TREATMENT OF PHENOLIC WASTES

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Abstract

The treatment of phenolic compounds from coal gasification plants using ultrafiltration and hyperfiltration is presented. Dynamically formed hydrous zirconium (IV) oxide membranes on several types of supports were the focus of the investigation. The pH variations of 6.5 to 11, pressure variations of 250 to 1000 psig (1724 to 6895 kPa) and concentration variations of 1 to 400 mg/l were examined. Phenol reductions greater than 95 percent were obtained with several membranes, and flux rates were greater than 100 gpd/sq ft (4.08 cu m/day/sq m).

INTRODUCTION

The energy problems which have developed recently in the United States have made it desirable to examine new methods of utilizing the lignite coal that is present in abundant quantities in western North and South Dakota, Montana and Wyoming. One of the solutions to this problem is seen in the conversion of coal to a clean fuel by the use of a coal gasification process. By gasifying the coal, a synthetic natural gas can be produced which is basically free of the sulfur present in the coal and is cleaner to use. A primary concern is that the treatment and/or conversion process that generates the clean fuel does not itself become a major pollution source. While the potential pollutants can be expressed in any or all of the three possible states of air emissions, solid wastes, and liquid effluents, all of them ultimately contribute to the wastewater effluents of the plant and its site. If coal gasification plants are to be constructed, the pollutants which are generated during their operation must be dealt with if their environmental effects are to be minimized.

Various types of processes have been developed to produce synthetic natural gas. Since the Lurgi gasification process is currently being planned for several sites in western North Dakota, the wastewater effluent concentrations produced by the Lurgi process was used as a basis of this study. However, the results should be applicable to many of the other processes also.

The purpose of this study was to determine the feasibility of utilizing hyperfiltration (reverse osmosis) or ultrafiltration to reduce the phenolic concentrations in the wastewater effluents for a coal gasification plant. Dynamically formed hydrous zirconium (IV) oxide membranes were the focus of the investigation. The applicability of Selas ceramic, Millipore and Acropor wrapped stainless steel, and carbon membrane supports were studied in relationship to the effects of pH variation, pressure variation, and phenolic compound concentrations.

COAL GASIFICATION PROCESS

The Lurgi coal gasification plants planned for construction in the United States are being designed to produce 250 million standard cubic feet (7.0 M cu m/day) of medium to high Btu synthetic natural gas that will yield about 970 Btu/std cu ft (36.14 MJ/cu m). The average consumption of coal in these plants is about 1000 to 1500 tons per hour (252 to 378 kg/s), and the annual water usage is about 17,500 acre-ft (21.58 M cu m).[1]

The coal is gasified with oxygen and superheated steam in the Lurgi pressure gasification process. The gasifier vessel consists of zones in which various gasification reactions take place. The combustion of the coal produces methane in a three-stage reaction: preheating and carbonization, gasification or devolitilization, and partial combustion. The temperature ranges from about 1150 to 1400° F (621 to 760° C) and the pressure ranges from about 350 to 400 psig (2413 to 2758 kPa).[2]

Most of the potentially hazardous materials are produced in the gasifiers, but there are no direct liquid or gaseous emissions of these materials from the units. Coal ash is the only direct waste discharge from the gasifiers. The ash is generally water quenched to cool and to prevent the production of airborne dust. The quenching water is considered a minor wastewater stream. A simplified flow diagram for wastewater treatment in the coal gasification process is shown in Figure 1.

The crude gas leaving the gasifier has a temperature of 700° to 1100° F (371° to 593° C), depending upon the type of coal used, and is under a pressure of about 400 psig (2758 kPa). It contains the carbonization products such as tar, oil, naphtha, phenols, ammonia, and traces of coal ash and dust. The crude gas is quenched by direct contact with a circulating gas liquor in a scrubber-decanter tower. The gas liquor effluent is sent to the gas liquor separator for the removal of tars and oils.

Following the removal of some of the tars and oils from the gas liquor in the Tar-Gas Liquor Separation unit, the water effluents are further treated in the Phenosolvan unit for the removal of phenolic compounds by passing through a multistage countercurrent extractor using isopropyl ether as the organic solvent. The waste effluent of the phenol recovery unit is subjected to ammonia recovery by fractionation and condensation to produce anhydrous ammonia.

Following this initial processing, the wastewater is to be subjected to further purification systems, such as ultrafiltration and hyperfiltration. Ideally, a wastewater cleaning system should be designed so that the water can be reclaimed for use as either boiler feed water or cooling tower makeup water. The removed and concentrated contaminants would also require a final safe disposal.

In the coal gasification operation the major sources of wastewater are the scrubber-decanter which follows immediately after the gasifier, and the condenser following the shift converter. The quantity of wastewater which will be produced is approximately as follows: 3.3 mgd (12.49 k cu m/day) will be generated in the scrubber-decanter, 1.1 mgd (4.16 k cu m/day) by the condenser following the shift converter, and 0.8 mgd (3.08 k cu m/day) by the steam stripping of the scrubber-decanter water to remove ammonia. Thus, approximately 5.3 mgd (19.68 k cu m/day) is produced which will require treatment. There are also some other relatively minor sources.[3]

WASTEWATER CHARACTERISTICS

During the gasification process, the by-products from the gasifiers are condensed along with the water. Oil and tar are separated from the aqueous phase of the gas liquor, and the latter eventually mixes with the phenol containing wastewaters from other parts of the plant. This effluent was considered "raw wastewater." Usually the raw wastewater goes through a filtration process, extraction of phenols, and the removal of ammonia. After this initial amount of treatment the effluent

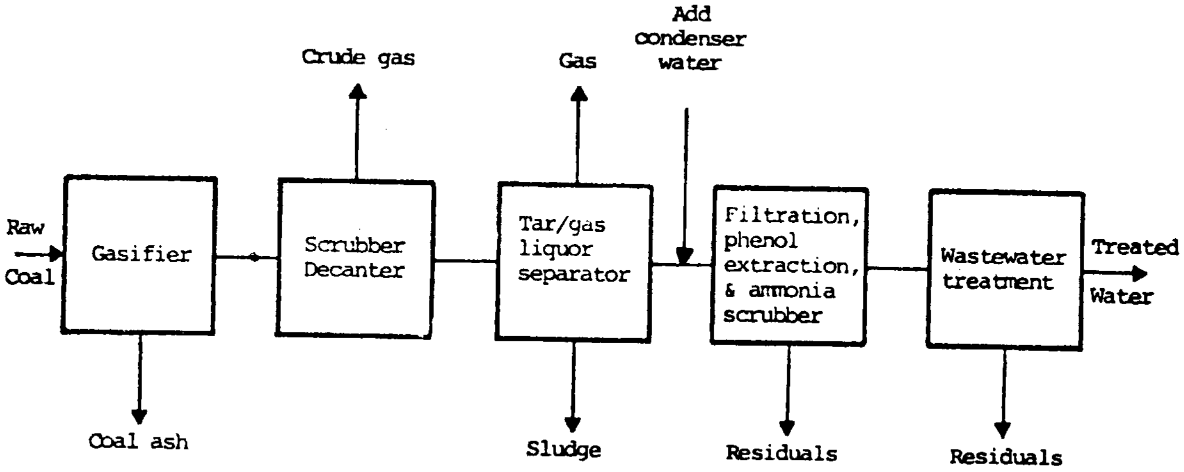

Figure 1. Flow diagram for wastewater treatment system.

"processed wastewater." When the processed wastewater had been subjected to biological treatment, it was designated as "bio-treated wastewater."

The concentration of phenolic compounds in the wastewater effluents of the Lurgi process plant of the South African Coal, Oil, and Gas Corp. Ltd., Sasolburg, South Africa (Sasol) has been reported by De W. Erasmus.[4] A typical analysis for their processed wastewater is 1- 0 mg/l for monohydric phenols (Koppeschaar method), and 170 to 240 mg/l for the total phenols. Experience at Sasol has shown that the ratio of multihydric to monohydric phenols is reasonably constant and on the order of 20 to 40:1.

Sources from the Lurgi gasification plant of St in Kollingas A. C. at Dorsten, German Federal Republic, reported 12-56 mg/l of monohydric phenols and 228-390 mg/l of total phenols. Cooke and Graham[5] also reported that in the processed wastewater from a Lurgi plant, the monohydric phenols (mostly phenol) comprise a minor part of the total phenols, while catechol and resorcinol (dihydric) account for the most of the fraction.

Barker and Hollingsworth[6] reported that catechol, resorcinol, hydroquinone, and their methylated derivatives in ammonical liquor are quite similar in composition to Lurgi processed effluent. They also indicated that trihydric species of phenol were also present in the same effluent.

Chambers et al.[7] made a study of the biochemical degradation of various phenol derivatives by bacteria adapted for the decomposition of phenol. They found that dihydric phenols may be oxidized quite easily along with monohydric phenols, while trihydric phenols were plainly resistant to decomposition by these bacteria.

Samples of the raw and processed wastewaters for the gasification of North Dakota lignite coal were obtained from Sasol by North Dakota State University. The analysis of the samples were conducted by Fleeker[8] and the biological oxidation of the processed water was performed by Bromel.[9] The rate of degradation of phenols was determined for a mixture of four Arthrobacter species and one Pseudomonas specie. From an initial total phenol concentration of 322 mg/l the bacteria reduced the concentration to 69 mg/l in a twenty-four hour period, and to 50 mg/l in five days; approximately 80 percent reduction. The monohydric phenols were reduced an equivalent amount from 69 mg/l to 8.3 mg/l. Bromel also reported that the residual recalcitrant compounds, possibly the multihydric phenols, may represent a potential problem in the effluents that will require chemical or physical treatment beyond biological treatment.

Although most of the phenols will be reduced in concentration to relatively low levels by the biological treatment methods, there will still be a large enough concentration remaining in the processed wastewater to potentially cause extensive contamination of the groundwater system. The standard recommended for phenol concentrations in potable water is 0.001 mg/l.[10] Phenols are highly toxic and increasingly so when chlorine is added to the water as most water treatment facilities do.[11] Concentrations of phenol on the order of 10 to 100 μg/l can cause undesirable tastes and odors. Trace amounts approaching 1 μg/l can impart an objectionable taste to a water following marginal chlorination.[12]

HYPERFILTRATION AND ULTRAFILTRATION

Osmosis and Reverse Osmosis

Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across an ideal semipermeable membrane. The membrane acts as a barrier to the flow of molecular or ionic species and permits a high permeability for the solvent, water, and a low permeability for the other species. If the pressure is increased above the osmotic pressure on the concentrated solution side, the solvent flow is reversed. Pure solvent will then pass from the solution into the solvent. This phenomenon is referred to as reverse osmosis.

Hyperfiltration and Ultrafiltration

Filtration separation can be classified into four families: (1) screening - removal of large particles; (2) filtration - removal of smaller particles; (3) ultrafiltration - removal of colloidal particles; and (4) hyperfiltration - removal of low-molecular-weight dissolved materials. The boundaries between the various classes are not precisely defined.

Much of the ultrafiltration mechanism can be interpreted in terms of selective sieving of particles through a matrix of pores of suitable dimensions. The removal of low molecular weight molecules cannot be reduced to geometric terms because there is no significant difference in the size of water molecules and the size of many inorganic ions. Therefore, ultrafiltration is unsuitable in this size range. The hyperfiltration membrane thus affects the thermodynamic and transport properties of solutes and solvents by forces, i.e., Van der Waals or Coulombic. These do not depend primarily on the difference in size of the ions and molecules to be separated. Hyperfiltration is commonly referred to as reverse osmosis, since there are substantial differences in osmotic pressure between feeds and filtrates which must be exceeded when appreciable differences of weight concentration of low-molecular-weight solutes exists.

Ultrafiltration and hyperfiltration differ primarily because ultrafiltration is not impeded by osmotic pressure and is effective at low pressure differentials of 5 to 100 psig (34.5 to 689 kPa). The osmotic pressure plays a larger role as the molecular size decreases. The term "hyperfiltration" is also applicable to the separation of solutes with different permeation rates when the solution is forced through a membrane under pressure. The term is descriptive even if the solute to be removed is a trace concentration and does not contribute significantly to the osmotic pressure.[13]

Membranes

Hyperfiltration membranes can be classified into two basic categories: neutral and ion-exchange. Both approaches to membrane development were recognized at about the same time. But because of the favorable properties of a specific neutral type (the Loeb-Sourirajan cellulose acetate membrane[13]); the cellulose acetate membranes have received most of the attention. Both flux and rejection of cellulose acetate membranes were high compared to those observed with available ion-exchange membranes which were designed for low water permeability. Since flux is inversely proportional to thickness, a much thinner ion-exchange layer was needed to realize the potential flux advantages that a more loosely structured membrane filtering by ion exclusion could provide.

Several membrane configurations have been proposed and tested. Many configurations involve preformed or precast membranes which require equipment disassembly for installation and removal. The type of membrane of concern in this paper is dynamically formed and does not require disassembly for formation or removal. Dynamically formed membranes are formed at the interface of a solution and a porous body from materials added to the solution as it circulates under pressure past the porous body.[13] Only limited success of dynamically formed membranes from neutral additives has been reported.[15]

The dynamic formation technique has made possible the development of thin dynamically formed ion-exchange membranes. Thus, the high permeability of 1400 gpd/sq ft (57.12 cu m/day/sq m) with a rejection of about 50 percent that was expected of thin ion-exchange membranes can be attained, particularly if they are formed with fast circulation of feed past the porous supports or with high turbulence.[13,16,17]

Several types of polyelectrolyte additives were found to form this type of ion-exchange membrane, e.g., synthetic organic polyelectrolytes,[18,19] hydrous oxides,[20,21] and natural polyelectrolytes such as humic acid.[19] Membrane formation is not limited to soluble polyelectrolytes or colloidal dispersions. It was found that particulates such as clays could form membranes as well.[19,22]

In many cases salt removal is unnecessary, or even undesirable; consequently, a membrane which passes salt while concentrating other matter is preferred. Several dynamically formed ultrafiltration membranes using hydrous oxide and polyvinyl priolidone have been tested successfully.[23]

Many materials can be used as porous supports: filter sheets such as Millipore and Acrepor, porous metal, carbon tubes[19]; ceramic tubes[24]; and woven fabric.[25] For most types of ion-exchange membrane additives, the favorable pore size range lies between 0.1 and 1.0 microns.[13]

Some attractive features of many dynamically formed membranes include the ability to operate at elevated temperatures, allowing treatment of waste streams at process temperatures and recycle of the hot water. A negative aspect is a deterioration of performance from polyvalent counter ions in feed.[13] Membrane regeneration can be relatively simple and inexpensive, since the deposit of active membrane can be removed by flushing and reformed by pumping through a dilute suspension of active material. Also, the higher fluxes that can frequently be obtained allow the use of tubular geometries without undue sacrifice in production rate per unit volume.[26]

EXPERIMENTAL

Procedure

The test equipment was so constructed that a pressurized solution, containing selected additives during membrane formation and consisting of the effluent to be studied during membrane evaluation, could be circulated past porous supports under controlled conditions of temperature, pressure, pH, and circulation velocity.

The feed solutions, a synthetic representation of the coal gasification wastewater, were prepared with reagent-grade phenol, resorcinol, o-cresol, and catechol. Tests included feed concentration variations of 1 to 100 mg/l for solutions prepared with all four phenolic compounds. Tests conducted solely with phenol ranged in feed concentration from 1 to 400 mg/l. Reagent grade pentachlorophenol was also used as a feed solution at 10 mg/l.

The range of pH used in testing varied from test to test between 5 and 12, and similarly the pressure ranged from 200 to 1000 psig (1379 to 6895 kPa). The temperature variation examined was 25° to 55° C for the ultrafiltration tests, and the hyperfiltration tests were conducted at a constant 30° C. Ultrafiltration tests were maintained at a constant pressure of 200 psig (1379 kPa). A constant flow rate past the membranes of 15 ft/sec (4.57 m/s) was maintained for all tests. Concentrated nitric acid and one normal sodium hydroxide were used to adjust the pH of the feed solution.

In each experimental run, the observed rejection was determined on the basis of salt conductivity and solute concentrations, and the results were expressed as a percent rejection. The flux or permeation rate through the membranes was determined and expressed as gpd/sq ft of membrane surface. While most of the test runs were conducted at specific operating conditions and were for a limited duration, several apparent optimum operating conditions were chosen for some extended-run experiments designed to measure the deterioration of the membrane with operating time.

Equipment

All of the experimental work conducted on this project was done at the Oak Ridge National Laboratory in Oak Ridge, Tennessee. The hyperfiltration loop at that facility is shown photographically and schematically in Figure 2. Feed solution was drawn from feed tank G by the Milroyal type C triplex pump C (5 gpm (0.32 l/s) at 1500 psig (10.34 MPa) capacity) and forced under pressure into the circulation pump B, a 100-A Westinghouse centrifugal pump which was rated at 100 gpm (6.31 l/s) at 100 psig (689 kPa) head. This pump circulated the feed solution through the loop and past the membrane supports, which were placed in test sections A and A' (only one test section is shown in the photograph). The test sections were designed to direct the feed solution through the annular region between a tubular porous support, upon which the membrane was formed, and the wall of a stainless steel cylindrical pressure jacket (Figure 3). Flow velocities past the membrane surfaces, typically 10 to 35 ft/sec (3.05 to 10.67 m/s), were monitored by meters at D, the temperature of the feed was controlled by the tube-in-tube heat exchanger E, and the pressure was regulated by a pneumatically controlled valve in the letdown line which returned the feed to the tank at atmospheric pressure. The product which permeated the membranes was monitored as to flux and composition, and was returned to the feed container to maintain constant feed composition.

All of the materials used in the loop were corrosion-resistant to minimize interference of corrosion products with the formation of the

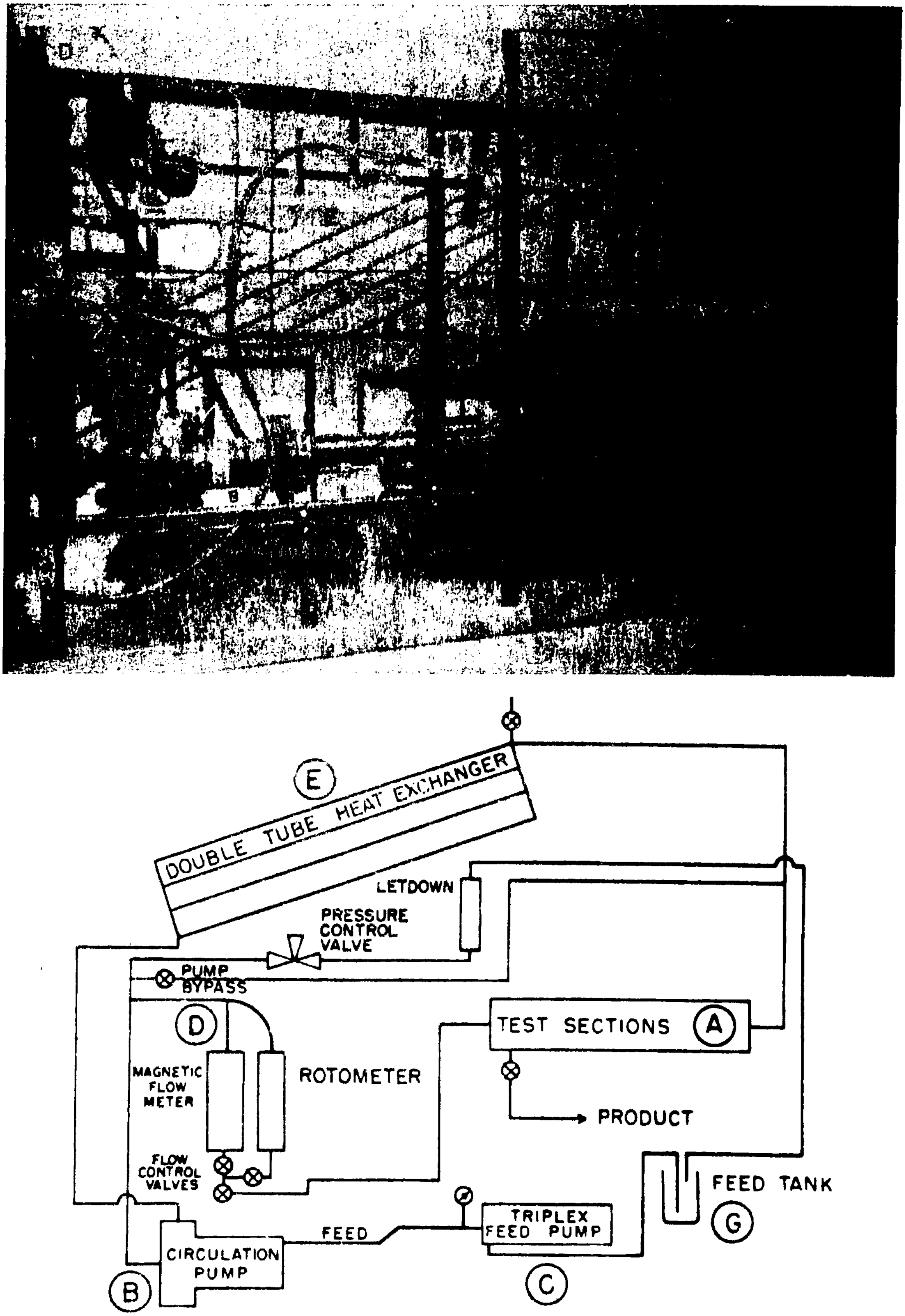

Figure 2. Hyperfiltration Loop.

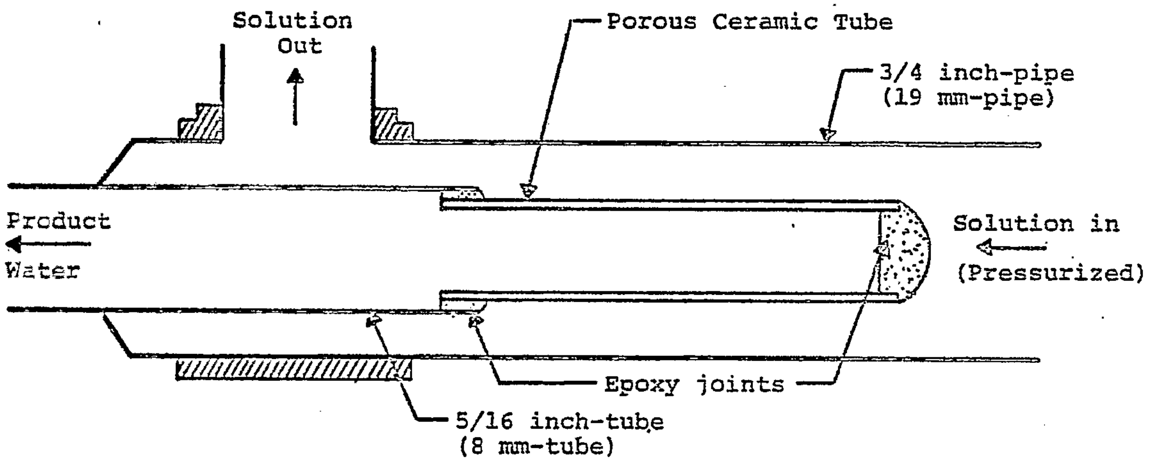

Figure 3. Mounting of typical test section with ceramic tube support.

membranes. The loop was designed to eliminate stagnant side volumes in which material might collect and contaminate subsequent experiments. The ultrafiltration loop consisted of a configuration similar to the hyperfiltration loop.

Porous Supports

Several different porous support materials were used. Acropor AN sheets, a copolymer of polyvinyl chloride and polyacrylonitrile on a nylon substrate made by Gelman Instrument Company, Ann Arbor, Michigan; and membrane filter sheets made from mixed esters of cellulose by Millipore Filter Company, Bedford, Massachusetts, were wrapped around 5/8 inch (15.9 mm) porous stainless steel tubes (pore size - 5 μm). Porous carbon tubes, Union Carbide Corporation's 563-6C (6.0 mm I.D., 10.25 mm O.D., undetermined pore size) and a porous ceramic tube, the Selas Ceramic filter element made by Selas Flotronics Corporation, Spring House, Pennsylvania, were also used.

Membrane Formation

The membranes were formed in carefully cleaned equipment to eliminate the possible interference of contaminants. Between each test run, the loop was cleaned by using a one molar sodium hydroxide wash, followed by a one molar nitric acid wash, and then distilled water.

The porous supports were inserted into the test sections. A solution of 0.04 molar sodium nitrate and 0.0001 molar zirconium oxide nitrate ($ZrO(NO_3)_2$, adjusted to a pH of 4, was circulated through the loop. As the hydrous oxide was deposited on the supports, the pressure increased. Once full pressure (900 psig (6205 kPa) to 1000 psig (6894 kPa)) was achieved, the salt rejection was monitored until it reached a value greater than 30 percent, which usually took an hour or more. Then a solution containing 50 mg/l of polyacrylic acid (PAA, Acrysol A-3 by Rohm and Haas) was added to the loop, and the pH was adjusted to 2. This solution was circulated past the membrane for about 30 minutes. After this time, the pH was raised to about 3, maintained there for another 30 minutes, and again raised a unit or so. This stepwise increase in pH was repeated until the solution was near neutral. At that time, the formation of the membrane was considered complete.

Two variations of the formation procedure included omitting the polyacrylic acid layer and substituting a silicate layer for the polyacrylic acid by adding 50 mg/l of sodium metasilicate (Na_2SiO_3).

Analytical Procedures

Routine monitoring of salt (observed) rejection was by conductivity with a conductance bridge and a cell with a precalibrated cell constant. Supplemental chloride analysis with a Buchler-Corlove chloridometer was performed in which the chloride ion concentration was determined by coulometric-amperometric titration with silver ion. This was done to check the mechanical integrity of the membrane for the absence of defects.

Phenol and phenolic compound combination concentrations were monitored by two methods. For test runs in which the feed concentration was greater than 10 mg/l phenol, the phenol concentration was determined by carbon analysis with a Beckman Model 915 Total Organic Carbon Analyzer. In this apparatus, the solution sample was injected into a high temperature (950° C) catalytic combustion chamber where the total carbon in the sample is oxidized in pure oxygen carbon dioxide which is analyzed by a Beckman Model IR-215A nondispersive infrared analyzer. Inorganic carbon was determined in a similar manner by injecting a sample into a 150° C combustion chamber and analyzing the carbon dioxide produced. The total organic carbon (TOC) was obtained from the difference between the total carbon and the inorganic carbon. Most of the feed solutions and many product solutions contained insignificant amounts of inorganic carbon. The analysis of total carbon was therefore essentially total organic carbon.

For a test run or a series of test runs in which the feed concentration of phenol was less than 10 mg/l, the Direct Photometric Method was used.[12] The principle of the method involved the reaction of phenol with 4-amino antripyrine at a pH of 10.0 ± 0.2 in the presence of potassium ferricyanide. The absorption of the prepared samples was measured on a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 510 nm. A standard calibration curve for phenol was prepared.

The color of the product and feed streams was determined with a Bausch and Lomb Spectronic 20 spectrophotometer at a wavelength of 465 nm and compared against platinum-cobalt standards.[12]

Pentachlorophenol concentrations were determined with a Cary Recording Spectrophotometer, Model 11 MS. The visible absorption spectra were scanned upward from 3000 angstroms to determine the exact wavelength for maximum absorption. This was found to be 3200 angstroms. All spectral measurements were made in a 10-cm silica glass cell. A calibration curve was prepared.

EXPERIMENTAL RESULTS

Hyperfiltration

The first hyperfiltration experiment utilized the zirconium oxide-polyacrylic acid (Zr(IV)-PAA) membrane with a feed solution composed of 100 mg/l each of phenol, catechol, resorcinol, and o-cresol. Six membrane support materials were tested. Three of these support materials, 6C carbon tube, 0.27-μ Selas ceramic tube, and 0.47-μ Acropor sheet on stainless steel tube, were used for the data presented in Figure 4. The tests were conducted at 25° C.

The results in the first three columns of Figure 4 indicate that the type of membrane support material has little effect on the performance of the dynamic membrane. The data are presented to show the effects of both pressure and pH on the operation of the membrane. The production of product water or flux rate is significantly increased by the increase of pressure, but the variation of pH has little effect on the flux rate.

The solute rejection rate increases from about 45 percent at a pH of 6.5 to about 80 percent at a pH of 10. It was expected that a pH of about 9.5 to 10 would produce the most significant reduction in the phenolic compounds because the phenolic compounds are sufficiently ionized at this pH to react favorably with the ion exchange properties of the membrane.

The salt rejection produced the opposite results by the rejection rate from about 92 percent to 85 percent as the pH is raised from pH 6.5 to 10. The maximum rejection of salt is best achieved near neutral pH. This characteristic is quite beneficial where the desire is to reduce the phenolic concentration without trying to remove all of the salt in the wastewaters.

The fourth column of Figure 4 presents data on the effect of different concentrations of the solute on the performance of the membrane. The Acropor membrane support produces a better flux rate than the other support materials, however, the variations in the con-

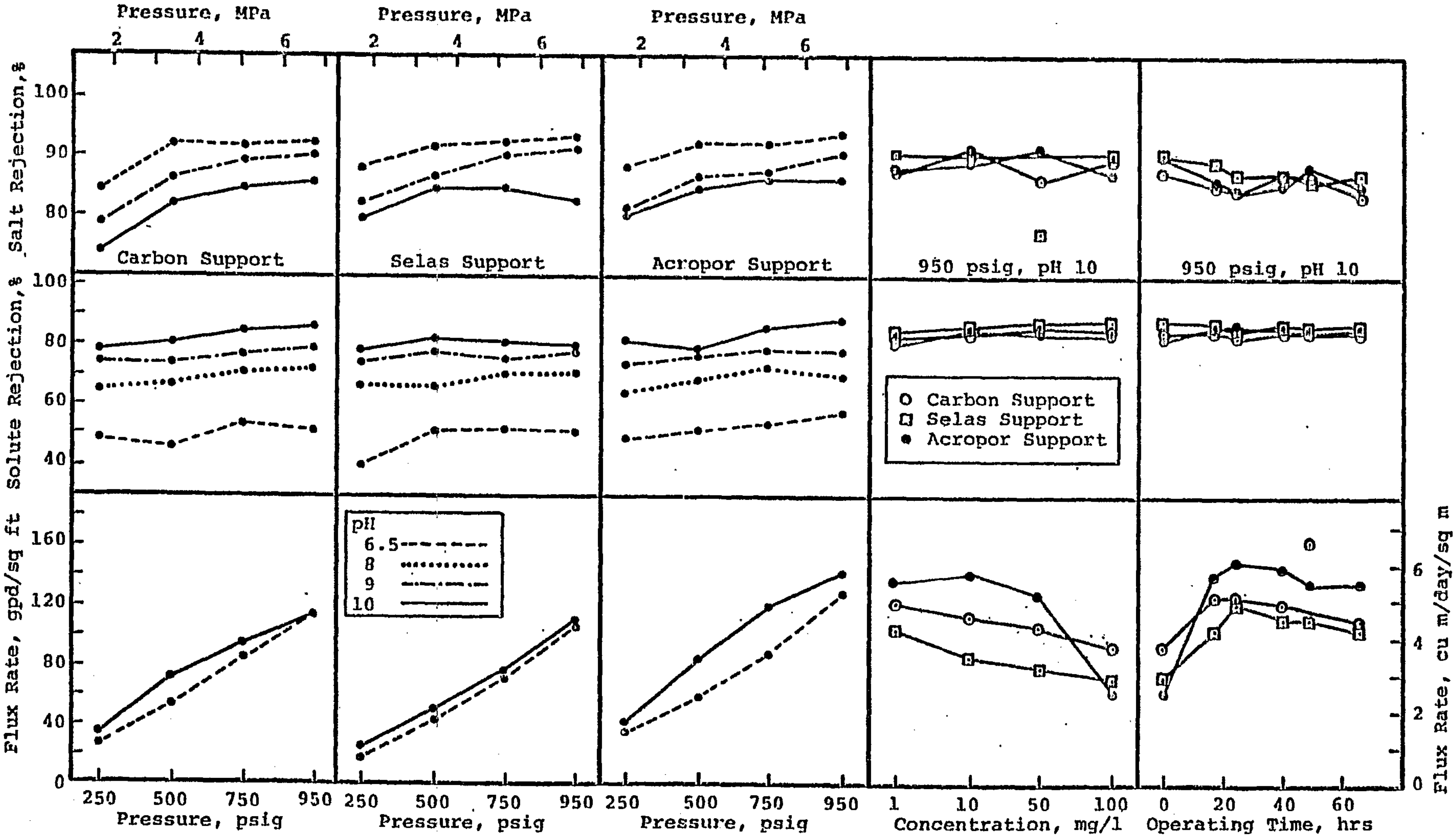

Figure 4. Hyperfiltration of Phenolic compounds (100 mg/l).

centration have little effect on the flux rate. The maximum flux rate is about 140 gpd/sq ft (5.7 cu m/day/sq m). The solute rejection and salt rejections remained constant at about 90 percent.

The final column of Figure 4 provides information about the long term effects of treatment on the operation of the membranes. The flux rate increased initially and then stabilized at about 150 gpd/sq ft (6.1 cu m/day/sq m). The solute rejection rates remained constant over the operating interval at about 90 percent. Salt rejection dropped slightly from 90 to 85 percent.

The next series of tests examined the suitability of zirconium oxide-polyacrylic acid (Zr(IV)-PAA), zirconium oxide-sodium silicate (Zr(IV)-Si), and zirconium (Zr(IV)) alone as membranes for the hyperfiltration of 10 mg/l of pentachlorophenol feed solution. The results are presented in Figure 5.

The first column of Figure 5 indicates that pH does have a significant effect on the flux rate of pentachlorophenol. While the zirconium membrane produced the highest flux rates, the solute rejection and salt rejection was far below the other membranes. The rejection of pentachlorophenol approaches 100 percent.

The second column of Figure 5 shows that the flux rate is virtually unchanged as pH increases, however, the solute rejection rate does increase with pH. The third column of Figure 5 indicates that flux rate rises with pressure. While the zirconium-silicate membrane produces the highest flux rate, the zirconium-polyacrylic acid provides the highest solute rejection at about 80 percent. The final column of Figure 5 again indicates that the membranes are stable for extended periods of time.

Ultrafiltration

Similar experimental parameters were examined under ultrafiltration. With a feed solution of 100 mg/l each of phenol, resorcinol, o-cresol, and catechol, tests were performed on three types of membranes on Selas ceramic supports: zirconium oxide (Zr(IV)), zirconium oxide-sodium silicate (Zr(IV)-Si), and silicate (Si). Figure 6 depicts a pH scan with the expected rejection increase at the higher pH. There is very little difference between the solute rejection rate for each type of membrane as the pH is increased. The data would indicate that it is the ionic state of the solute rather than the membrane that is the controlling factor in the rejection rate. The 75 percent solute rejection is below the 80 percent indicated on Figure 5 at a pressure of 950 psif (6.5 MPa).

As shown in column two of Figure 6, temperature of the feed water has a significant effect on the flux rate for some membranes. The flux for the zirconium oxide membrane increased from 60 gpd/sq ft (2.45 cu m/day/sq m) at 25° C to 160 gpd/sq ft (6.53 cu m/day/sq m) at 55° C. However, the salt and solute rejections appeared to be unaffected by the temperature changes.

Operating the filtration process for extended periods of time indicated a slight reduction of flux rate with time initially, followed by a long period of stable flow. The solute and salt rejections were unaffected by the operating time.

The sensitivity of the operation to variations in concentration was evaluated. Over a range of 1 mg/l to 400 mg/l of phenol, not significant variations in the data were noted.

A final test of the membranes, as shown in column five of Figure 6, was a pH scan from 6.5 to 12. Destruction or deterioration of the membranes was expected at the high pH values. The flux rate declined slightly as the pH was increased. The solute rejection increased significantly as the pH was increased above 8, but started to fall beyond pH 11. The salt rejection rate was the greatest at about a pH of 9, and fell down in both directions. In general the zirconium membrane outperformed the silicate membrane for the solute being tested.

CONCLUSIONS

The points of most general importance which have emerged from the foregoing studies are, briefly, as follows:

1. The carbon support tube produced slightly better rejection rates, but lower flux rates.
2. Increasing the pH of the feed increased the solute rejection rate, decreased the salt rejection rate, and had little effect on the flux rate.

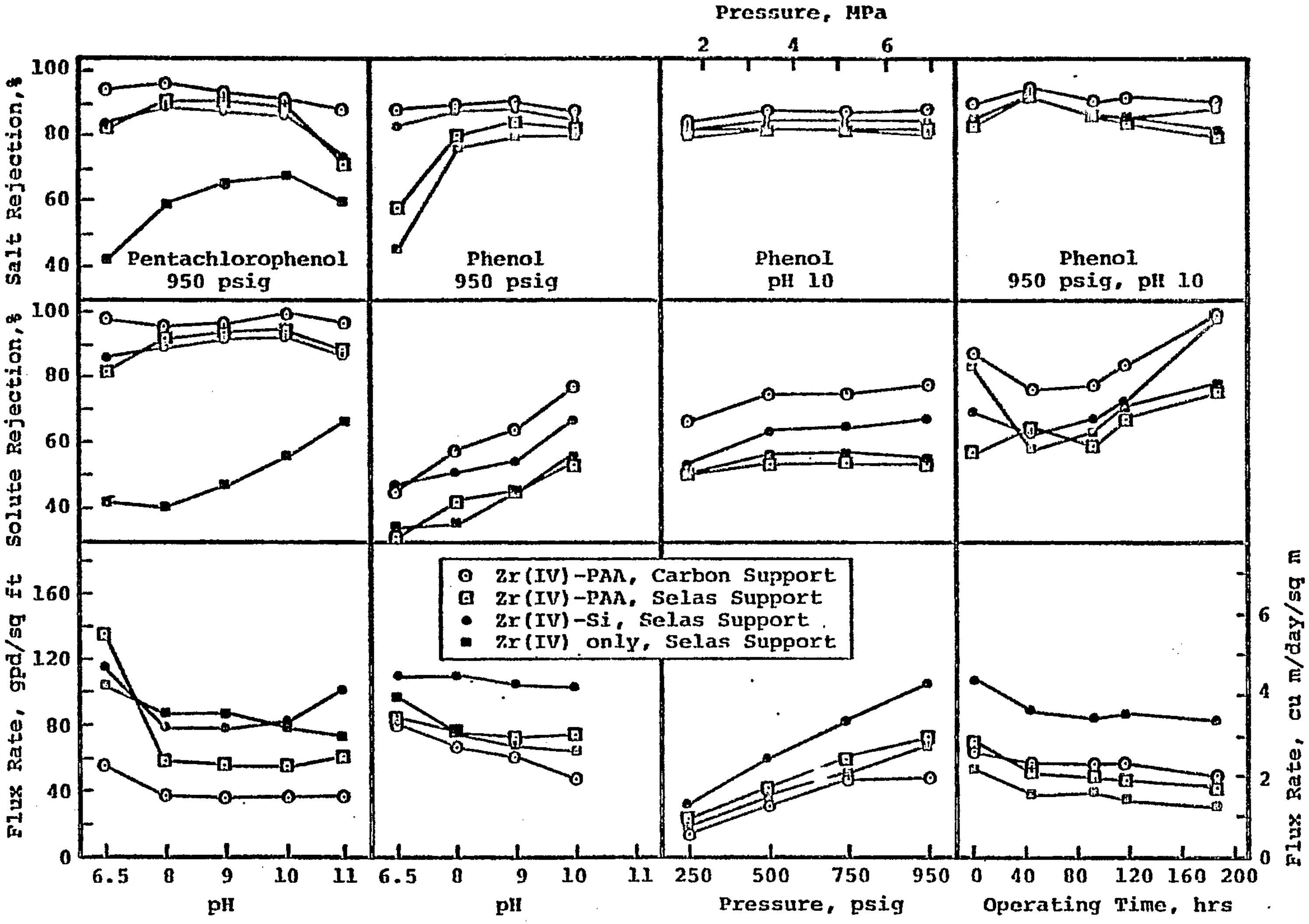

Figure 5. Hyperfiltration of pentachlorophenol and phenol (10 mg/l).

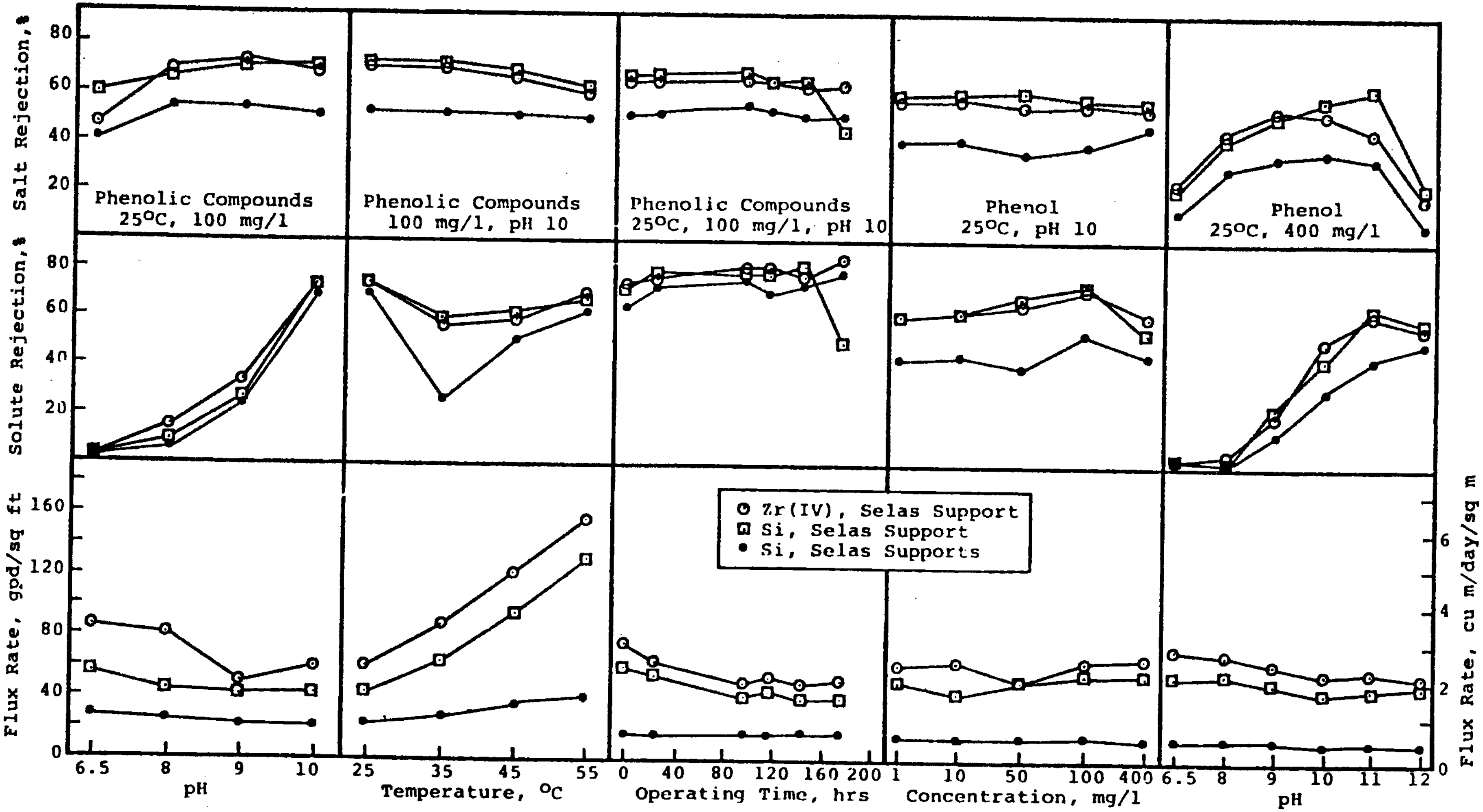

Figure 6. Ultrafiltration of phenolic compounds and phenol (200 psig, 1.38 MPa).

3. Increasing the pressure of the feed significantly increased the flux rate but had little effect on the solute and salt rejection rates.
4. Variations in concentration produced little change in rejection rates but did cause a slight decrease in flux rates as concentration increased.
5. Long-time operation of the processes indicated that the rejection rates and flux rates stabilize after a short period of time.
6. Increasing the temperature of the feed resulted in an increase in the flux rate but very little change in the rejection rates.
7. The best rejection of the phenolic compounds was obtained with a pH of 10, pressure of 950 psig (6.5 MPa), and zirconium oxide-polyacrylic acid on carbon supports.

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