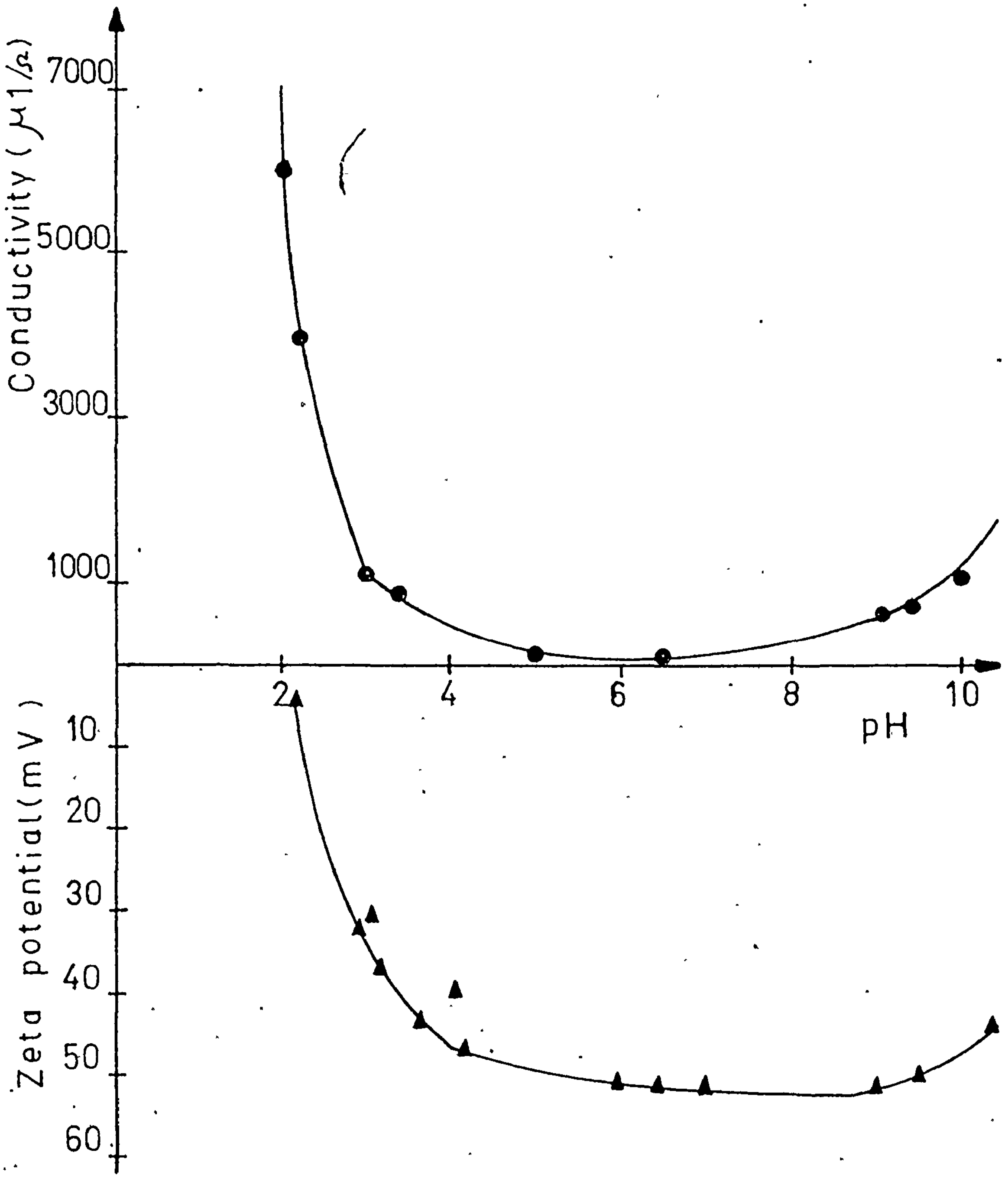
The potential difference between a colloid and the surrounding liquid consists of two parts; the difference between the surface of the colloid and the layer nearest to it and the difference between this and the bulk of the liquid. The latter is called the zeta-potential or the electrokinetic potential. The following Table (Table 14) given by Riddick (1968) lists the stability of electronegative colloids.

Five to ten lignin colloids were timed at different pH's in the zeta-potential gel. Zeta-potentials were read each time from a set of curves in the Zeta-Meter-Manual and corrected to 25°C. The results are shown in Figure 36.

Table 14 Stability Characteristics of Colloids

	Average ZP in mV
maximum agglomeration and precipitation	+ 3 to 0
range of strong agglomeration and precipitation	+ 5 to - 5
threshold of agglomeration	- 10 to - 15
threshold to delicate dispersion	- 16 to - 30
moderate stability	- 31 to - 40
fairly good stability	- 41 to - 60
very good stability	- 61 to - 80
extremely good stability	- 81 to -100

FIGURE NO 36. THE ZETA POTENTIAL OF LIGNIN COLLOIDS AND THE CONDUCTIVITY AS FUNCTION OF THE pH



Lignin colloids are stable at pH more than 4. The Zeta-potential at pH 3 is still as high as -30 mV which explains the difficulties in the precipitation of lignin from its solutions. Between pH 2 and 3 the zeta-potential drops sharply from -30 to 0 mV, making lignin particles easier to precipitate.

Lignin could be precipitated on a carbon anode without lowering the pH due to the zeta potential, as was found in one experiment. However, this topic was not pursued further.

Appendix 9

The Pulp Mill Samples

Some of the characteristics of the sulfite mill effluent samples, spent sulfite liquor and bleach plant effluent are listed in table 15. Precipitation of lignin was tried from both samples by using sodium hydroxide. No precipitate formed at pH up to 11. By using calcium hydroxide at pH 11 only a small amount of solids precipitated from both samples and the colour remained unchanged.

Some characteristics of the combined kraft mill effluent sample are shown in table 16. The sample was over one month old on arrival from Smooth Rock, and therefore, maybe not very representative. Lignin did not precipitate from the sample by lowering the pH to 3, but the colour changed from 0.28 to 0.25 at 465 mm.

Table 15 Sulfite Mill Samples

	Spent Sulfite Liquor	Bleach plant effluent
conductivity [μ'/Ω]	4000	1200
pH	2.5	3.6
zeta-potential [mV]	-25	-37
suspended solids [mg/ℓ]	122	120
TC [mg/ℓ]	3450	800
TOC [mg/ℓ]	3450	800
IC [mg/ℓ]	2	2
total solids [g/ℓ]	9.1	1.7
inorganic solids [mg/ℓ]	250	470
volatile solids [g/ℓ]	8.85	1.23
colour	brown	brown

Table 16 Some Characterization of the Kraft Mill Sample

pH	6.9
suspended solids	60 mg/ℓ
TC	187 mg/ℓ
TOC	143 mg/ℓ
IC	44 mg/ℓ
Total solids	900 mg/ℓ
inorganic solids	670 mg/ℓ
volatile solids	230 mg/ℓ
BOD	180 mg/ℓ
Colour	yellow-brown

Appendix 10

The Rejection of Selected Species by a Lignin Membrane

The rejection of species other than lignin by a lignin membrane was examined at conditions, pH 9, 30°C, 150 psi, 1000 mg/ℓ. The results are shown in Table 17.

The greater rejection of aluminum over copper and manganese is possible caused by the presense of large hydroxyl molecules $Al(OH_4)^-$. The high rejection of potassium implies that potassium reacts with lignin. Ions of higher charge are rejected better than those with a low charge, approximately proportionally to the cube of the charge. The LAS used had a molecular weight of 325.5. It was rejected far better than phenol with a molecular weight of 94 as could be expected considering the different size of the molecules.

Table 17 The Rejection of Selected Species by a Lignin Membrane

Ion	Feed Concentration mg/ℓ	Product Concentration mg/ℓ	R %
Al^{3+}	30	10	66
Cr^{2+}	70	25	64
Mn^{2+}	10	4	60
K^{+}	89	6.2	93
PO_4^{3-}	37.5	9	76
SO_4^{2-}	89	47	54
F^{-}	32	30	6
phenol	200	172	12
dodecyl benzene sulfonic acid	200	18	90

Appendix 11

Table of Runs

No.	T °C	P psi	pH	R %	F_W gal/ft^{2}day	Remarks
1	30	150	11			Backwash
2	"	"	3			"
3	"	"	7			"
4	"	"	5			"
5	30	95	9	99	5.6	diff. p
6	"	150	"	99	5.6	"
7	"	200	"	99	5.6	"
8	"	300	"	99.2	6.1	"
9	"	50	"	98.8	3.7	"
10	40	150	7	99.3	6.7	diff. T
11	55	"	"	99	11.5	"
12	70	"	"	98.8	16.3	"
13	25	"	"	99.1	7.3	"
14	30	"	"	99	9.8	"
15	"	40	"	99	4.1	diff. p
16	"	250	7.9	99.3	5.3	"
17	"	250	7.5	99.1	7	"
18	"	100	7.4	98	4.8	"
19	"	150	7	98.6	5.3	"
20	"	200	"	99.2	6.4	"
21	"	25	"	98.2	1.8	"
22	"	250	7.9	99.2	7.5	"
23	"	150	3	97.5	37	diff. pH
24	"	"	9	98.5	5.6	"
25	"	"	5	98.5	21	"
26	"	"	3	98	16	"
27	"	"	"	98	13	"
28	"	"	"	96.5	8	"
29	"	"	"	–	–	"
30	"	"	5	98.5	7.5	"
31	"	"	9	98	5.7	CH_2O
32	"	150	3	–		low pH
33	"	100	2	98.5	42	CH_2O
34	"	100	2	97.5	28	low pH
35	"	150	11	95	7.1	diff. pH
36	"	150	9	–	5.7	Standard
37			3	98	33	decanted
38			9	97.5	8.4	E-22

No.	T °C	p psi	pH	R %	F_W gal/ft^{2}day	Remarks
39		100	3	90	13.5	E-22
40		150	9	99	6	E-22
41			9	92	11	new tube
42				55	7	cooking liq.
43				70	3.7	E-22
44					3.1	Bleach plant
45				70-1	-	"
46		150	9	98.5	6.7	standard run
47			9	98.5	15.5	acid pretreat
48			9	98.5	12.5	"
49			9	98	7.1	diff. v
50			9	98.3	7.6	diff. c
51		40	9	98.3	6.4	low p
52			9	99	6.0	standard run
53		60	9	98	6.1	low p
54		35	9	98	5.1	"
55		150	3.6	99	7.7	org. acid
56			2.5	98	11.1	Whalen comp.
57			9	95	22	Carborundum
58			9	97	9.4	"
59			9	99	3.1	High C_{15}
60			9	-	-	acid pretreat
61			9	-	-	"
62			9	-	-	R of other comp.
63			9	-	-	"
64			9	-	-	"
65			9	-	-	"
66			9	-	-	"
67			6.9	98	9	Kraft effluent
68			3	92	6	"
69			1.9		9	"

Temperature 30°C, pressure 150 psi unless otherwise indicated, feed concentration usually 1000 mg/ℓ.

APPENDIX 12

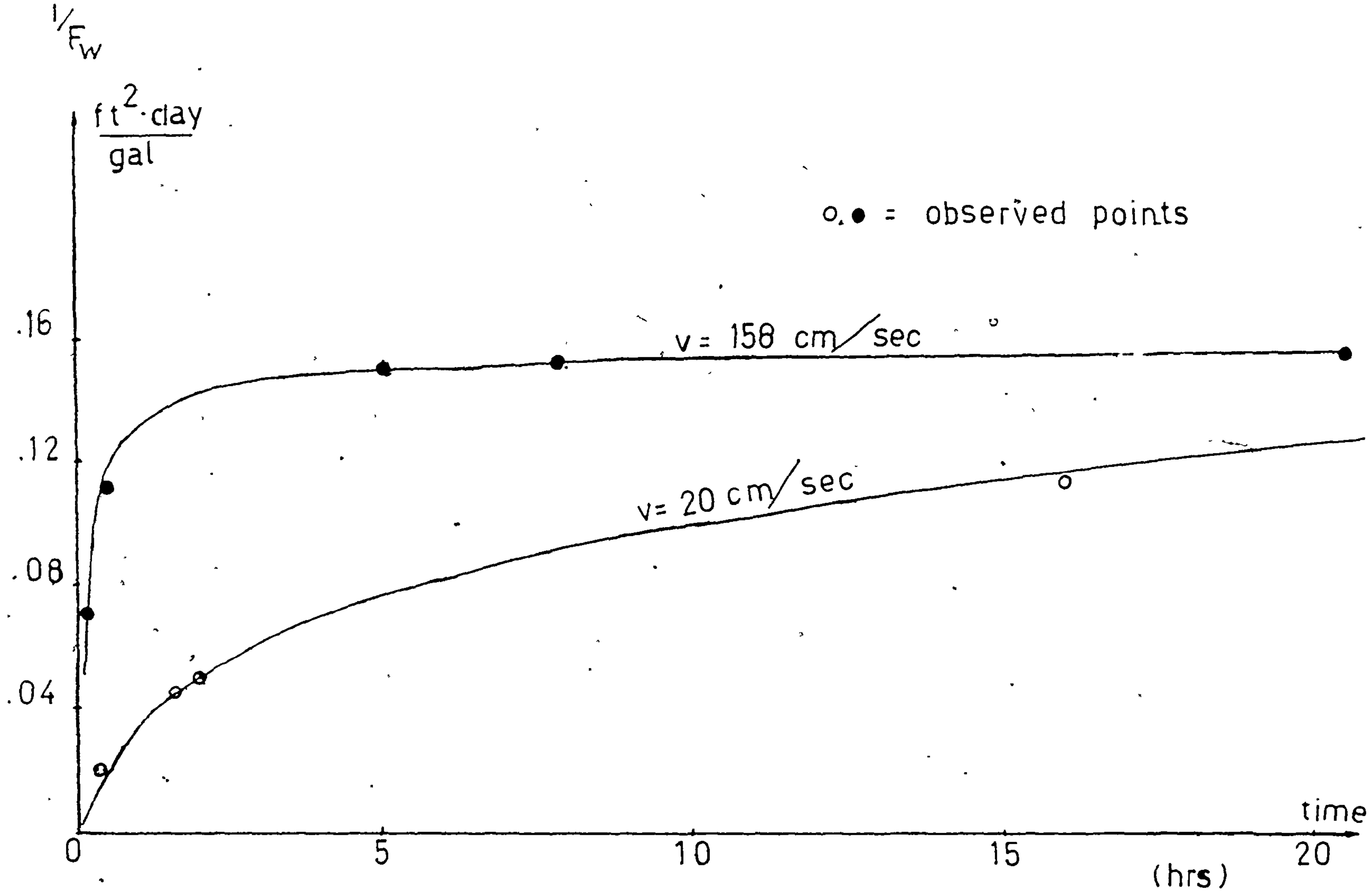
APPLIED THEORY

Equation 17 can be written in the form,

$$L = \frac{-k_2 t + \sqrt{k_2^2 t^2 + 8tk_1}}{2} \qquad (56)$$

Constants k_1 and k_2 can be calculated from experimental results, when the membrane thickness is replaced by the inverse values of the product flux at two different points. The curves in Figure 37 are calculated using values $k_1 = 0.058$ $(\mathrm{ft}^2\text{-day-hr/gal})^2$, $k_2 = 0.736$ ft^2-day-hr/gal at a cross-flow velocity 158 cm/sec and, $k_1 = 0.00071$ $(\mathrm{ft}^2\text{-day-hr/gal})^2$ and $k_2 = 0.0042$ ft^2-day-hr/gal at a cross-flow velocity 20 cm/sec. The constants are calculated at product flux values after 5 and 10 hours of operation in both cases. The difference between the calculated and observed values at other operating times is smaller than the experimental error.

FIGURE NO 37 EQUATION 56 AND OBSERVED POINTS



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NOMENCLATURE

A = critical pressure

B = solute transport coefficient

C = concentration

D = diffusion coefficient

F = flux

L = thickness of membrane

N = number of molecules

N_{Sc} = Schmidt number

N_{Re} = Reynolds number

P = pressure

Q = indicator of the state of formation of the membrane

S = surface area of membrane

R = gas constant, rejection

R_m = membrane resistance

T = temperature

V = volume

W_p = solvent permeation coefficient

Indexes:

f = final

n = solvent

s = solute

1s = solute on high pressure side
2s = solute on low pressure side
f = final
ms = solute in the membrane
3s = solute on the membrane
$b_{1,2}$ = integration constant
d = diameter
e = Neper's number
a = pore radius
n = number of moles, constant
m = constant mass
r = radius of a colloid
t = time
u = velocity of solvent through the membrane
v = cross-flow velocity
$k_{1,2,3}$ = constant
x = distance
p = constant
y'' = second derivative
y' = first derivative
y = function of t
π = osmotic pressure
ϕ = osmotic pressure coefficient
δ_m = membrane thickness (effective)
τ = tortuosity

μ = viscosity

ζ_{ℓ} = density of solvent

ν = kinematic viscosity