

**SUMMARY REPORT ON PHYSICAL AND CHEMICAL TREATMENT
OF UCG CONDENSATE AND AFFECTED GROUNDWATERS**

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TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES	iii
LIST OF FIGURES.....	iv
ACKNOWLEDGMENT	vi
DISCLAIMER.....	vii
RESEARCH SUMMARY.....	viii
INTRODUCTION.....	1
Coagulation-Precipitation Experiments.....	1
Reverse Osmosis Experiments.....	2
Cross Flow-Filtration Experiments.....	2
Carbon-Adsorption Experiments.....	3
Objectives.....	4
EXPERIMENTAL METHODS	5
RESULTS AND DISCUSSION.....	7
Coagulation-Precipitation Experiments.....	7
Reverse Osmosis Experiments.....	9
Cross-Flow Filtration Experiments.....	24
Carbon-Adsorption Experiments.....	31
Equilibrium-Uptake Tests.....	38
Batch-Isotherm Tests.....	38
CONCLUSIONS.....	42
Coagulation-Precipitation.....	42
Reverse Osmosis.....	42
Cross-Flow Filtration.....	42
Carbon Adsorption.....	43
REFERENCES.....	44

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Levels of Various Parameters in Supernatants from Jar Tests with UCG Condensate.....	10
2. Effect of Variable Purifloc C-31 Dose on Removal of Particles and Acetone-Soluble Tar from Hanna IVB Condensate.....	11
3. Effect of Variable DEAE-Dextran Dose on Removal of Particles and Acetone-Soluble Tar from Hanna IVB Condensate.....	11
4. Levels of Various Parameters in the Hanna Groundwater Sample and the Preburn Hanna Coal-Seam Aquifer, Compared with Wyoming Groundwater Standards and Treatment Objectives.....	12
5. Characterization of Influent, Permeate, and Concentrate from Reverse Osmosis Experiment with Hanna Groundwater Affected by UCG (400 PSI and 75% Conversion).....	19
6. Concentrations of Metals in Influent, Permeate, and Concentrate from Reverse Osmosis Experiment with Hanna Groundwater Affected by UCG.....	22
7. Analysis of Simulated Wastewater Treated by Ultrafiltration and Microporous Filtration with PAC addition (50% Conversion).....	25
8. Results of Pressure-Excursion Ultrafiltration Experiment Performed with Simulated Wastewater and Constant Feed Circulation Rate (50% Conversion).....	27
9. Results of Flow-Excursion Ultrafiltration Experiment Performed with Simulated Wastewater and Constant Transmembrane-Pressure Difference (50% Conversion).....	27
10. Concentrations of Metals in Influent and Effluent from Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion).....	30
11. Adsorptive Constants and Correlation Coefficients from Langmuir and Freundlich Isotherms Resulting from Batch-Adsorption Tests.....	39
12. TOC and Phenol Removal Data from Batch-Adsorption Tests with Coal and Char.....	40

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Schematic of Membrane-Separation Apparatus.....	6
2. Apparatus for Simulating Single Reverse Combustion of Coal.....	8
3. Effect of Operating Pressure on Deionized-Water Flux during Reverse Osmosis Tests with Hanna Groundwater.....	14
4. Effect of Operating Pressure on Conductivity and TDS Reduction during Reverse Osmosis Treatment of Hanna Groundwater (50% and 75% Conversion).....	15
5. Effect of Operating Pressure on Product Flux during Reverse Osmosis Treatment of Hanna Groundwater with and without Pretreatment (50% and 75% conversion).....	17
6. Effect of Operating Pressure on Deionized-Water Flux during Reverse Osmosis Tests with Pretreated Hanna Groundwater.....	18
7. Effect of Operating Pressure on Reduction of Total Dissolved Solids during Reverse Osmosis Treatment of Pretreated Hanna Groundwater (75% Conversion).....	20
8. Effect of Elapsed Time on Product Flux during Reverse Osmosis Treatment of Pretreated Hanna Groundwater (400 psi and 75% Conversion).....	23
9. Effect of Variable Transmembrane-Pressure Difference on Treatment of Simulated Wastewater by Ultrafiltration (50% Conversion; $P_{loss} = 8$ psi).....	26
10. Effect of Variable Feed-Circulation Rate on Product Flux during Treatment of Simulated Wastewater by Ultrafiltration (50% Conversion; $\Delta P = 15$ psi).....	28
11. Effect of Variable Transmembrane-Pressure Difference on Product Flux during Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion; $P_{loss} = 10$ psi).....	32
12. Effect of Variable Feed-Circulation Rate on Product Flux during Treatment of Simulated Wastewater by Microporous Filtration with PAC addition (50% conversion); $\Delta P = 19$ psi).....	33
13. Effect of Elapsed Time on Product Flux during Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion).....	34

14.	Log Concentrations of Particles in Untreated Simulated Wastewater and Effluents Treated by Cross-Flow Filtration.....	35
15.	Cumulative and Frequency Distributions from Particle-Size Analysis of Untreated Simulated Wastewater.....	36
16.	Cumulative and Frequency Distributions from Particle-Size Analysis of Simulated Wastewater Treated by Ultrafiltration.....	37

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement.

RESEARCH SUMMARY

Several unit operations were evaluated for ability to treat Hanna IVB UCG condensate and UCG-affected groundwaters. These treatment processes included coagulation-precipitation, reverse osmosis (RO), ultrafiltration (UF), microporous filtration (MPF), and carbon-adsorption with coal and char. The objectives of the experiments were to remove colloidal and suspended solids, dissolved inorganics, and soluble organics from UCG wastewaters.

In coagulation-precipitation experiments, a 60 mg/L dose of polymer Purifloc C-31 resulted in removal of 99.0% of the 2-90 μ m-diameter particles and 92.9% of the acetone-soluble tar from Hanna IVB condensate. Similarly, addition of 50 gm/L of polymer DEAE-Dextran resulted in removal of 98.3% of the 2-90 μ m-diameter particles and 95.2% of the acetone-soluble tar. Reverse osmosis treatment of Hanna groundwater reduced sulfate and total dissolved solids by 99.4% and 98.9%, respectively. An operating pressure of 400 psi and feed conversion rate of 75% were used with this RO experiment. Acetone-soluble tar was reduced by 77.0% during a UF experiment performed with a 50% conversion rate. Removals of soluble organics by UF were negligible, however. Treatment of simulated wastewater by MPF with powdered-activated-carbon addition effected much greater removals of dissolved organic carbon and phenols. Metals were also successfully removed by this configuration. Total organic carbon (TOC) and phenols in simulated wastewater were effectively adsorbed onto coal and char. The TOC removals by adsorbents were 71.4-92.6% with simulated wastewater and 11.2-37.5% with Hanna IVB condensate. The absolute quantities removed were greater for the Hanna IVB condensate, however.

The adsorption of TOC from simulated wastewater onto coal was well described by both the Langmuir and Freundlich isotherm models ($r^2 = 0.951$ and 0.953 , respectively). The Freundlich isotherm best described the adsorption of TOC from simulated wastewater onto char ($r^2 = 0.934$). The adsorption of contaminants from Hanna IVB UCG condensate was poorly described by both isotherm models.

INTRODUCTION

Treatment of UCG condensates by physical, chemical, and biological methods has been the focus of past UCG environmental research. Also of concern, however, is the potential for contamination of groundwaters by UCG. The Western Research Institute has conducted research to evaluate selected processes for ability to remove UCG-induced contaminants from groundwaters and from process condensate.

The unit operations evaluated include coagulation-precipitation, reverse osmosis (RO), ultrafiltration (UF), microporous filtration (MPF) with addition of powdered activated carbon (PAC), and adsorption of organics onto coal and char. Coagulation-precipitation and carbon-adsorption experiments were performed with Hanna IVB condensate from an underground coal gasification (UCG) experiment near Hanna, Wyoming. Reverse osmosis experiments were performed with groundwater from the same site. Ultrafiltration, microporous filtration, and carbon-adsorption experiments were performed on a synthesized wastewater. This wastewater, designed to simulate groundwater recently affected by the UCG process, was comprised of 95.2% Hanna groundwater and 4.8% Hanna IVB UCG condensate. The addition of an organic spike to the groundwater was necessary to raise concentrations of organics to levels resulting from recent UCG operations. A target level of 230 mg/L dissolved organic carbon was set for the simulated wastewater, based on postburn water quality analyses at Hoe Creek, Wyoming (Campbell et al. 1978).

Coagulation-Precipitation Experiments

Removal of solids and acetone-soluble tar from Hanna IVB condensate may be required before further processing by hot-gas stripping, carbon adsorption, and reverse osmosis. Colloidal materials can foul adsorption media and membrane surfaces, severely reducing the efficiency of carbon adsorption, ion exchange, and membrane-separation processes (Klein and Barker 1978). Further, these materials can coat the tower-packing media in a gas stripping column and impair stripping efficiency by reducing the surface area of the packing.

Coagulation-precipitation may be an effective pretreatment step for removing colloidal materials from Hanna IVB condensate. Successful coagulation and flocculation cause particles too small for effective gravity settling to agglomerate into larger masses. During flocculation, many of the colloids not involved in the initial reaction with the coagulant are enmeshed in the larger aggregates and subsequently removed (Klein and Barker 1978). The tar remaining after coagulation-precipitation is water-soluble and adsorbable (Johnson et al. 1977).

Experiments were performed to evaluate the feasibility of treating Hanna IVB condensate by coagulation-precipitation. Dow Purifloc C-31 and Sigma DEAE Dextran, cationic polymers successfully used to treat coal conversion wastewater (Singer et al. 1979), were

tested for their ability to remove acetone-soluble tar and solids from Hanna IVB condensate.

Reverse Osmosis Experiments

Reverse osmosis is an effective method for the removal of total dissolved solids (TDS) and sulfate from coal conversion wastewater. Recently, RO was used in combination with other unit operations to treat coal gasification wastewater (Campbell et al. 1983). The gas condensate was treated with activated carbon for removal of soluble organics. The effluent contained 2,540 mg/L of sulfate, similar to UCG-affected groundwater. This effluent was then treated by reverse osmosis using an operating pressure of 400 psi and a 75% conversion rate. Both Dupont polyamide and Dowex cellulose-triacetate membranes were evaluated in these RO experiments. The polyamide membrane, found to be superior to the cellulose triacetate membrane, yielded an effluent with 10 mg/L of sulfate.

The feasibility of using RO to remove TDS and sulfate from Hanna groundwater was evaluated in the research reported herein. A Filmtch polyamide membrane was used for all experiments.

Cross-Flow Filtration Experiments

Cross-flow filtration (CFF), a promising alternative to more conventional treatments, has been shown to be less expensive than treatment by chemical precipitation (Patterson 1985). Cross-flow filtration, including ultrafiltration (UF) and microporous filtration (MPF), can remove emulsified and colloidal substances from oily wastes. The UF membrane has a pore size of 0.005 μm , and the MPF membrane has a pore size of 0.2 μm . The larger porosity of the MPF membrane allows higher product flux, hence more efficient wastewater processing.

Microporous filtration was recently used to treat complex, organic-laden wastewater from industrial laundries. Oil and grease, chemical oxygen demand (COD), and suspended solid concentrations in the influent were 1,100, 5,000, and 1,000 mg/L, respectively. These levels were reduced to 10, 100, and 0 mg/L, respectively, by pretreatment and microporous filtration. Also, lead, zinc, copper, chromium, nickel, and iron were reduced to <0.1 mg/L by the treatments. Pretreatment consisted of chemical conditioning to convert the contaminants to filterable form. The low operating pressures, increased pore size, and greater flux associated with microporous filtration made this process more efficient than ultrafiltration (Tran 1985).

Both ultrafiltration and microporous filtration were evaluated during this research for their effectiveness in treating simulated UCG-affected groundwater. A tubular membrane configuration was used with all experiments.

Carbon-Adsorption Experiments

Coal and char have been evaluated in past studies as possible substitutes for activated carbon (Johnson et al. 1977, Klein 1979). These media can substantially reduce the cost of carbon-adsorption treatment. Further, constants derived from tests with coal and char can be used to characterize adsorptive and desorptive processes occurring in aquifers affected by UCG operations.

Lignitic coal was investigated as a substitute for activated carbon in a recent study (Klein 1979). The Oak Ridge National Laboratory (ORNL) tested the adsorption of naphthalene and phenanthrene from synthetic solutions onto coal. Wastewater from the ORNL hydrocarbonization facility was also tested. Concentrations of phenols (50-200 mg/L) and polyaromatic hydrocarbons (1-3 mg/L) in this wastewater were reduced by 99 and 95%, respectively.

Another study featured the use of char from the Synthane process as an adsorbent (Johnson et al. 1977). This char, with a surface area of approximately 325 M²/g, was used to remove residual organics from treated Synthane coal-gasification condensate. The condensate had been previously subjected to air stripping at elevated pH, dilution, and biological treatment. The influent TOC concentration of the treated condensate ranged from 80 to 490 mg/L. An adsorbent dose ranging from 2 to 40 g/L removed all of the solution color and 88 to 97% of the TOC concentration.

Batch isotherm tests can be used to ascertain the degree of treatment attainable by carbon adsorption. The data from these tests may be correlated to Freundlich or Langmuir isotherms. The Freundlich isotherm is defined as (Humenick 1977)

$$X/M = KC^{1/n}$$

where:

X/M = unit weight of contaminant adsorbed per unit weight of carbon, mg/mg

C = equilibrium contaminant concentration, mg/L

K = value of X/M at C = 1

n = slope⁻¹ of plot of ln(X/M) versus ln C

The Langmuir isotherm is defined as (Humenick 1977)

$$\frac{X}{M} = \frac{(X/M)_m bC}{1 + bC}$$

where:

X/M = unit weight of contaminant adsorbed per unit weight of carbon, mg/mg

C = equilibrium contaminant concentration, mg/L

$(X/M)_m = y\text{-intercept}^{-1}$, mg/mg

$b = 1/\text{slope} \cdot (X/M)_m$, L/mg

Coefficients calculated from isotherm plots may be used to characterize the behavior of both the carbon and the adsorbate (Eckenfelder 1980). The Freundlich constants K and n generally decrease with increasing complexity of the wastewater. Low values of n indicate substantial adsorption of solute from concentrated solution and poor adsorption from dilute solution, whereas high K and n values indicate substantial adsorption of solute throughout the concentration range of the test.

Batch-isotherm, equilibrium-uptake, and leaching tests were employed during this research to describe adsorptive characteristics of contaminants in groundwater affected by UCG. Data from batch tests were correlated to both the Freundlich and Langmuir isotherms. The relative abilities of these isotherms to describe the adsorption of selected contaminants from the simulated wastewater were then assessed.

Objectives

The objectives of the coagulation-precipitation experiments were

- to identify effective polymer doses and corresponding pH ranges for treating Hanna IVB UCG condensate
- to determine removals of acetone-soluble tar and particles from polymer-treated Hanna IVB condensate

The objectives of the reverse osmosis experiments were

- to reduce TDS and sulfate concentrations in UCG-affected Hanna groundwater to pregasification levels
- to identify effective pretreatments for RO treatment of Hanna groundwater
- to evaluate the effect of variable operating pressure on product flux
- to assess the degree of fouling or compaction of the RO membrane
- to characterize UCG-affected groundwater treated by RO

The objectives of cross-flow filtration tests were

- to reduce acetone-soluble tar, solids, and soluble organics concentrations in simulated wastewater
- to identify effective pretreatments for CFF treatment of simulated wastewater
- to evaluate the effect of variable feed circulation rate and transmembrane-pressure difference on product flux
- to characterize simulated wastewater treated by CFF

The objectives of the carbon-adsorption experiments were

- to generate adsorption-desorption coefficients, using Langmuir and Freundlich isotherms, for use in modeling
- to evaluate the potential of coal and char to remove soluble organics from simulated wastewater and Hanna IVB condensate

EXPERIMENTAL METHODS

Coagulation-precipitation experiments were performed with a Phipps and Bird, Inc., model 300 six-paddle stirrer. Particle-size measurements were made with a HIAL/ROYCO PA-720 24-channel analyzer equipped with an ASAP liquid sampler. An HR-120 sensor, which detects particles having diameters of 2 to 120 μm , was used with the sampler. Acetone-soluble tar was measured using procedures described in a recent treatability study (Singer et al. 1979).

Reverse osmosis experiments were performed with a Village Marine model PW 150 apparatus and a Filmtec 30-2521 spiral-wound membrane. Wastewater was concentrated using a semi-batch, nonsteady-state mode of operation (Figure 1). Permeate was recycled to the feed reservoir in subsequent parametric tests. Calcium, total hardness, and magnesium determinations were made according to Standard Methods (American Public Health Association 1980). Reverse osmosis influent was softened with calcium hydroxide and sodium carbonate to reduce scale formation at the wastewater-membrane interface. Best doses of these chemicals were determined by jar tests. An AMF Cuno 5.0-micron filter was used to filter softened wastewater before RO treatment. Finally, residual calcium was complexed with sodium metaphosphate, $(\text{NaPO}_3)_6$, to minimize precipitation of calcium sulfate at the concentrated boundary layer. Feed temperature was maintained at 25°C with a cooling coil coupled with a Forma Scientific model 2067 circulating bath. Conductivity was measured at 25°C using a YSI model 32 conductance meter, and TDS was measured using procedures outlined in Standard Methods (American Public Health Association 1980).

Cross-flow filtration experiments were performed with a Koch-Abor UF-4 apparatus and two tubular membranes providing a total surface area of 2.2 ft^2 . The HFM-251 membranes, having a molecular weight

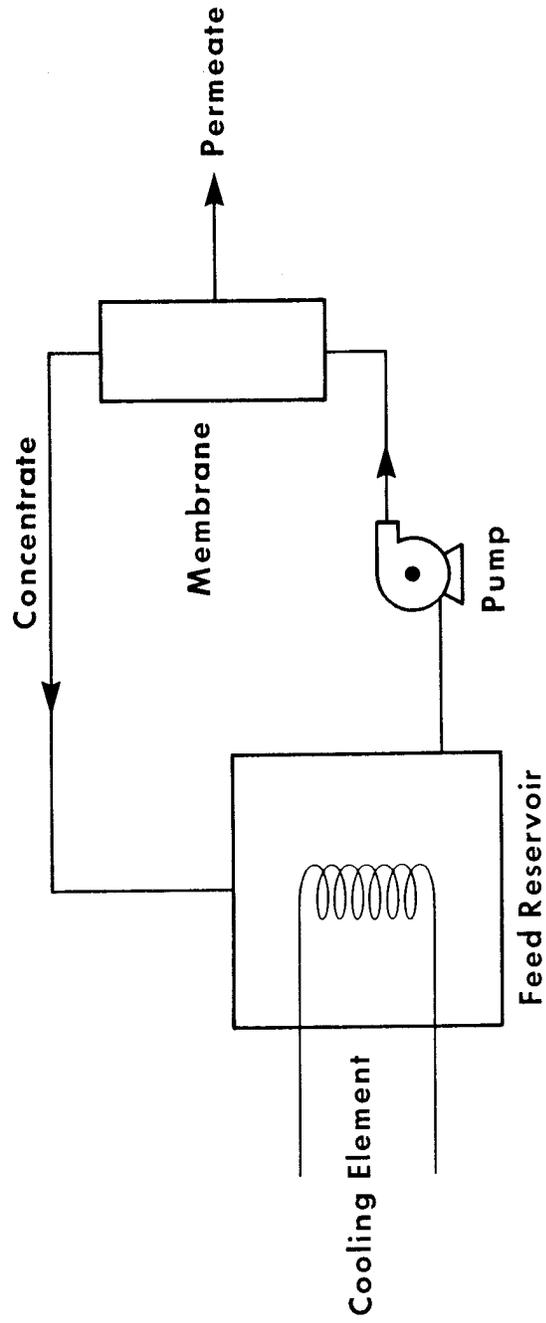


Figure 1. Schematic of Membrane-Separation Apparatus

cutoff of 18,000, were used in UF experiments. The MMP-406 membranes, with a nominal porosity of 0.2 μm , were used in MPF experiments. For all CFF experiments, the semi-batch nonsteady-state mode of operation was used to concentrate wastewater (Figure 1). Wastewater temperature was maintained at 25°C with a cooling coil immersed in the feed tank. Cold tap water was delivered through the cooling coil and continuously discharged. The PAC doses were determined with jar tests employing a six-paddle stirrer manufactured by Phipps and Bird, Inc. Particle-size analysis was performed using equipment described earlier. An HR-346BCL sensor, which can detect particles sized from 0.4 to 24 μm , was used for submicron particle-size determinations. Phenols were assayed with a Hewlett-Packard model 5830A gas chromatograph equipped with a flame-ionization detector. Gas chromatographic procedures for measuring phenols were similar to those outlined in Standard Methods (American Public Health Association 1980). Because phenol was the only quantitative standard used with this research, relative response factors were used to calculate the weight concentrations of other phenolic compounds. The total organic carbon was measured using a Coulometrics, Inc. model 5020 total carbon apparatus coupled with a model 5010 CO₂ coulometer. Both TOC and total solids were measured according to procedures outlined in Standard Methods (American Public Health Association 1980), and the acetone-soluble tar was measured by the methods of Singer et al. (1979).

Coal was procured from the Rosebud mine near Hanna, Wyoming, for use in carbon-adsorption experiments. The coal was ground, sieved to 25-60 mesh, and washed with tap water. Char was produced in an apparatus in which the single-reverse combustion UCG process was simulated (Figure 2). Procedures and equipment were similar to those used in a recent study by Manahan et al. (1980). The combustion apparatus consisted of a three-foot Vycor tube with heat-resistant stoppers at the inlet and outlet. The Vycor tube was tightly packed with 25-60 mesh coal that had been washed and vacuum-filtered to remove most of the water. Oxygen was passed through the tube (3 psig), and the coal was ignited near the tube outlet. Combustion proceeded toward the tube inlet and was usually complete in 20 minutes. The char was sieved to 16 mesh and dried at 65°C until used in adsorption tests.

Leaching and adsorption experiments were performed with 0.5 to 20 g of adsorbent contacted with 100 mL of solution. Samples were agitated on an Eberbach shaker table at 5°C for 96 hours. Equilibrated samples were filtered with 0.7 μm filters before analysis. Phenols measurements were made with a Hewlett-Packard 5790A gas chromatograph equipped with a flame-ionization detector. Procedures for measuring TOC were the same as described earlier.

RESULTS AND DISCUSSION

Coagulation-Precipitation Experiments

Variable-pH jar tests were performed on UCG condensate with polymers DEAE-Dextran and Purifloc C-31 to identify optimum pH ranges

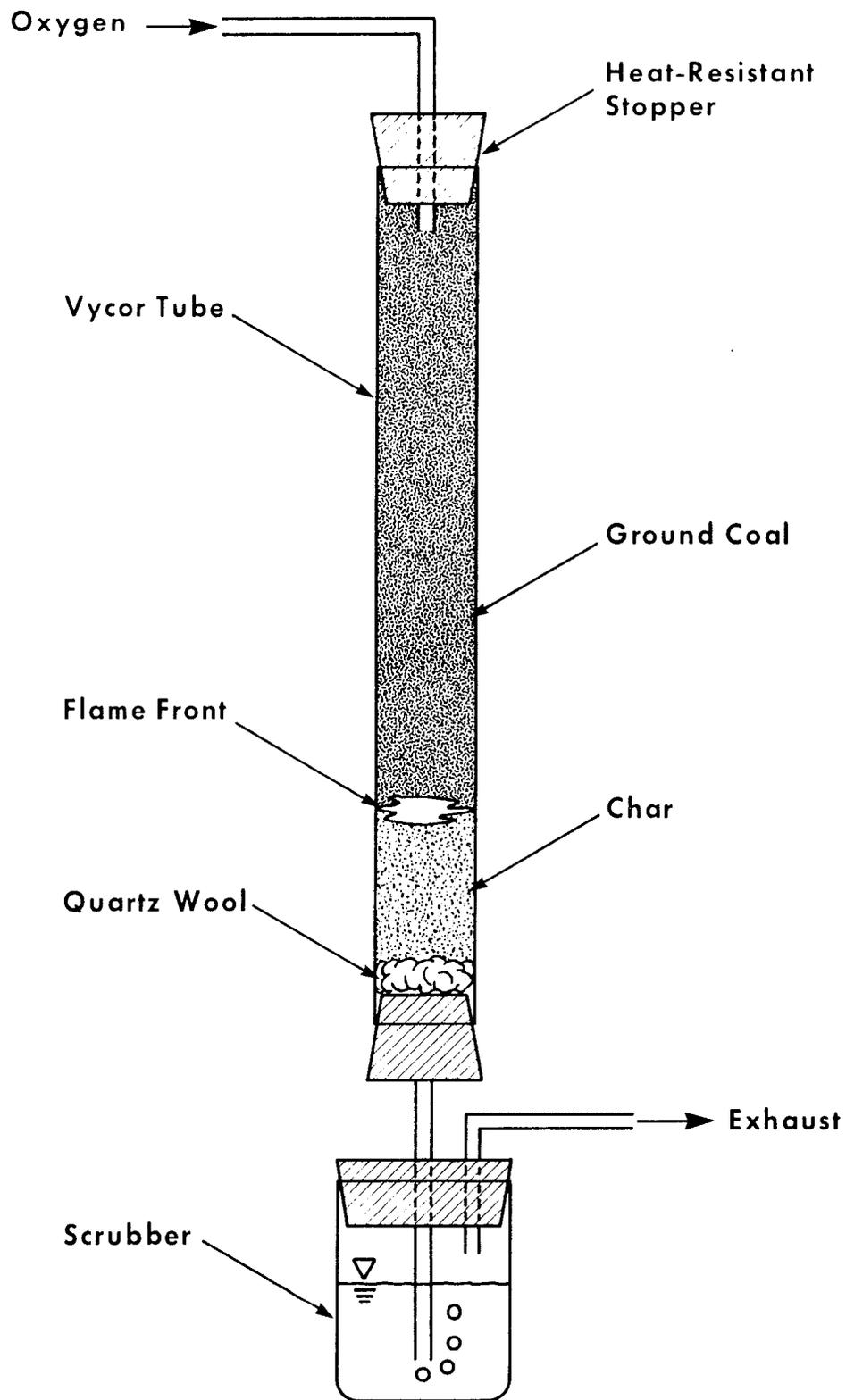


Figure 2. Apparatus for Simulating Single Reverse Combustion of Coal

for contaminant removal. The results of these tests, shown in Table 1, indicate that particle removals first increased, then decreased, with increasing pH. Particle enumeration for these experiments used total counts of 2-90 μm -diameter particles. Purifloc C-31 yielded the highest particle removals (99.5%) and the highest acetone-soluble tar removals (92.2%) at pH 5. These data, corroborated with visual observations, indicate that acidic conditions in the UCG condensate caused precipitation of coal tars, which, upon polymer addition, coagulated and settled from the wastewater.

Excellent particle removals were obtained with polymer DEAE-Dextran (99.8%) at pH 9. This result was surprising because the supernatant was dark brown and turbid. Excellent removal of particles (99.7%) also occurred at pH 6. This result was consistent with those of earlier experiments performed with Purifloc C-31 in that the acidic condition precipitated coal tars. These tars were then removed by coagulation, flocculation, and settling.

Best removals of acetone-soluble tar occurred at pH 5 for both polymers. The removals were 92.2 and 91.0%, respectively, for Purifloc C-31 and DEAE-Dextran.

Variable-dose jar tests were performed at pH 5 with polymers DEAE-Dextran and Purifloc C-31 to identify optimum coagulant doses. Tests were conducted with Purifloc C-31 doses of 40-140 mg/L and DEAE-Dextran doses of 10-110 mg/L. Purifloc C-31 yielded the best removal of acetone-soluble tar (92.9%) with the 60 mg/L polymer dose (Table 2). Additionally, 99.0% of the particles were removed at this polymer dose. The optimum DEAE-Dextran dose (50 mg/L) removed 95.2% of the acetone-soluble tar and 98.3% of the particles (Table 3).

For both polymers tested, particle and acetone-soluble tar concentrations first decreased, then increased, as polymer dose was increased. These results suggest that contaminant removal was caused by charge neutralization of the colloidal suspension. The negative charge of the suspension was reduced as cationic polymer was initially added to the wastewater, allowing coagulated particles to agglomerate and settle. However, the net charge of the colloids was reversed as the polymer dose was further increased. This caused the suspension to restabilize, resulting in higher residual contaminant levels with higher polymer doses.

Reverse Osmosis Experiments

Reverse osmosis experiments were conducted with Hanna groundwater, designated 85-(Hanna)-01W-010C. This groundwater was first composited and subjected to detailed characterization (Table 4). The data indicate that TDS and sulfate levels are greater than preburn levels. The treatment objective, therefore, was to reduce concentrations of TDS and sulfate to pregasification levels in the Hanna coal-seam aquifer.

Before exposing the membrane to Hanna groundwater, the RO membrane was tested with deionized water to derive a pure water

Table 1. Levels of Various Parameters in Supernatants from Jar Tests with UCG Condensate

Solution pH	Purifloc C-31 ^a		DEAE-Dextran ^b			
	Visual Obs.	Particle Count ^c	Acetone-Sol. Tar, mg/L	Visual Obs.	Particle Count ^c	Acetone-Sol. Tar, mg/L
Influent, 8.9	Brown, Turbid	56,284	734	Brown, Turbid	59,222	984
4	Amber, Clear	464	220	Amber, Turbid	2,118	112
5	Amber, Clear	300	57.5	Amber, Clear	276	89
6	Amber, Turbid	8,338 ^d	145	Amber, Turbid	204	131
7	Amber, Turbid	566	410	Amber, Turbid	408	178
8	Brown, Turbid	1,289	293	Brown, Turbid	703	--
9	Brown, Turbid	1,806	532	Brown, Turbid	131	--

^aPurifloc C-31 dose constant at 90 mg/L

^bDEAE-Dextran dose constant at 30 mg/L

^cTotal particle count, 2-90 μ m-diameter, per 43 mL-volume of diluted sample

^dSupernatant was disturbed when sampled

Table 2. Effect of Variable Purifloc C-31 Dose on Removal of Particles and Acetone-Soluble Tar from Hanna IVB Condensate^a

Purifloc C-31 Dose, mg/L	Particles ^b		Acetone-Sol. Tar	
	Conc. (# counts)	% Removal	Conc. (# counts)	% Removal
--	71,200	--	888	--
40	3,260	95.4	245	72.4
60	690	99.0	63	92.9
80	382	99.5	186	79.0
100	328	99.5	172	80.6
120	292	99.6	224	74.8
140	394	99.4	118	86.7

^a experiments conducted at pH 5

^b total particle count, 2-90 μm -diameter, per 43 mL of diluted sample

Table 3. Effect of Variable DEAE-Dextran Dose on Removal of Particles and Acetone-Soluble Tar from Hanna IVB Condensate^a

DEAE- Dextran Dose, mg/L	Particles ^b		Acetone-Sol. Tar	
	Conc., # counts	% Removal	Conc., mg/L	% Removal
--	64,600	--	942	--
10	2,630	95.9	180	80.9
30	1,870	97.1	145	84.6
50	1,130	98.3	45	95.2
70	3,430	94.7	192	79.6
90	9,200	85.8	205	78.2
110	18,600	71.2	265	71.9

^a experiments conducted at pH 5

^b total particle count, 2-90 μm -diameter, per 43 mL of diluted sample

Table 4. Levels of Various Parameters in the Hanna Groundwater Sample and the Preburn Hanna Coal-Seam Aquifer Compared with Wyoming Groundwater Standards, and Treatment Objectives

Parameter, mg/L	Hanna Groundwater Sample	Pregasifi- cation Level ^a	Wyoming Groundwater Standard (Livestock) ^b	Treatment Objective
Total organic carbon	9	41	NE ^d	NA ^e
Phenols (µg/L)	< 6	< 10	NE ^d	NA ^e
Chemical oxygen demand	< 10	NS ^c	NE ^d	NA ^e
Ammonia	11.9	1.15	NE ^d	1.15
Conductivity (millimhos/cm)	4.3	NS ^c	NE ^d	NA ^e
Sulfate	1,960	19	3,000	19
Total suspended solids	4.9	NS ^c	NE ^d	NA ^e
Total dissolved solids	3,600	1,220	5,000	1,220
Alkalinity (as CaCO ₃)	502	1,110	NE ^d	NA ^e
Chloride	56	NS ^c	2,000	NA ^e
Boron	1.1	0.04	5.0	0.04
Calcium	147	NS ^c	NE ^d	NA ^e
Mercury	0.172	< 0.0001	0.00005	< 0.0001
Magnesium	65.3	NS ^c	NE ^d	NA ^e
Sodium	833	NS ^c	NE ^d	NA ^e
Selenium	0.0990	NS ^c	0.05	NA ^e
Calcium hardness (as CaCO ₃)	374	NS ^c	NE ^d	NA ^e
Total hardness (as CaCO ₃)	673	NS ^c	NE ^d	NA ^e
pH (standard units)	8.47	NS ^c	6.5-8.5	NA ^e

^asource: Cooke and Oliver

^bsource: Division of Environmental Quality 1980

^c not sampled or otherwise unavailable

^d standard not established

^e not applicable

permeability constant. The results, shown in Figure 3, indicate a trend of increasing product flux with increasing operating pressure. The slope of the line yields a permeability constant of 5.81×10^{-6} gpm/ft²-psi, with a correlation coefficient (r^2) of 0.972. These are baseline values; subsequent calculations performed after exposure of the membrane to groundwater were expected to yield smaller permeability values if membrane fouling or compaction had occurred.

Product flux obtained with RO treatment of the Hanna groundwater was invariant as operating pressure was increased from 100 to 600 psi, indicating that significant membrane fouling had occurred. Flux ranged from 9.6×10^{-3} to 9.9×10^{-3} gpm/ft² for an experiment involving 50% recovery of wastewater. The percent recovery of wastewater is defined as the volume of RO feed converted to permeate divided by the initial feed volume and expressed as percent. Fouling of the RO membrane by the Hanna groundwater resulted in smaller reductions of conductivity and TDS than desired. Conductivity and TDS reductions were only 30-35% with operating pressure equal to 400 psi and conversion rate equal to 75% (Figure 4). Reductions of conductivity and TDS increased to 46.8% and 44.4%, respectively, at 550-600 psi (Figure 4). Corresponding levels of conductivity and TDS in the effluent were 4.86 millimhos/cm and 4810 mg/L, respectively. Sulfate determinations were not made during these experiments because RO feed volume was limited.

To assess the degree of membrane fouling or compaction, deionized water experiments were repeated following treatment of the Hanna groundwater at the 50% and 75% recovery rates. This experiment yielded a pure-water permeability constant of 1.22×10^{-7} gpm/ft² compared with 5.81×10^{-6} gpm/ft²-psi before the groundwater treatment. Product flux was essentially invariant, ranging from 1.10×10^{-2} to 1.4×10^{-2} gpm/ft², confirming that extensive compaction or fouling of the membrane had occurred during treatment of the Hanna groundwater (Figure 3). The membrane was then subjected to rigorous cleaning with 24 hours of exposure to 0.1% HCl acid solution. Product flux was restored to the level shown in Figure 1 after the cleaning step, indicating that the flux decline was caused by membrane fouling rather than compaction. The pure water permeability constant obtained with this experiment was 6.05×10^{-6} gpm/ft²-psi, with r^2 equal to 0.978.

Membrane fouling was caused by high levels of calcium hardness in the groundwater, resulting in precipitation of calcium sulfate in the concentrated boundary layer. Although sodium metaphosphate had been added to the groundwater to complex calcium, the initial calcium hardness concentration (374 mg/L) was too high. Experiments were performed to assess the effectiveness of pretreating the groundwater with calcium hydroxide (hydrated lime) before RO treatment. Calcium hydroxide reduces calcium hardness in wastewater, thus reducing the potential for the precipitation of calcium sulfate.

Appropriate doses of hydrated lime and sodium carbonate (soda) were determined during initial pretreatment efforts. These chemicals removed carbonate and noncarbonate hardness, respectively, from the

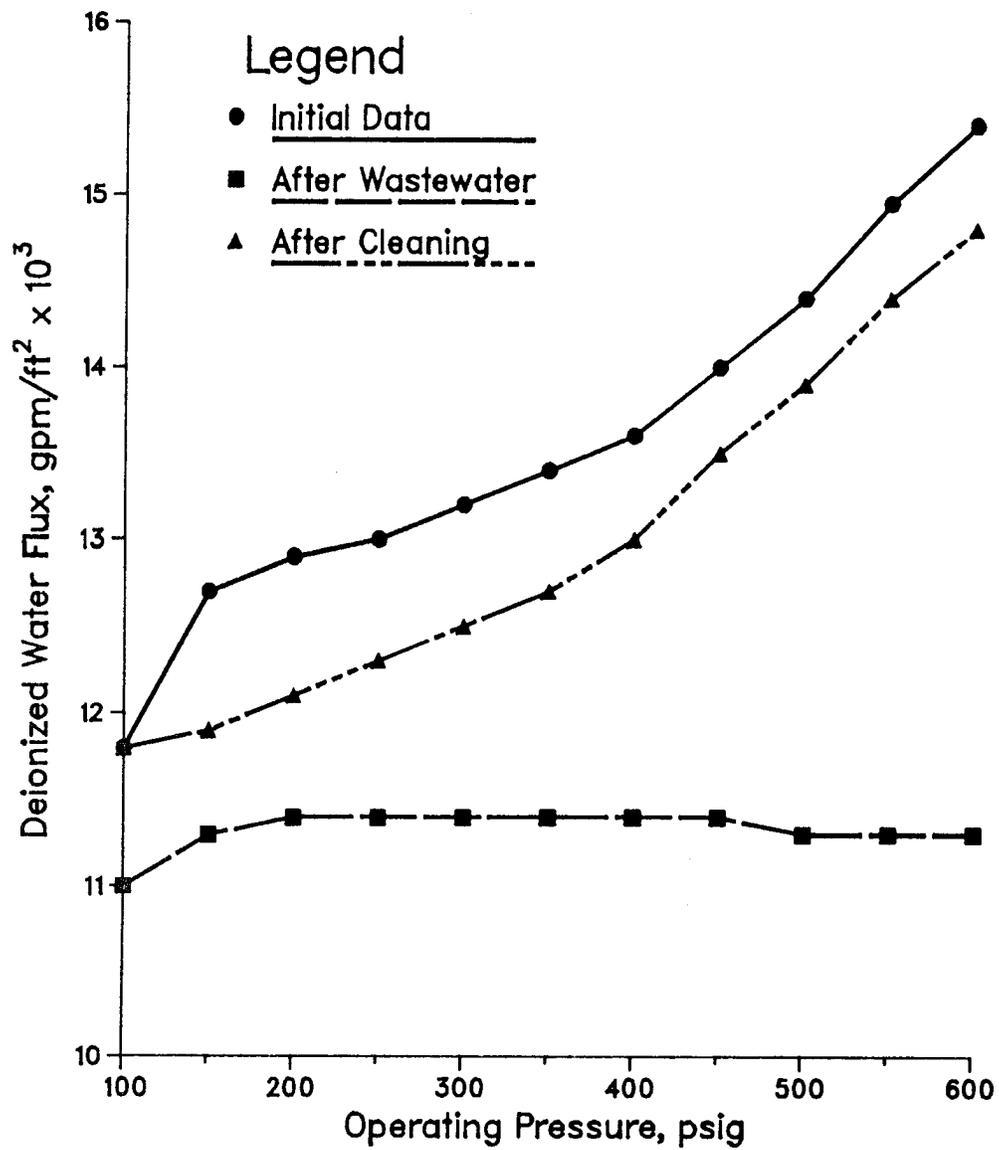


Figure 3. Effect of Operating Pressure on Deionized-Water Flux During Reverse Osmosis Tests with Hanna Groundwater

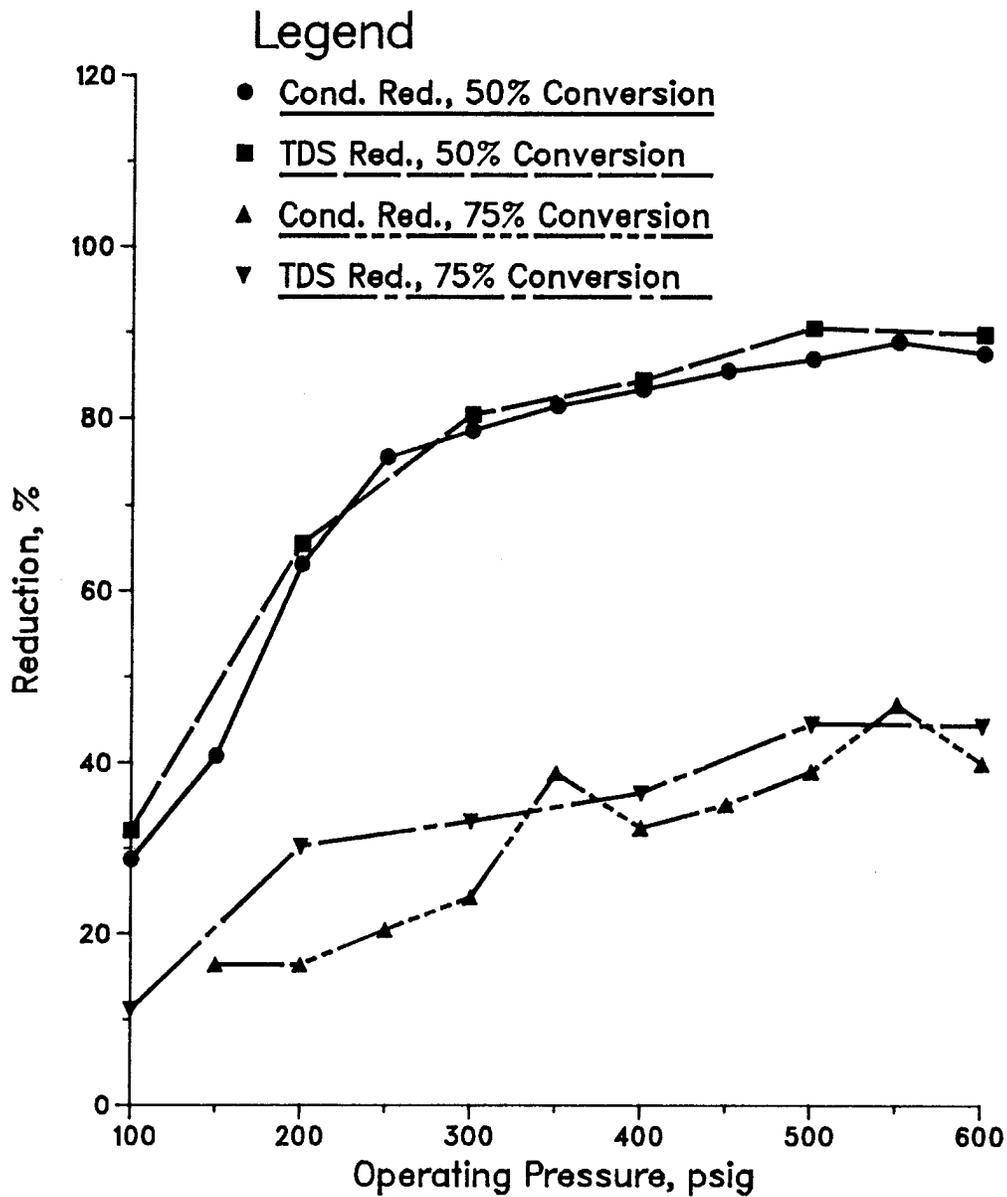


Figure 4. Effect of Operating Pressure on Conductivity and TDS Reduction During Reverse Osmosis Treatment of Hanna Groundwater (50% and 75% Conversion)

groundwater. Lime and soda doses of 480 and 370 mg/L, respectively, were calculated from the levels of calcium and magnesium hardness and alkalinity in the Hanna groundwater. This combined lime-soda dose yielded an effluent with 80 mg/L of calcium hardness, considered high for RO feedstock. A target range of 25-45 mg/L calcium hardness was based on a recent RO study (Campbell et al. 1983). Variable-dose jar tests were performed to identify more effective coagulant doses. Doses of 1,080 mg/L lime and 820 mg/L soda produced an effluent containing 42 mg/L of calcium hardness and were thus selected to pretreat the Hanna groundwater.

A 50% conversion RO experiment was performed on the pretreated Hanna groundwater. The results of this experiment are shown in Figure 5. Product flux increased as operating pressure was increased, indicating that the RO membrane did not experience severe fouling during this experiment. The addition of lime-soda to the wastewater, in conjunction with sodium metaphosphate, apparently prevented the precipitation of calcium sulfate at the membrane surface. The permeability constant, calculated from the product flux and operating pressure data, was 4.8×10^{-6} gpm/sq. ft.-psi, with a correlation coefficient (r^2) of 0.938. This permeability constant is somewhat less than the value reported for pure water before exposure of the membrane to wastewater (5.81×10^{-6} gpm/ft²-psi), indicating that the expected slight fouling or compaction of the membrane occurred. The RO process very effectively reduced total dissolved solids in the Hanna groundwater. Conductivity was reduced by 99.0% to 0.0731 millimhos/cm, and TDS was reduced by 98.9% to 63.4 mg/L.

Product flux also increased as operating pressure was increased during a reverse osmosis experiment with 75% converted Hanna groundwater (Figure 5). Pretreatment of the Hanna groundwater by lime-soda addition protected the membrane from severe fouling in the presence of the more concentrated feed. The product rate was 3.7×10^{-6} gpm/sq. ft.-psi, with r^2 equal to 0.964. Product flux was slightly less at 75% conversion than at 50% conversion because of the increased TDS concentration in the feed (Figure 5). Slight fouling of the RO membrane occurred under these conditions. Excellent reductions of conductivity (99.2%) and TDS (99.6%) were obtained at 400 psi, corresponding to 0.0898 millimhos/cm of conductivity and 38.2 mg/L of TDS in the RO effluent.

To assess the degree of membrane fouling or compaction, permeability experiments with pure water were repeated after exposure of the RO membrane to pretreated Hanna groundwater. The permeability constant for this experiment was 3.1×10^{-6} gpm/sq. ft.-psi, which is 46% less than the value determined for pure water before exposure of the RO membrane to wastewater (Figure 6). Some fouling or compaction of the membrane had occurred, although not as severe as during past work. Increasing deionized-water flux was observed for all pure-water experiments performed during tests with pretreated wastewater.

An acid solution was then used to clean the reverse osmosis membrane, and the permeability experiment with pure water was repeated. Product flux was restored to levels consistent with initial

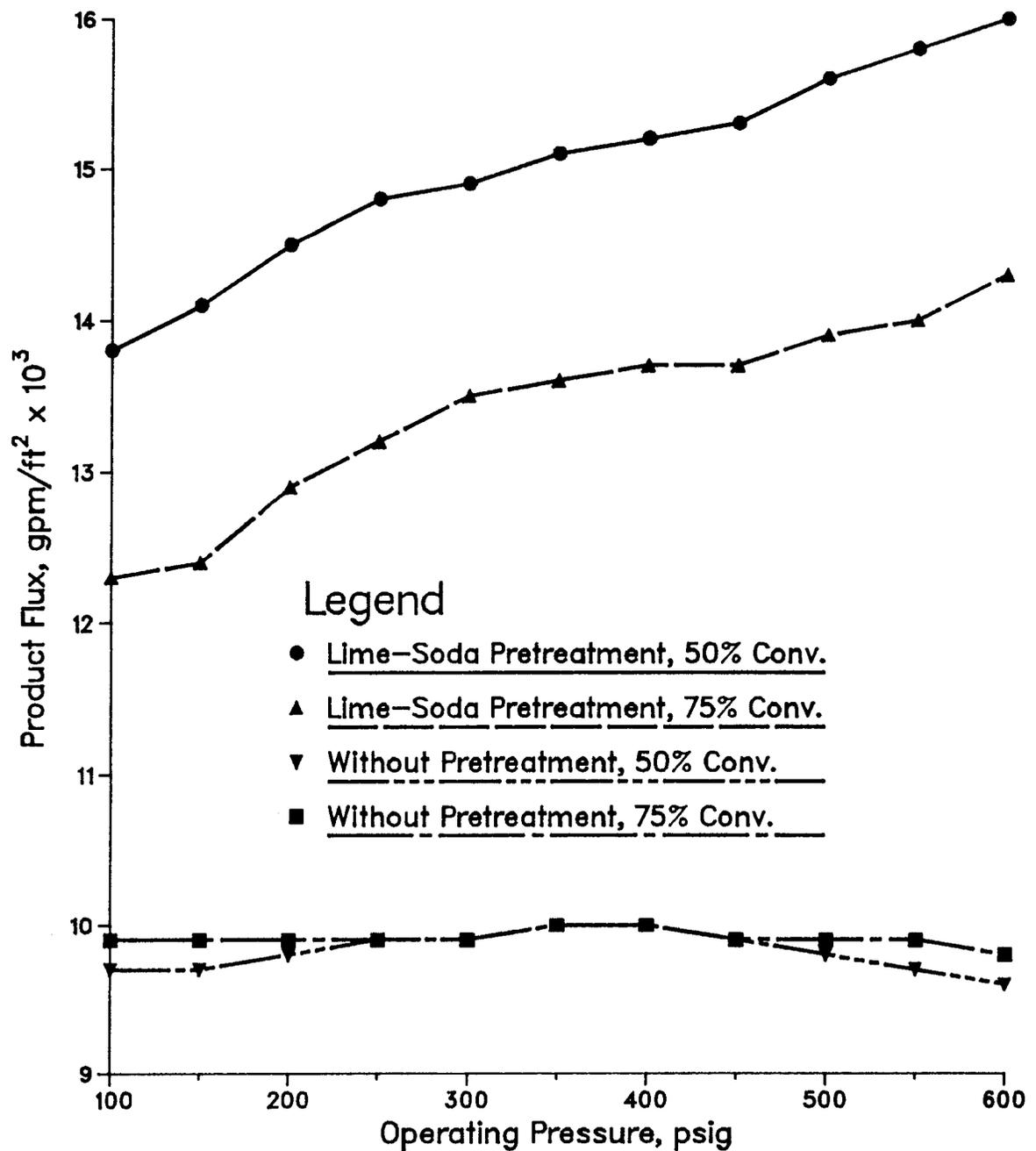


Figure 5. Effect of Operating Pressure on Product Flux During Reverse Osmosis Treatment of Hanna Groundwater with and without Pretreatment (50% and 75% Conversion)

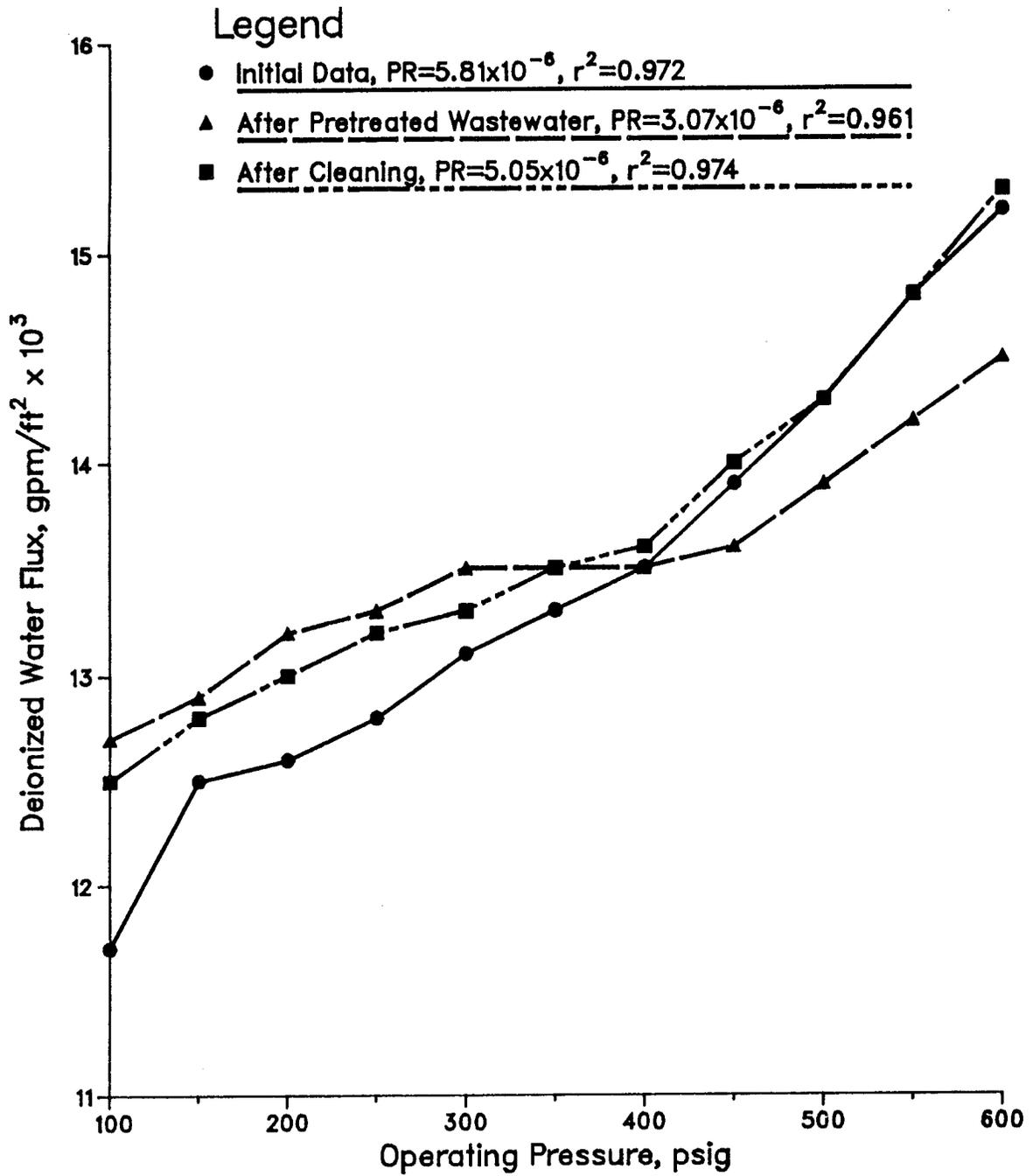


Figure 6. Effect of Operating Pressure on Deionized-Water Flux During Reverse Osmosis Tests with Pretreated Hanna Groundwater

pure water experiments. The permeability constant for this experiment was 5.1×10^{-6} gpm/sq. ft.-psi, only 12% less than the initial permeability constant for pure water (Figure 6). The small, irreversible decrease in product flux was probably caused by compaction rather than fouling.

Excellent reductions of conductivity and TDS were realized for all RO experiments using pretreated Hanna groundwater. Data from these tests indicate that best removals of conductivity and TDS occurred with operating pressure equal to 400 psi (Figure 7). This condition was selected for generating RO effluent for more detailed characterization.

Characteristics of the RO influent, effluent, and concentrate are shown in Table 5 for an experiment during which operating pressure

Table 5. Characterization of Influent, Permeate, and Concentrate from Reverse Osmosis Experiment with Hanna Groundwater Affected by UCG (400 psi and 75% Conversion)

Parameter, mg/L	Lime-Precipitated Influent	Reverse-Osmosis Concentrate	Reverse-Osmosis Permeate	Removal, %
Conductivity (millimhos/cm)	4.89	12.73	0.0643	98.7
Total dissolved solids	3,650	10,600	40	98.9
Calcium	12	INT ^a	1.6	86.7
Calcium hardness (as calcium carbonate)	30	INT ^a	4.0	86.7
Total hardness (as calcium carbonate)	76	INT ^a	10	86.8
Magnesium	11	INT ^a	1.5	86.3
Sulfate	2,050	6,300	12	99.4
Ammonia	< 0.5	< 0.5	< 0.5	--
pH (s.u.)	11.5	6.76	5.26	NA ^b

^a interference
^b not applicable

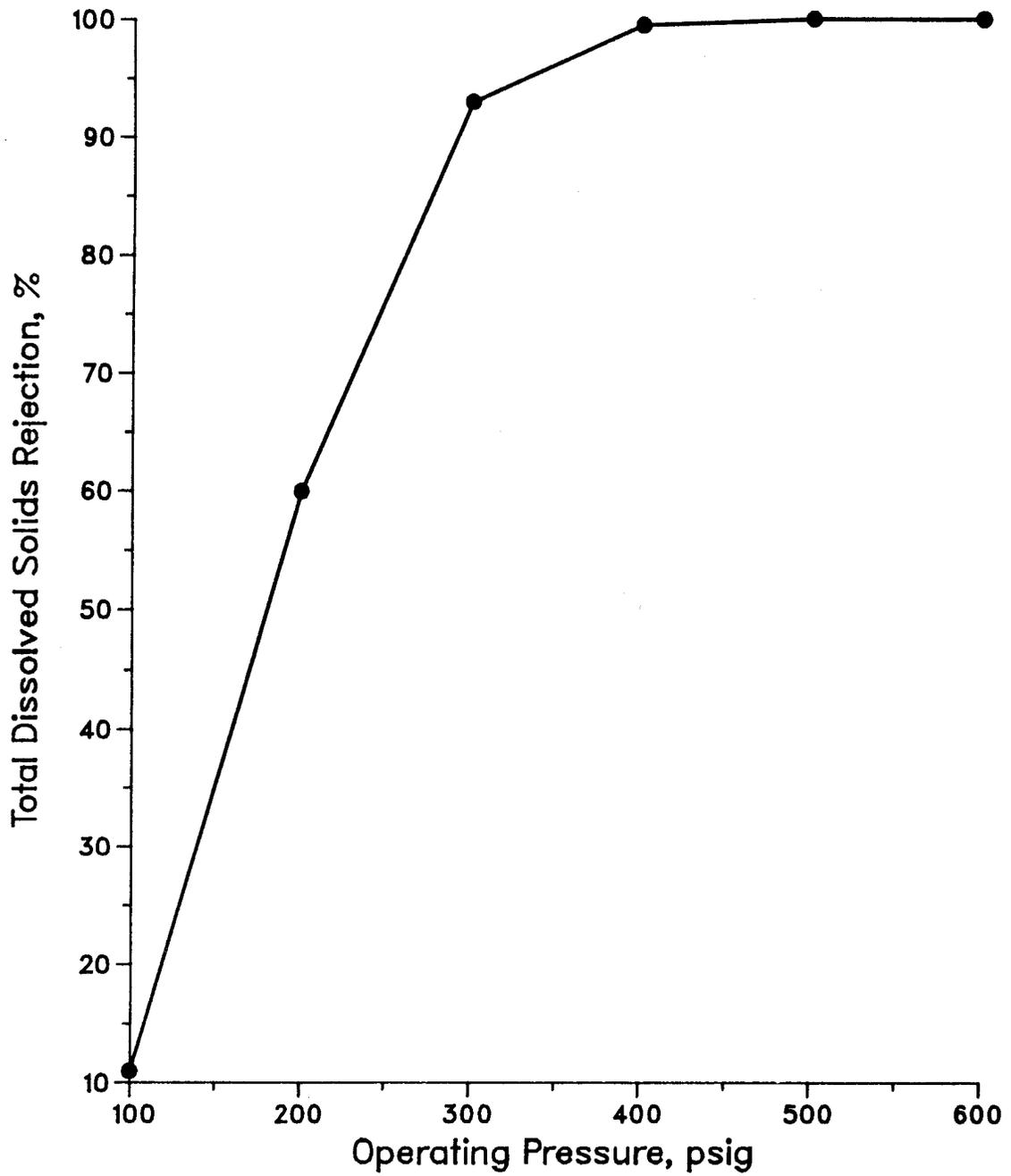


Figure 7. Effect of Operating Pressure on Reduction of Total Dissolved Solids During Reverse Osmosis Treatment of Pretreated Hanna Groundwater (75% Conversion)

equaled 400 psi and the conversion rate equaled 75%. The sulfate concentration in the Hanna groundwater was reduced to 12 mg/L, a level similar to the Hanna pregasification concentration of 19 mg/L. TDS was reduced to 40 mg/L, well below the pregasification level of 1,220 mg/L.

A metals analysis was performed on lime-softened influent, permeate, and concentrate samples from the RO experiment described above. The inductively coupled plasma (ICP) method was used for this analysis. High rejections of calcium, lithium, molybdenum, sodium, silicon, and strontium were realized, based on the influent and effluent analyses (Table 6). Concentrations of aluminum, arsenic, barium, potassium, magnesium, nickel, phosphorus, selenium, and vanadium were also reduced. Used in conjunction with a calcium hydroxide-precipitation step, RO should effectively remove metallic contaminants from UCG-affected groundwater.

The RO concentrate contains elevated concentrations of most of the metallic species analyzed (Table 6). Except for copper, however, the concentrations are below the maximum allowed in the Wyoming class III groundwater quality standards. The RO concentrate is likely to be toxic, even though the concentrations of most metals are less than the amounts allowed in livestock standards. Concentrate from RO treatment of simulated wastewater was very toxic to aquatic test organisms during a recent study (Nolan et al. 1986). This waste requires an environmentally sound method of disposal.

The copper concentration in the RO concentrate is 0.883 mg/L. The copper concentration in the RO permeate (0.069 mg/L) is four times that in the lime-softened RO influent. Copper may have been contributed to the wastewater by a copper cooling coil used during past RO experiments.

A long-term (100 hours) experiment was performed to assess the effect of elapsed time on RO treatment of the softened Hanna groundwater. Results indicate that no significant decline in product flux occurred during this experiment (Figure 8). The minimum product flux was 0.0133 gpm/sq. ft.

A phenol spike of 46 mg/L was added to the groundwater before the long-term experiment to determine if phenols could be effectively removed by RO. Phenol removal varied from 46.2 to 76.8% during the experiment, and the minimum effluent phenol concentration was 11.7 mg/L. These rejection values are in agreement with those reported by other researchers. Phenol is inefficiently removed by RO partly because of its low molecular weight (94.1). Other factors affecting rejection of organic solutes are the degree of branching and the electrical charge. Effective treatment of UCG-affected groundwater containing phenols may require treatment by activated-carbon adsorption or ion exchange. Alternatively, carbon adsorption used in conjunction with the RO process can effectively treat wastewaters containing soluble organic and inorganic contaminants.

Table 6. Concentrations of Metals in Influent, Permeate, and Concentrate from Reverse Osmosis Experiment with Hanna Groundwater Affected by UCG

Parameter, mg/L	Lime-Precipitated Influent	Concentrate	Permeate	Removal, %
Ag	<0.01	<0.01	<0.01	--
Al	0.054	0.508	<0.03	>44
As	0.120	0.107	<0.1	>17
B	0.654	1.61	0.270	59
Ba	0.011	<0.01	<0.01	>9.1
Be	<0.01	<0.01	<0.01	--
Bi	<0.1	<0.1	<0.1	--
Ca	19.5	24.6	2.94	85
Cd	0.010	0.029	0.010	--
Co	<0.01	0.018	<0.01	--
Cr	<0.01	0.028	<0.01	--
Cu	0.016	0.883	0.069	--
Fe	<0.1	0.110	0.048	
K	29.4	66.8	<10	>66
Li	0.605	1.13	0.108	82
Mg	13.8	57.6	5.34	61
Mn	<0.01	0.013	<0.01	--
Mo	0.049	0.045	<0.01	>80
Na	940	1590	173	82
Ni	0.013	0.044	0.012	7.7
P	0.5	<1	<0.1	
Pb	<0.1	<0.05	<0.025	
Sb	<0.1	0.132	<0.1	--
Se	0.108	<0.1	<0.1	>7.4
Si	6.15	18.9	1.43	76
Th	<0.05	0.198	0.035	
Sr	0.106	0.201	0.020	81
V	0.022	0.030	0.016	27
Zn	0.033	4.31	0.336	--

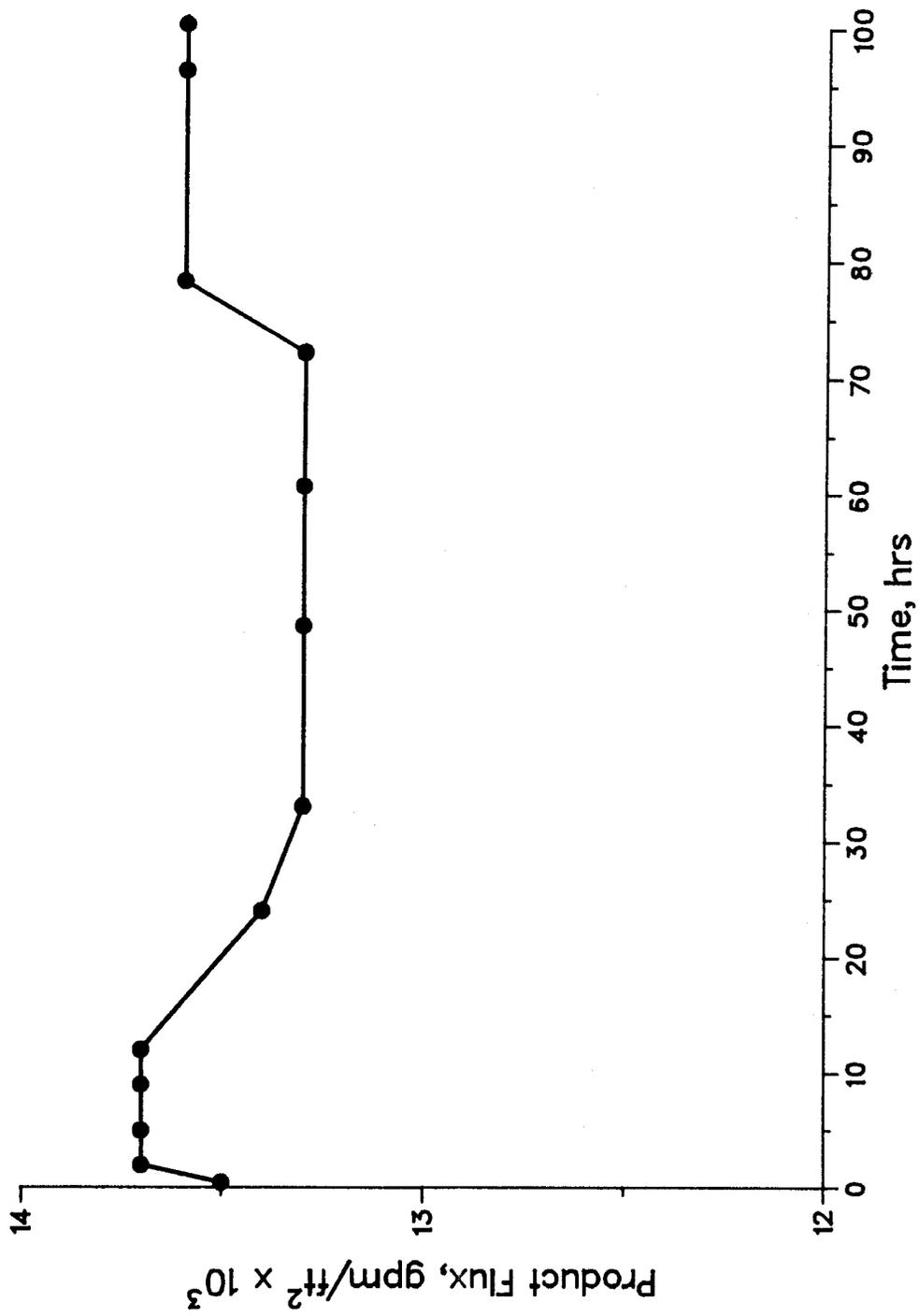


Figure 8. Effect of Elapsed Time on Product Flux During Reverse Osmosis Treatment of Pretreated Hanna Groundwater (400 psi and 75% Conversion)

Cross-Flow Filtration Experiments

Simulated wastewater was used for all CFF experiments. Hanna-84-01W-01C groundwater was spiked with Hanna IVB condensate to simulate subsurface water contaminated by UCG-induced organics (Table 7). Most of the organic carbon was in the dissolved state.

Ultrafiltration was tested for its ability to remove emulsified tars and colloidal materials, measured as acetone-soluble tars (AST), from the simulated wastewater. If effective, ultrafiltration could be less costly than chemical methods of treatment.

Pressure- and flow-excursion experiments were performed with a 50% wastewater conversion rate. Pressure-excursion experiments involved variable transmembrane pressure difference, and flow-excursion experiments involved variable feed circulation rate. Transmembrane pressure difference, the pressure differential across the membrane, is defined as $P_{inlet} - 0.5\Delta P_{loss}$, where P_{inlet} is the system inlet pressure and ΔP_{loss} is the inlet pressure minus the outlet pressure. A cleaning solution prepared from detergent supplied by the manufacturer was applied to the ultrafiltration membranes after each experiment.

Transmembrane pressure difference was varied and product flux measured in the pressure-excursion experiment. As the transmembrane pressure difference was increased, product flux increased (Figure 9). Acetone-soluble tar removals, however, remained relatively constant, and the maximum removal of AST was 46.6% (Table 8).

A flow-excursion experiment was performed in which feed circulation rate was varied. Increasing pressure loss in the system increases the feed circulation rate and usually increases product flux. But product flux remained constant during this experiment (Figure 10), suggesting concentration polarization, the accumulation of substances at the membrane-wastewater interface. Concentration polarization is caused by application of pressure-dependent materials to the membranes (Hayes 1985). This response usually indicates that true cross-flow filtration was not achieved, but that conventional filtration, characterized by flow occurring perpendicular to the filter, has instead occurred. Nevertheless, removal of AST was greater than obtained during the pressure-excursion experiment. A maximum removal of 77.0% was obtained, probably resulting from more efficient filtration caused by accumulation of colloidal substances at the surface of the membrane (Table 9). Product flux, however, was less than desired. Pretreatment of the ultrafiltration feedstock will be necessary to prevent concentration polarization and, thus, more efficiently remove acetone-soluble tar and colloidal substances from the wastewater.

Only negligible amounts of TOC, dissolved organic carbon (DOC), phenol, and total solids were removed by any of the UF experiments (Table 7). Most of the organic components were too small for effective filtration by the HFM-251 membrane, which has a molecular weight cutoff equal to 18,000.

Table 7. Analysis of Simulated Wastewater Treated by Ultrafiltration and Microporous Filtration with PAC Addition (50% Conversion)

Parameter, mg/L	Untreated Simulated Wastewater	Ultrafiltration Exp.		Microporous Filt. Exp. with PAC		
		Flow- Excursion Effluent ^a	Pressure- Excursion Effluent ^b	Flow- Excursion Effluent ^c	Pressure- Excursion Effluent	PAC-treated and 0.45- Micron Filtered (Control)
Total organic carbon	196	196	183	32.5	34.9	76.5
Dissolved organic carbon	195	195	189	34.2	37.0	68.4
Acetone-soluble tar	65.0	23.8	49.5	30.0	66.0	17.5
Phenol	70.2	67.5	92.5	< 1.0	< 1.0	19.2
o-Cresol	14.6	15.9	16.9	< 1.0	< 1.0	< 1.0
m,p-Cresol	15.1	26.4	27.4	< 1.0	< 1.0	< 1.0
p-Ethyl and 2,5-dimethylphenol	6.4	8.8	7.9	< 1.0	< 1.0	< 1.0
pH (s.u.)	8.5	8.4	8.2	8.25	8.74	8.37
Total solids	3,240	2,880	3,120	980	2,520	3,135

^a transmembrane-pressure difference = 15 psi

^b pressure loss = 8 psi

^c transmembrane-pressure difference = 19 psi

^d pressure loss = 10 psi

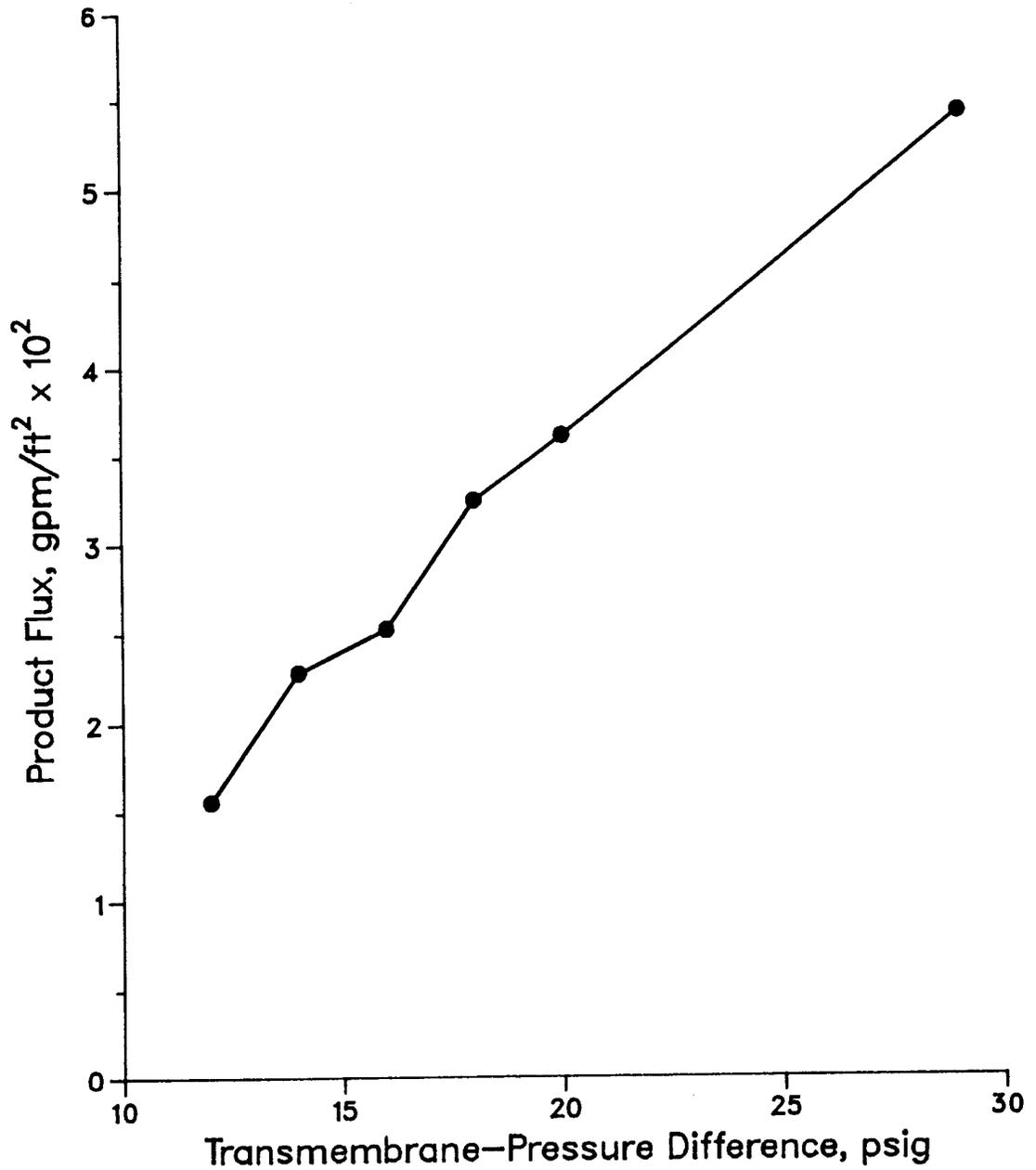


Figure 9. Effect of Variable Transmembrane-Pressure Difference on Product Flux During Treatment of Simulated Wastewater by Ultrafiltration (50% Conversion; $P_{Loss}=8$ psi)

Table 8. Results of Pressure-Excursion Ultrafiltration Experiment Performed with Simulated Wastewater and Constant Feed Circulation Rate (50% Conversion)^a

Transmembrane Pressure Difference, psi	Effluent Acetone-Soluble Tar, mg/L ^b	% Removal ^c
12	53.0	23.2
14	37.0	46.4
16	55.5	19.6
18	52.5	23.9

^a Pressure loss was 8 psi.

^b Influent acetone-soluble tar was initially 69.0 mg/L; after conversion, tar was 112 mg/L.

^c Based on initial influent concentration

Table 9. Results of Flow-Excursion Ultrafiltration Experiment Performed with Simulated Wastewater and Constant Transmembrane-Pressure Difference (50% Conversion)^a

Pressure Loss, psi	Feed Circulation Rate, gpm	Effluent Acetone-Soluble Tar, mg/L ^b	% Removal ^c
2	29	14.0	77.0
6	36	19.0	68.8
10	47	14.0	77.0
14	47	48.0	21.3

^a Transmembrane-pressure difference was 15 psi.

^b Influent acetone-soluble tar was initially 61.0 mg/L; after conversion, influent tar was 117 mg/L.

^c Based on initial influent concentration

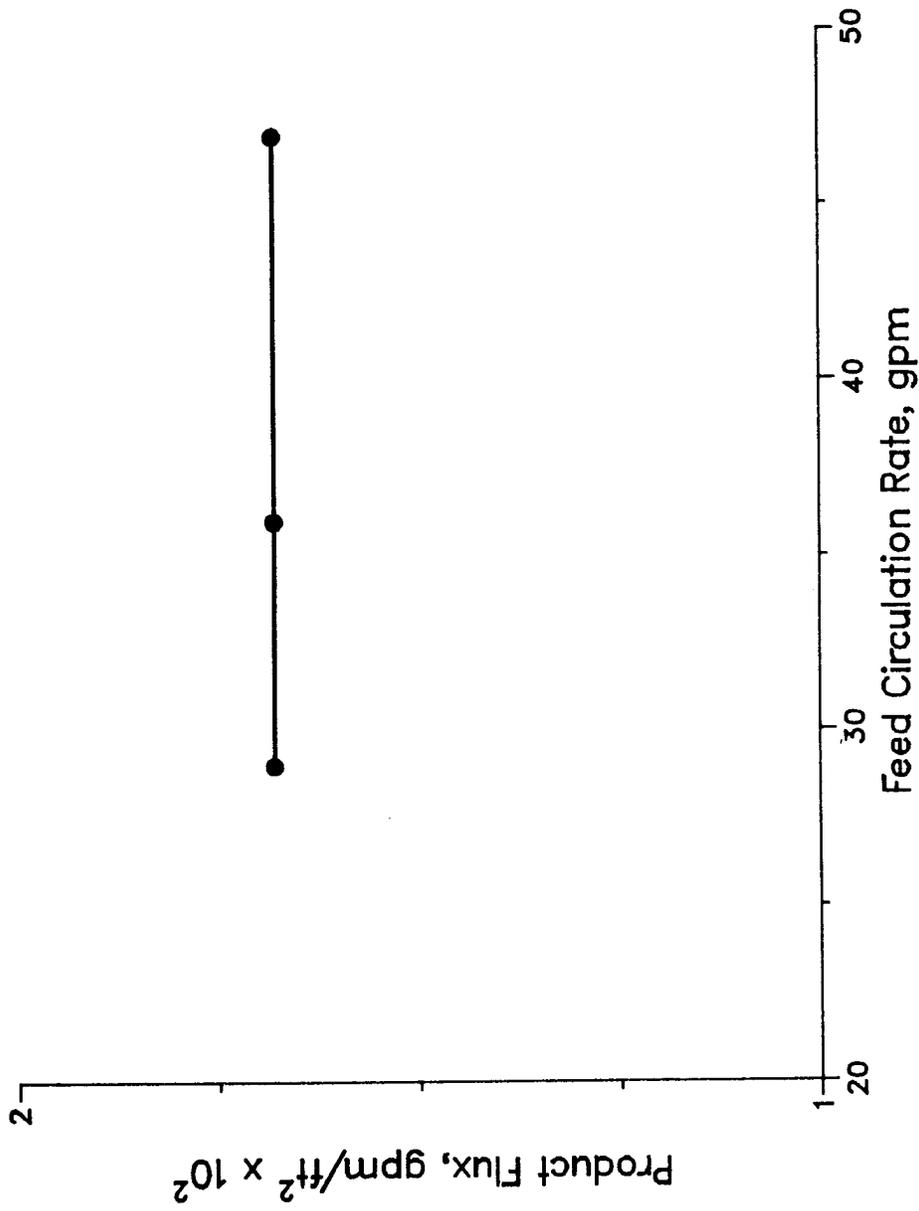


Figure 10. Effect of Variable Feed-Circulation Rate on Product Flux During Treatment of Simulated Wastewater by Ultrafiltration (50% Conversion; $\Delta P=15$ psi)

Pretreatment of the simulated wastewater was initiated to improve rejections of dissolved organics and to solve apparent fouling problems associated with the UF membranes. Powdered activated carbon (1,500 mg/L) was added to the wastewater to convert soluble contaminants into filterable form. Residual PAC and adsorbed contaminants were filtered from the wastewater using a microporous membrane with a nominal porosity of 0.2 microns, small enough to reject residual carbon fines, yet large enough to allow increased flux rates.

Levels of contaminants in effluents from MPF experiments are shown in Table 7. Removals of TOC, DOC, and phenols were much greater than those occurring with unassisted UF. Individual concentrations of phenol, o-cresol, m, p-cresol, p-ethylphenol and 2,5-dimethylphenol were less than 1 mg/L. (Because m- and p-cresol coeluted during the gas chromatographic analysis, these constituents are reported as m, p-cresol.) Most of the organic components were adsorbed onto the PAC, which was subsequently removed from solution by filtration with the microporous membranes.

Microporous filtration with PAC addition also effectively removed several metals from the simulated wastewater. Levels of aluminum, boron, cadmium, chromium, copper, potassium, lithium, magnesium, manganese, sodium, selenium, thorium, strontium, and zinc were less than in untreated simulated wastewater (Table 10). Levels of aluminum, boron, cadmium, chromium, selenium, and zinc were less than the maximum allowed in Wyoming class III (livestock) groundwater quality standards. However, the MPF effluent contained 1.20 mg/L of copper, exceeding the class III standard of 0.5 mg/L. Precipitation with calcium hydroxide will probably be necessary to obtain a further reduction of copper.

Simulated wastewater treated with PAC was passed through a 0.45- μ m cartridge filter to serve as a control for the MPF experiment. Concentrations of aluminum, arsenic, barium, cadmium, copper, molybdenum, phosphorous, silicon, and zinc were less than obtained in the MPF effluent. With the control, removal of metals may have been increased by the perpendicular flow of the fluid to the cartridge filter. This may have caused solids to accumulate on the surface of the filter enhancing removals of fine particles and dissolved species. Whether similar removals could be obtained in practice with a conventional sand filter is unknown. Overall, the performance of the MPF configuration with PAC addition was very satisfactory.

Product flux was significantly greater with the MPF configuration than with earlier UF experiments. A maximum flux of 0.175 gpm/sq. ft. was observed during the MPF experiment compared with a maximum flux of 0.0360 gpm/sq.ft during a similar UF experiment. Product flux increased as transmembrane-pressure difference was increased (Figure 11).

Product flux remained constant as feed-circulation rate was increased (Figure 12). This result was unexpected because pretreatment with PAC was used to adsorb soluble organics and should

Table 10. Concentrations of Metals in Influent and Effluent from Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion)

Parameter, mg/L	Untreated Simulated Wastewater	Microporous Filtration- and PAC-Treated Effluent ^a	PAC-Treated, 0.45- μ Filtered
Ag	<0.01	<0.01	<0.01
Al	0.163	0.078	0.064
As	0.113	0.146	0.125
B	0.955	0.541	0.831
Ba	0.068	0.077	0.022
Be	<0.01	<0.01	<0.01
Bi	<0.1	<0.1	<0.1
Ca	43.7	42.6	61.0
Cd	0.015	0.011	<0.01
Co	<0.01	<0.01	<0.01
Cr	0.015	<0.01	<0.01
Cu	2.03	1.20	0.020
Fe	<0.5	<0.1	<0.2
K	27.8	15.7	26.6
Li	0.588	0.348	0.576
Mg	44.9	25.1	41.2
Mn	0.191	0.118	0.185
Mo	0.046	0.054	0.037
Na	637	405	631
Ni	<0.01	0.018	0.016
P	<0.5	0.720	<0.5
Pb	<0.1	<0.1	<0.1
Sb	<0.15	<0.1	<0.15
Se	0.175	<0.1	0.131
Si	0.827	5.70	2.37
Th	0.117	<0.05	0.096
Sr	0.479	0.328	0.470
V	0.022	0.022	0.023
Zn	0.484	0.243	0.142

^a composited permeate sample from pressure-excursion experiment

have mitigated fouling effects. The lack of a response to increasing feed-circulation rate may have been caused by operating limitations of the equipment. The maximum pressure drop attainable with the UF-4 apparatus is 12 psi, which may be insufficient to achieve high feed-circulation rates, turbulent flow within the membrane, and greater product flux.

A long-term MPF experiment with PAC addition was performed to assess the effect of time on product flux. The 50% conversion rate was used for this experiment, which lasted 100 hours. As time elapsed, product flux decreased as a result of membrane fouling (Figure 13). However, most of the flux decline occurred early in the experiment, after which the system operation essentially stabilized.

Submicron-particle size analyses were performed on simulated wastewater, concentrated feed, UF-treated effluent, and MPF-treated effluent (Figure 14). Results are expressed as the logarithm of the number of particles per mL of wastewater. The UF effluent contained the smallest number of particles 0.5-5.0 μm in diameter. The HFM-251 membrane used in UF experiments has a porosity of approximately 0.005 μm and filters out most particles greater than 0.005 μm . Concentrated MPF feed (50% conversion) contained the largest number of particles 0.5-5.0 μm in diameter because of the PAC fines remaining in suspension; the MPF effluent contained significantly fewer particles because most of the PAC fines and adsorbed contaminants had been removed by the MMP-406 membrane. However, the MPF effluent contained more particles (1.2 μm -diameter and larger) than untreated simulated wastewater, probably because residual PAC fines remained in suspension. Future research should involve UF treatment of PAC-treated influent for more effective separation of PAC fines.

Ultrafiltration reduced the volumetric mean of the particles from 15.4 to 4.0 μm . Cumulative population-frequency, and volume-frequency distributions for untreated and UF-treated wastewaters are shown in Figures 15 and 16, respectively. Larger particles are more likely to be removed by UF whereas submicron particles (colloids) can permeate the UF membrane. The tendency of the UF system to remove larger particles is reflected in the observed shift of the volumetric mean.

Carbon-Adsorption Experiments

Before evaluating coal and char as adsorbents, studies were performed to assess the degree of leaching of organics from coal and char into solution. Samples were agitated for 96 hours in tap water, used to provide a degree of solution-ionic strength. The amount of leaching from coal was below detection limits for both phenols (< 1 mg/L) and TOC (< 10 mg/L). The amount of phenols leached from char was also below detection limits, but there was observable leaching of TOC. A maximum TOC concentration of 14 mg/L was leached when 200 g of char was equilibrated with tap water, and a linear response was observed. As more char was added to tap water, the equilibrium TOC concentration increased, so that 0.739 mg/L of TOC were leached per gram of char. Therefore, high doses of char used with dilute wastewaters could result in substantial leaching of organics into

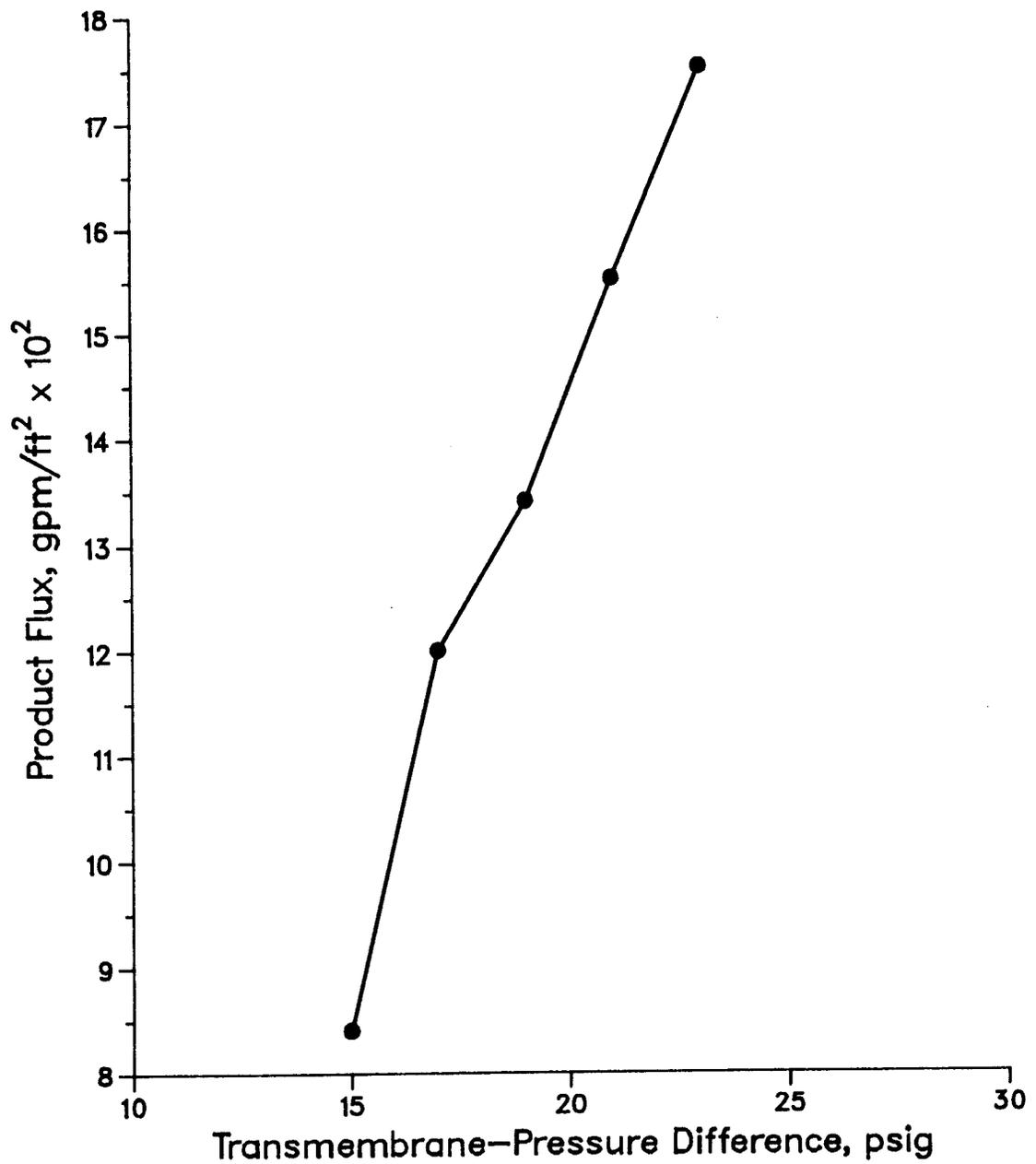


Figure 11. Effect of Variable Transmembrane-Pressure Difference on Product Flux During Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion; $P_{Loss}=10$ psi)

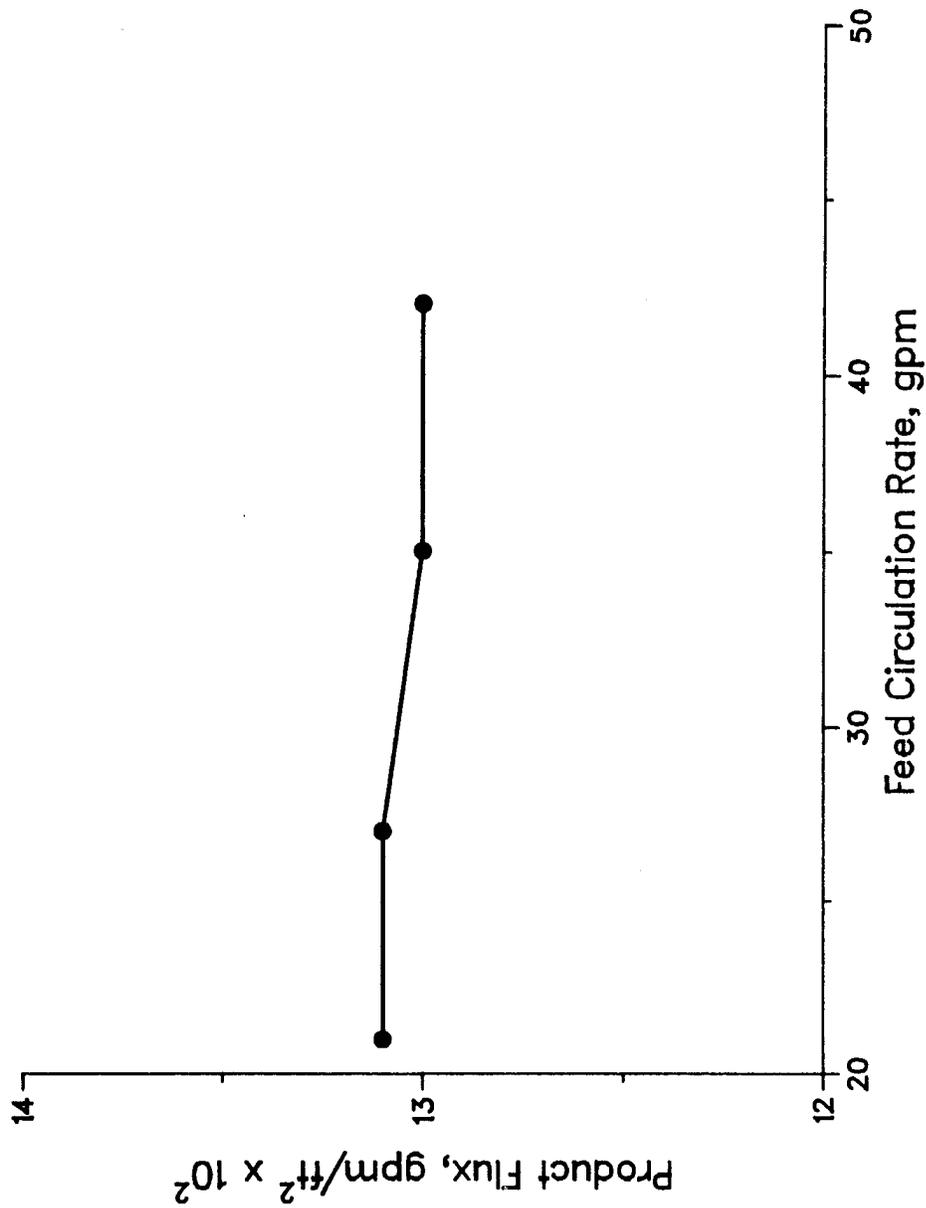


Figure 12. Effect of Variable Feed-Circulation Rate on Product Flux During Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion; $\Delta P=19$)

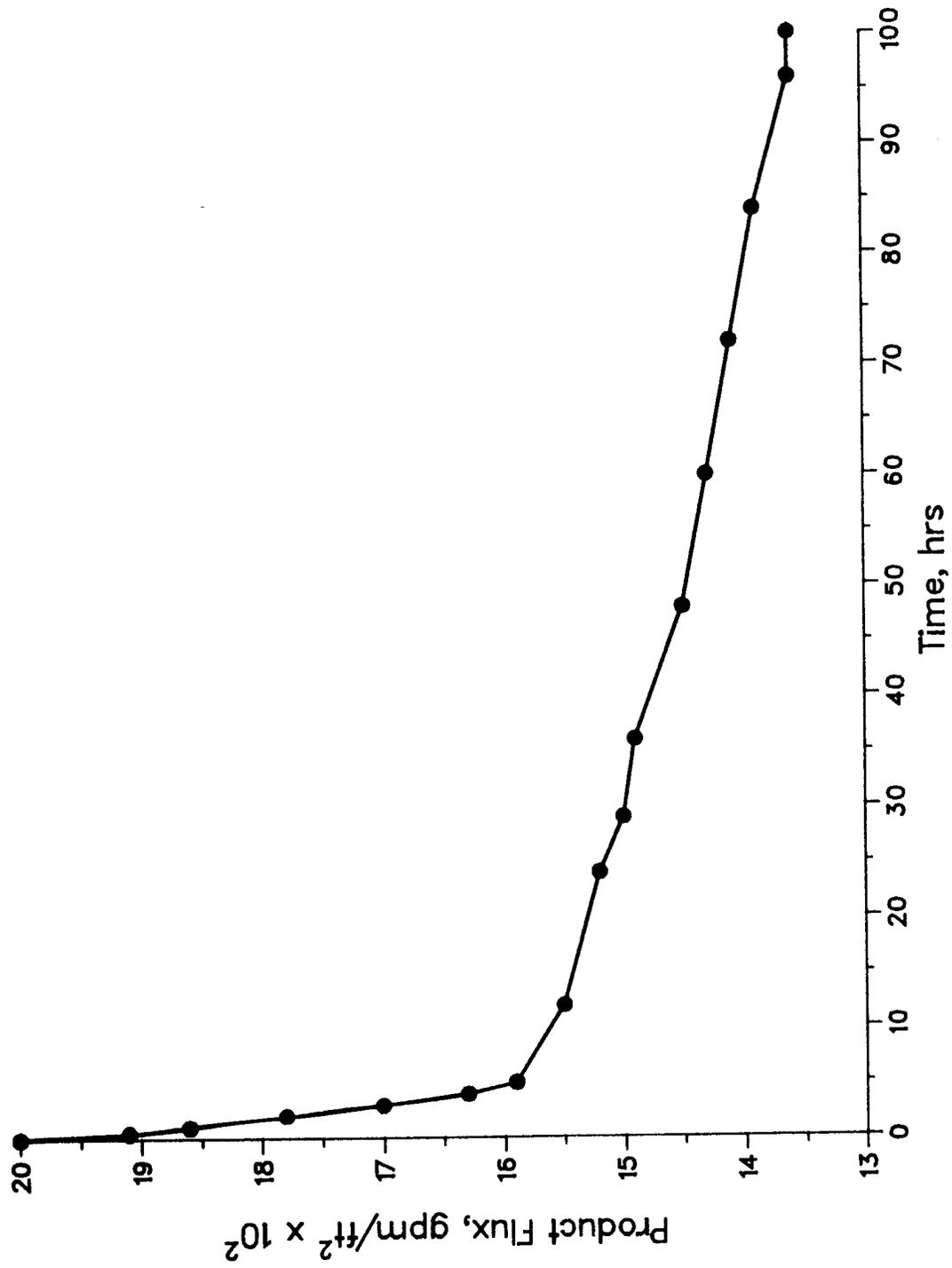


Figure 13. Effect of Elapsed Time on Product Flux During Treatment of Simulated Wastewater by Microporous Filtration with PAC Addition (50% Conversion)

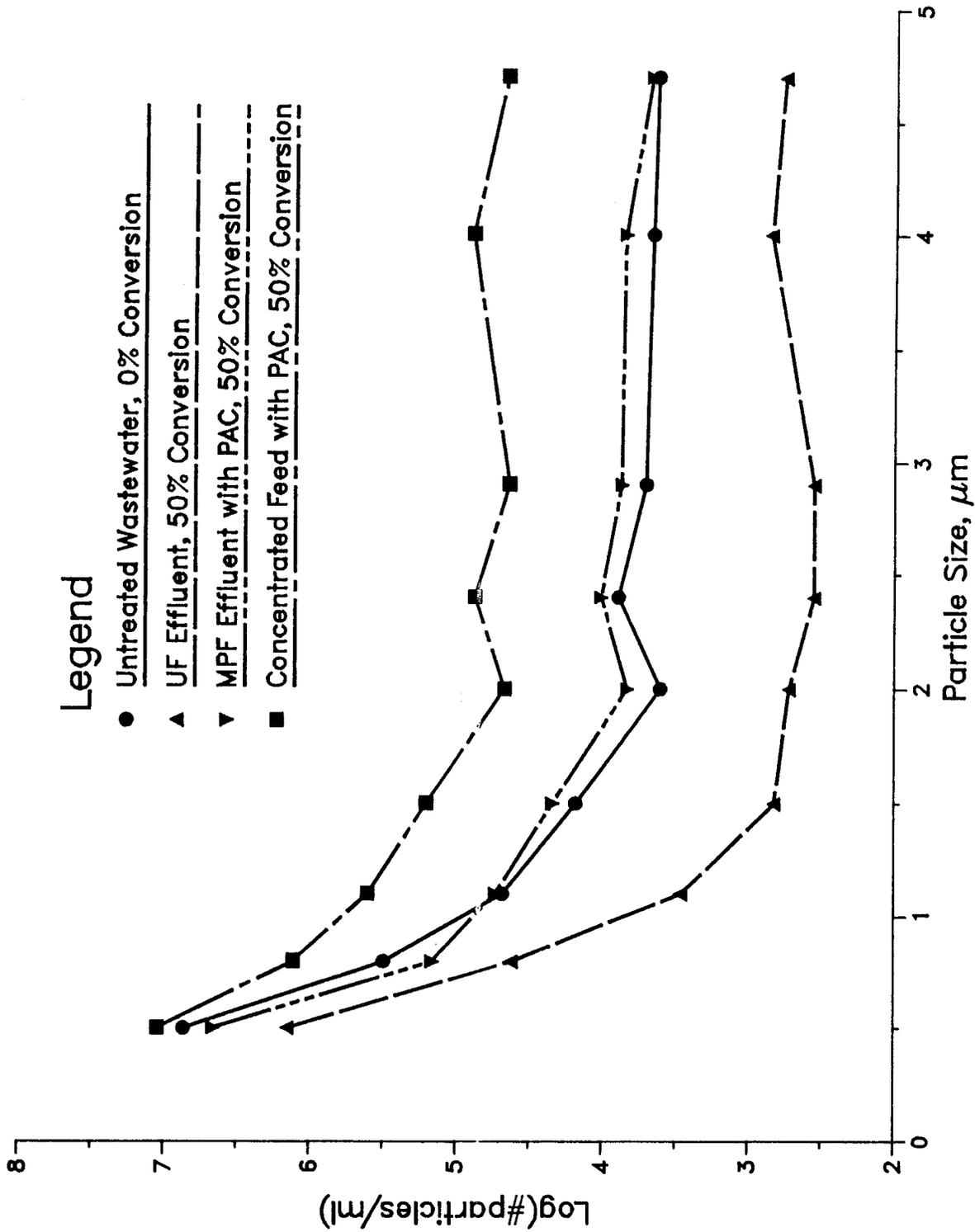


Figure 14. Log Concentrations of Particles in Untreated Simulated Wastewater and Various Effluents Treated by Cross-Flow Filtration

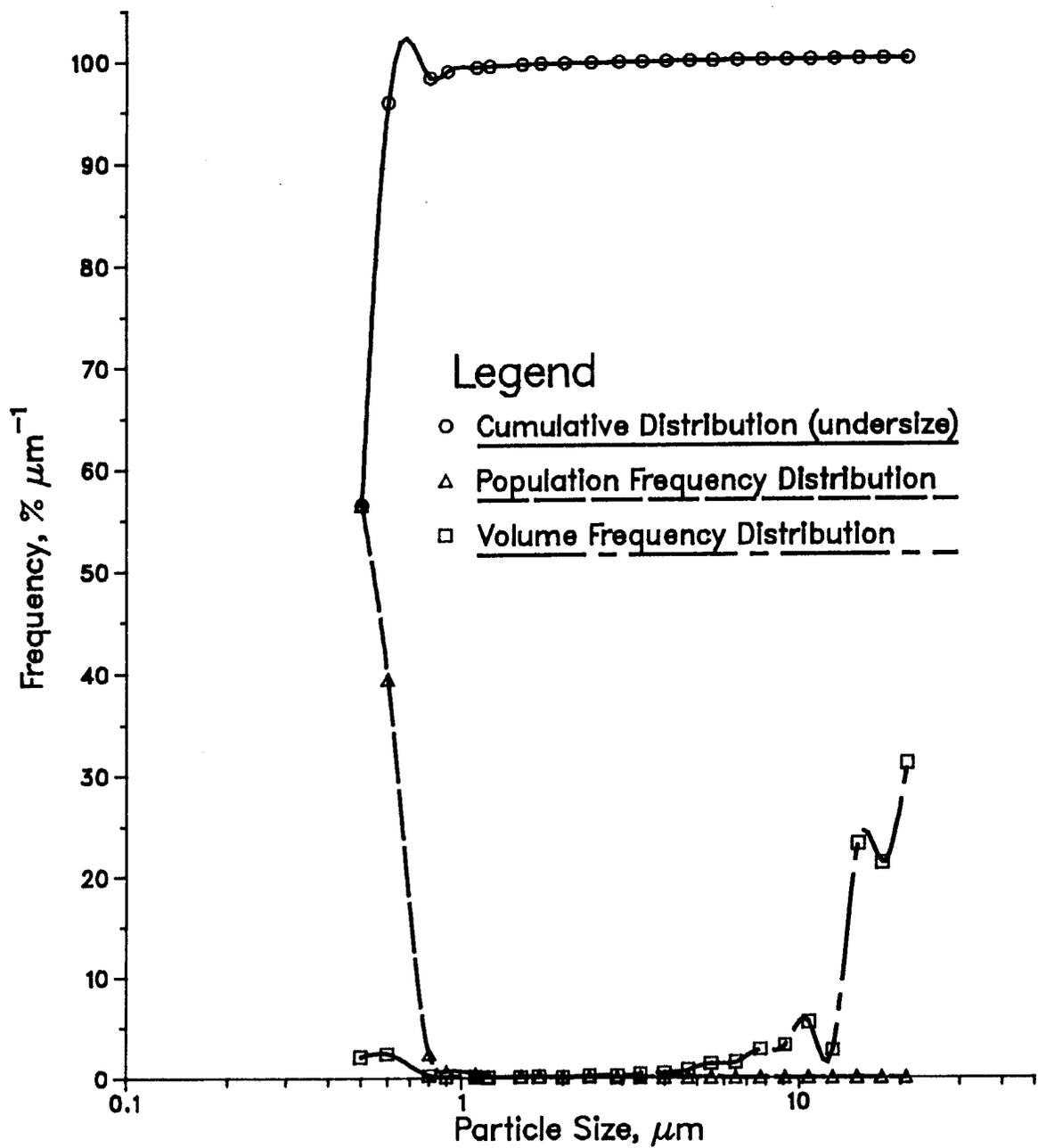


Figure 15. Cumulative and Frequency Distributions from Particle Size Analysis of Untreated Simulated Wastewater

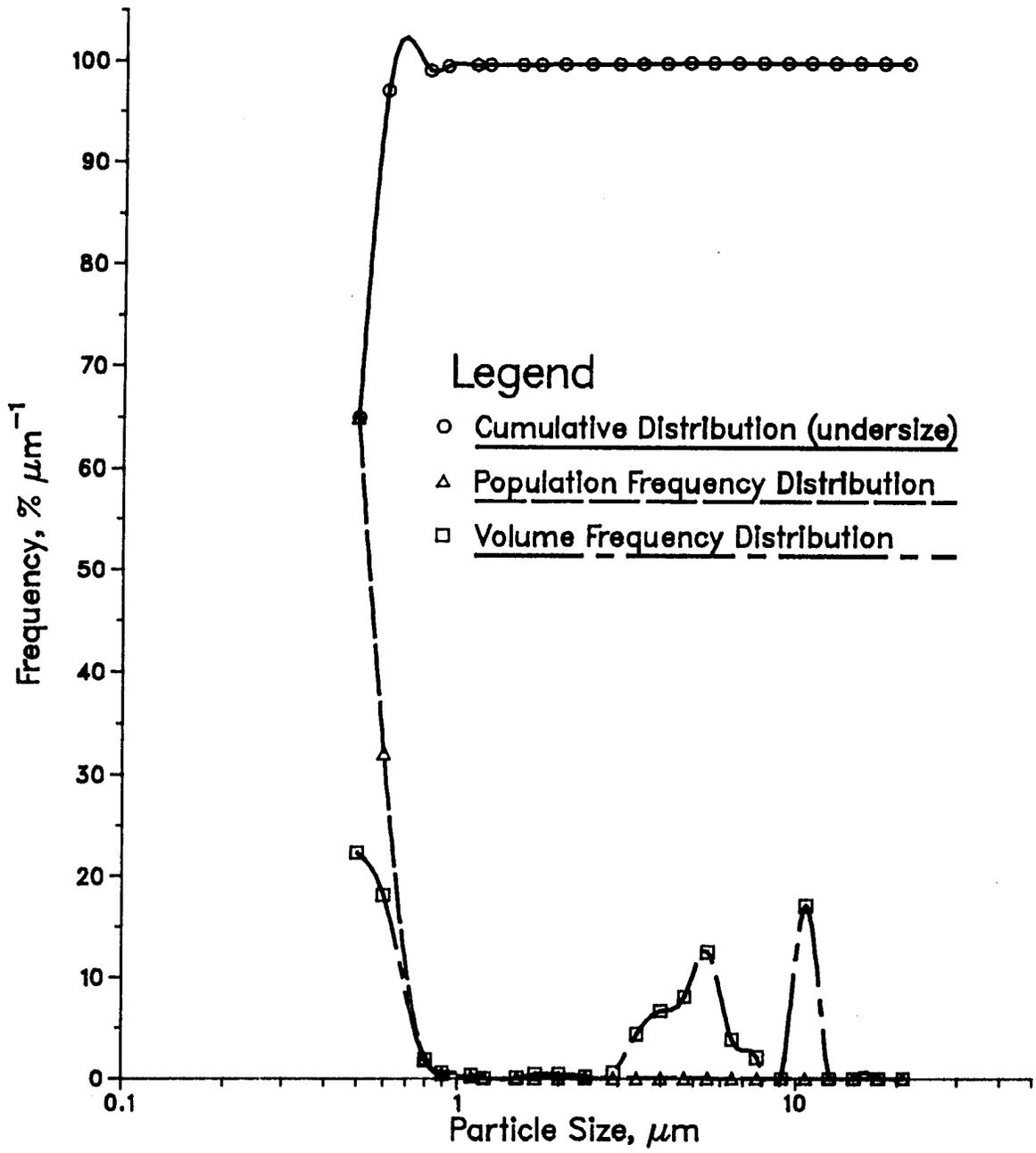


Figure 16. Cumulative and Frequency Distributions from Particle Size Analysis of Simulated Wastewater Treated by Ultrafiltration

solution. This could impair the effectiveness of char as an adsorbent.

Equilibrium-Uptake Tests

Equilibrium-uptake tests were performed with coal and char in simulated wastewater to determine the time required for most of the contaminants to be adsorbed. Adsorbent dose was 100 g/L. Most of the TOC and phenol were adsorbed onto coal after 96 hours. Equilibrium o-cresol and m-, p-cresol concentrations occurred after 48 hours. Equilibrium-uptake tests using char yielded similar results, except that the concentrations equilibrated after 24 hours.

Batch-Isotherm Tests

Batch-isotherm tests were performed to derive data for Langmuir and Freundlich adsorption models. The tests lasted 96 hours to ensure that all components had equilibrated with the wastewater. Either coal or char was added to simulated wastewater or Hanna IVB condensate. The characteristics of the simulated wastewater, comprised of Hanna IVB condensate and Hanna groundwater, are shown in Table 7. Carbon dose was varied from 0.57 to 20 g/L during the batch-isotherm tests. The Langmuir constants, b and $(X/M)_m$, and the Freundlich constants, n and k , were derived from the batch tests (Table 11). Linear-correlation coefficients (r^2), calculated for each isotherm, indicate how well the experimental data fit the models.

Coal in Simulated Wastewater. Batch tests of coal in simulated wastewater indicate that, for TOC, the isotherm data fit the Langmuir and Freundlich models equally well. The Langmuir isotherm yielded an r^2 value of 0.951 and the Freundlich isotherm an r^2 of 0.953 (Table 11). Adsorption of phenol from the simulated wastewater, however, yielded a nonlinear response for both isotherms, probably because phenol does not dominate the adsorption characteristics of the simulated wastewater. Because the simulated wastewater is a complex mixture, adsorption onto coal may be best described by the TOC isotherms.

Adsorption of o-cresol from the simulated wastewater onto coal was better described by the Langmuir isotherm ($r^2 = 0.922$) than the Freundlich isotherm ($r^2 = 0.868$). The adsorption of m-, p-cresol from simulated wastewater onto coal was not adequately described by either isotherm.

The maximum TOC removal obtained with batch tests employing coal and simulated wastewater (71.4%) occurred with the 200 g/L coal dose (Table 12). Phenols removals varied from >94.4 to >98.9% with carbon doses of 170-200 g/L.

Char in Simulated Wastewater. Batch tests employing char in simulated wastewater indicate that the Freundlich isotherm better describes the adsorption of TOC ($r^2 = 0.934$). The Langmuir isotherm yielded an r^2 value of 0.890 (Table 11). A nonlinear response was obtained for all other components in the simulated wastewater.

Table 11. Adsorptive Constants and Correlation Coefficients from Langmuir and Freundlich Isotherms Generated by Batch-Isotherm Tests

Test	Constituent	Langmuir Isotherm			Freundlich Isotherm		
		r^2	b, L/mg	(X/M) _m , mg/mg	r^2	n	K
Coal in Simulated Wastewater	TOC	0.951	0.00197	0.0067	0.953	1.16	2.05×10^{-5}
	Phenol	NL ^a	--	--	NL ^a	--	--
	o-Cresol	0.922	0.204	2.41×10^{-4}	0.868	3.04	7.42×10^{-5}
	m, p-Cresol	0.594	0.436	6.01×10^{-4}	0.512	4.18	2.78×10^{-4}
Char in Simulated Wastewater	TOC	0.890	0.00633	0.0113	0.934	1.18	1.00×10^{-4}
	Phenol	NL ^a	--	--	NL ^a	--	--
	o-Cresol	NL ^a	--	--	NL ^a	--	--
	m, p-Cresol	NL ^a	--	--	NL ^a	--	--
Coal in Hanna IVB condensate	TOC	0.321	-1.65×10^{-4}	4.74×10^{-4}	0.215	0.280	1.79×10^{-15}
	Phenol	0.886	-4.10×10^{-4}	-8.22×10^{-4}	0.863	0.0820	1.73×10^{-43}
	o-Cresol	0.876	-0.00225	-1.96×10^{-4}	0.888	0.0885	9.00×10^{-33}
	m, p-Cresol	0.929	-7.04×10^{-4}	-8.39×10^{-4}	0.884	0.120	1.02×10^{-28}
Char in Hanna IVB condensate	TOC	0.243	1.36×10^{-4}	0.323	0.369	0.789	3.47×10^{-7}
	Phenol	0.686	-3.10×10^{-4}	-0.00258	0.660	0.221	4.72×10^{-18}
	o-Cresol	0.717	-7.25×10^{-4}	-0.00508	0.689	0.514	2.12×10^{-8}
	m, p-Cresol	0.665	-7.59×10^{-5}	-0.0576	0.664	0.633	8.82×10^{-8}

^a nonlinear response

Table 12. TOC and Phenol Removal Data from Batch Isotherm Tests with Coal and Char

Test	Constituent	Minimum Effl. Conc., mg/L	Removal, %	Amount of Contaminant Removed, mg ^a	Carbon Dose, g/L
Coal in simulated wastewater	TOC	50	71.4	125	200
	Phenol	< 1	> 98.9	> 89.9	170
	o-Cresol	< 1	> 94.4	> 16.9	200
	m, p-Cresol	< 1	> 97.5	> 39.0	170
Char in simulated wastewater	TOC	13	92.6	163	160
	Phenol	< 1	> 99.0	> 99.0	120
	o-Cresol	< 1	> 94.0	> 15.7	90
	m, p-Cresol	< 1	> 97.0	> 32.3	90
Coal in Hanna IVB condensate	TOC	3,620	11.2	457	200
	Phenol	1,990	24.9	660	200
	o-Cresol	351	28.4	139	200
	m, p-Cresol	1,040	31.1	470	200
Char in Hanna IVB condensate	TOC	3,120	37.5	1,870	200
	Phenol	1,850	47.8	1,690	200
	o-Cresol	256	30.2	111	200
	m, p-Cresol	753	50.1	757	200

^afor indicated dose

Leaching of organics may have increased the complexity of the wastewater during these tests, so specific constituents inadequately represent the adsorption characteristics of this system.

The maximum removal of TOC during this test (92.6%) occurred with the 160 mg/L char dose (Table 12). Removals of phenols from the simulated wastewater onto char varied from >94.4 to >99.0% with carbon doses of 90 to 120 g/L.

Char was more efficient than coal for adsorbing TOC and phenols from the simulated wastewater. This contradicts results of Manahan et al. (1980), who reported coal to adsorb organic contaminants more efficiently than char. In Manahan's study, relatively high levels of TOC were leached from char into distilled water and simulated wastewater, reducing net adsorption. Smaller amounts of TOC were leached from char during the research reported herein.

Coal in Hanna IVB Condensate. Batch tests performed with coal and Hanna IVB condensate indicate that both the Langmuir and Freundlich isotherms effectively describe the adsorption of phenols o-cresol, and m-, p-cresol (Table 11). Values of r^2 for these

constituents ranged from 0.876 to 0.929 with the Langmuir isotherm and from 0.863 to 0.888 with the Freundlich isotherm (Table 11). The Freundlich isotherm calculated from phenol adsorption data yielded a K value of 1.73×10^{-4} . The extremely low values of K from the Freundlich isotherms suggest that the combination of char and Hanna IVB condensate is very complex.

Phenols were less efficiently removed by coal from Hanna IVB condensate (24.9 to 31.1%) than from simulated wastewater (>94.4 to >98.9%) (Table 12). Absolute removal of phenols was greater with the Hanna IVB condensate, however. For example, 660 mg of phenol was absorbed from Hanna IVB condensate, while approximately 90 mg of phenol was adsorbed from simulated wastewater, at the indicated coal doses.

Adsorption of TOC from Hanna IVB condensate onto coal was inadequately described by either isotherm. The Langmuir isotherm yielded an r^2 value of 0.321, while the Freundlich isotherm yielded an r^2 of 0.215 (Table 11). The reason for the poor response with TOC is not known, but the number of solutes, relative adsorbabilities, relative contributions to total TOC, and extent of competition among solutes for adsorption sites all affect the shape of an isotherm (Perrich 1981). Thus, phenol may better indicate the adsorptive characteristics of the Hanna IVB condensate because it is the dominant organic solute in the wastewater.

The maximum TOC removal by coal (11.2%) occurred with the 200 g/L dose (Table 12). This percentage is much less than obtained with simulated wastewater (71.4%). Absolute removal of TOC was greater with Hanna IVB condensate (457 mg) than with simulated wastewater (125 mg), however, for the indicated coal doses.

Char in Hanna IVB Condensate. Batch tests revealed that the Langmuir and Freundlich isotherm models inadequately described the adsorption of organic contaminants from Hanna IVB condensate onto char. Values of r^2 for phenols varied from 0.665 to 0.717 with the Langmuir isotherm and from 0.660 to 0.689 with the Freundlich isotherm (Table 11). Leaching of contaminants from char may have increased the complexity of the wastewater, so use of specific constituents to describe adsorptive characteristics was inappropriate.

Phenols removal varied from 30.2 to 50.1% during these tests, less than observed with simulated wastewater (Table 12). However, absolute removal of phenols was greater with Hanna IVB condensate.

Values of r^2 generated with TOC adsorption data from tests with char and Hanna IVB condensate were very low. These were 0.243 and 0.369, respectively, for the Langmuir and Freundlich isotherms (Table 11). The complexity of the Hanna IVB condensate may have been increased by leaching of organics from char, causing the poor response observed with TOC.

Maximum TOC removal by char from Hanna IVB condensate was 37.5% (Table 12), which is significantly less than TOC removal by char from

simulated wastewater, 92.6%. Absolute removal of TOC was greater with the more concentrated wastewater, however.

CONCLUSIONS

Coagulation-Precipitation

Polymers DEAE Dextran and Dow Purifloc C-31 effectively removed particles and acetone-soluble tar from Hanna IVB UCG condensate. The optimum dose for the two polymers was 50 and 60 mg/L, respectively. Increasing polymer dose resulted in first decreasing, then increasing levels of particles and acetone-soluble tar. This suggests that colloid destabilization occurred by the mechanisms of charge neutralization and interparticle bridging. Coagulation-precipitation is recommended to treat Hanna IVB condensate before further processing by hot-gas stripping, carbon adsorption, and membrane-separation methods.

Reverse Osmosis

Reverse osmosis processing of untreated Hanna groundwater resulted in significant fouling of membranes, declining product flux, and smaller reductions of conductivity and TDS. Pretreatment, consisting of hydrated-lime and soda addition to the Hanna groundwater, greatly improved the effectiveness of the RO process. No significant decline in flux was observed during experiments for which pretreatment was used. Reductions of conductivity and TDS were greater than 99% with operating pressure equal to 400 psi and conversion rate equal to 75%. Reverse osmosis is recommended for reduction of sulfate and TDS in UCG-affected groundwater to prior-use conditions. After processing by reverse osmosis and subsequent pH adjustment, the groundwater should be suitable for injection into the aquifer.

Cross-Flow Filtration

Ultrafiltration experiments with simulated wastewater yielded moderate removals of acetone-soluble tar. Acetone soluble tar was reduced by 77.0% during a flow-excursion experiment for which the 50% conversion rate was used. This value is similar to those reported for coagulation-precipitation experiments with simulated wastewater (Nolan and Wolf 1985). Removal of soluble organics by UF was less than desired, however. Total organic carbon, dissolved organic carbon (DOC), and phenols permeated the UF membrane.

Pretreatment with PAC markedly improved rejections of TOC, DOC, and phenols by MPF. Phenol, o-cresol, and m, p-cresol were reduced to less than 1 mg/L with this configuration.

Ultrafiltration, because of the smaller pore size of the UF membrane, more effectively removed 0.5-5.0 μm -diameter particles than MPF. Volume-frequency distributions indicated that larger particles are more likely to be removed by UF. Concentrated MPF feed contained the largest number of particles because PAC fines remained in

suspension. Microporous filtration removed most of the particles, but residual fines remaining in the wastewater caused MPF effluent to contain slightly more particles ($>1.1 \mu\text{m}$) than untreated wastewater. Further research is recommended to evaluate the ability of UF to remove PAC fines from pretreated wastewater before processing by other treatment methods.

Carbon Adsorption

No TOC or phenols were detected in tap water during leaching tests with coal. Leaching tests with char indicated that 0.739 mg/L of TOC per gram of adsorbate was released into tap water. Equilibrium-uptake tests with coal and char indicated that most of the TOC and phenols in the simulated wastewater were adsorbed after 96 hours. Total organic carbon data from tests using coal and simulated wastewater were described very well by both Langmuir and Freundlich isotherms. The characteristics of TOC adsorption onto char were best described by the Freundlich isotherm. Neither isotherm model adequately described the adsorption of TOC from Hanna IVB condensate onto coal or char. The extremely low K values obtained during batch isotherm tests with coal and Hanna IVB condensate suggest that this wastewater is very complex. This complexity may have caused the poor response observed with the TOC data. Char adsorbed TOC from simulated wastewater more efficiently than coal on a percentage basis, but high removals occurred with both adsorbents. Relatively low removals of TOC and phenols occurred when coal and char were equilibrated with Hanna IVB condensate. Char may be less expensive than conventional activated carbon. Further research is recommended to assess the suitability of this adsorbent with continuous-flow operations.

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