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Research Report No. 120

CHARGED MEMBRANE, LOW PRESSURE ULTRAFILTRATION TO TREAT ACID MINE DRAINAGE WATERS

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May 1979

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ABSTRACT

Title: Charged Membrane, Low Pressure Ultrafiltration to Treat Acid Mine Drainage Waters

Low-pressure ultrafiltration with negatively-charged, non-cellulosic membranes is shown to be a feasible process in terms of achieving the simultaneous separation of dissolved metals (and sulfate) and of suspended solids from acid mine drainage water. The process is evaluated in terms of the simultaneous achievement of good water flux without membrane fouling and of adequate ultrafiltrate quality at high water recovery for water reuse operation.

At a transmembrane pressure of 5.6×10^5 N/m^2, water fluxes in the range of 5.8×10^{-4} cm/sec to 12.5×10^{-4} cm/sec could be obtained at 97% water recovery. The results of the ultrafiltration investigations are compared with the reported results from lime precipitation-settling and reverse osmosis treatment field studies in terms of treated water quality, reusability, concentrate (sludge) production rates, water recovery and membrane flux behavior. With a lime precipitation-settling process the treated water would be saturated with calcium sulfate.

Descriptors: Acid Mine Water, Membrane Processes, Chemical Precipitation, Water Reuse, Waste Water Treatment, Reverse Osmosis

Identifiers: Charged Membrane Ultrafiltration, Water Recovery

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

Figure Page

Figure Page

I. INTRODUCTION

Acid mine water is a problem of critical significance in most of the coal producing regions. The construction of coal conversion plants will produce a greatly increased demand for both coal (1) and water and will provide a great impetus for the recycle and reuse of treated acid mine drainage water. Acid mine water is produced by oxidation and hydrolysis of pyrite (FeS_2) exposed during coal mining. The resulting acid water, containing H_2SO_4, Fe^{2+}, and Fe^{3+}, dissolves various metals (Ca, Mg, Al, Mn, etc.) from the surrounding strata and produces highly contaminated water containing SO_4^{2-}, H^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, and other heavy metal ions.

Charged membrane ultrafiltration provides a unique and broadly-applicable technique for the simultaneous separation of various inorganic metal ions (including precipitates) present in industrial wastewaters. Negatively-charged, anistropic, non-cellulosic membranes (10×10^{-8} cm to 20×10^{-8} cm pore widths) provide high water flux and adequate rejections of metals (and sulfate) at low transmembrane pressures (5×10^5 N/m^2 to 7×10^5 N/m^2). This process is particularly appropriate for applications requiring water reuse in which completely demineralized water is not warranted.

The separation of ionic solutes by charged ultrafiltration membranes is due to repulsion of coions by the fixed charged groups in the membrane skin. The attainment of adequate separation at low pressure without membrane compaction problems and the non-fouling nature with solutions containing high concentrations of suspended solids are attractive features of charged membranes. These membranes are primarily suitable for dilute to moderately-concentrated solutions of low effective osmotic pressures. Reverse osmosis membranes (operated at pressures above 3×10^6 N/m^2), in contrast, are used for water desalination and/or for wastewaters of high osmotic pressures for which very high rejections (98.0 to 99.9%) of all inorganic ions are desired.

The treatment of acid mine waters by charged membrane ultrafiltration for the purpose of water reuse is a very promising application. Various physicochemical treatment methods have been reported in the literature and are summarized in Table 1. Most treatment methods are primarily directed towards removal of acidity and iron (the lime neutralization process) or for the production of a very high quality water (the reverse osmosis process). The lime (or limestone) neutralization process produces water containing high dissolved solids, saturated calcium sulfate (leading to scale formation problems), and colloidal hydroxide

TABLE 1

Acid Mine Water Treatment Processes

Process	Reference
Lime precipitation	2,3
Limestone precipitation	2,3,4,5
Lime-limestone precipitation	3,4
Sodium hydroxide precipitation	6
Soda ash precipitation	2
Lime-soda precipitation	7
Alumina-lime-soda	8
Ion Exchange	9
Reverse Osmosis	10-19
Reverse Osmosis + Lime precipitation (Neutrolosis)	10,20
Electro-biochemical neutralization	21

precipitates, and the treated water is not suitable for industrial reuse. The high pressure reverse osmosis process produces a high quality demineralized water, but the water flux drop due to the calcium sulfate and iron hydroxide fouling problem limits water recovery.

II. OBJECTIVES OF THIS INVESTIGATION

The overall objective of this investigation is the experimental evaluation and development of the ultrafiltration unit to treat acid mine waters (over a broad concentration range), providing a degree of treatment sufficient for water reuse and for the concommitant elimination of some of the problems inherent to the reverse osmosis and/or lime neutralization processes.

Extensive bench-scale experiments with non-cellulosic, negatively-charged ultrafiltration membranes (with broad pH tolerance limits) in a bench-scale, continuous flow unit are conducted with synthetic and actual acid mine wastes to determine solute rejection and ultrafiltrate water flux characteristics. Laboratory studies involving lime precipitation-settling process and precipitation-settling-ultrafiltration process are also made to establish the feasibility of designing a combination ultrafiltration-settling operation. Computer simulations are also conducted to establish metal removals at various water recoveries, and to establish the feasibility of using an ultrafiltration process to reuse the treated mine waste. The results of the ultrafiltration investigations are compared with the reported results from the lime precipitation-settling and reverse osmosis treatment processes in terms of treated water quality, reusability, concentrate (sludge) production rates, water recovery, and membrane flux behavior.

The stoichiometry of Equation (1) shows that one mole of iron disulfide oxidizes in the presence of oxygen and water to produce two moles of acidity. The ferrous iron (Fe^{2+}) oxidizes further to form ferric (Fe^{3+}) iron, which reacts with water to form a ferric hydroxide precipitate and three additional moles of acidity are generated in accordance with Equation (3). It has also been shown that the iron disulfide can reduce the ferric iron according to Equation (4) with the release of sixteen moles of acidity. The overall reaction is:

$$2FeS_2(s) + 15/4\ O_2 + 14Fe^{3+} + 11\ 1/2\ H_2O \rightarrow 4SO_4{}^{2-} + 20H^+ + 15Fe^{2+} + Fe(OH)_3(s) \qquad (5)$$

It can be seen that only two moles of iron disulfide can produce sixteen moles of acidity, yielding the extreme acidity of the resulting drainage.

A schematic diagram illustrating the steps in the oxidation process for an underground mine appears in Figure 1 (25). During the mining process the pyrite may not be completely exposed; it may still be covered by shale or other porous media. The oxygen is transported to the pyrite surface by either forced convection, if there is a forced draft of air through the porous media, or molecular diffusion. If there is a water film covering

III. FORMATION OF ACID MINE WASTE

The occurrence of acid mine drainage in a particular mine and its quality are highly dependent upon the chemical content of the coal and its paleoenvironment. Some coals and the surrounding strata contain iron disulfide in the form of pyrite that, when exposed to oxygen in a humid environment oxidizes to form hydrous iron sulfates. The natural water movement in the mine dissolves these sulfates which react to form the highly acidic drainage. Although this explanation is generally accepted as the mechanism by which acid mine drainage is formed, due to the many factors affecting the formation, the exact chemical equations are not fully understood.

A. Qualitative Model

Singer and Stumm (24) have shown the reaction of iron disulfide (pyrite) and the generation of acidity are given by the following equations:

$$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightleftarrows Fe^{3+} + 1/2\ H_2O \qquad (2)$$

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3(s) + 3H^+ \qquad (3)$$

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15\ Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

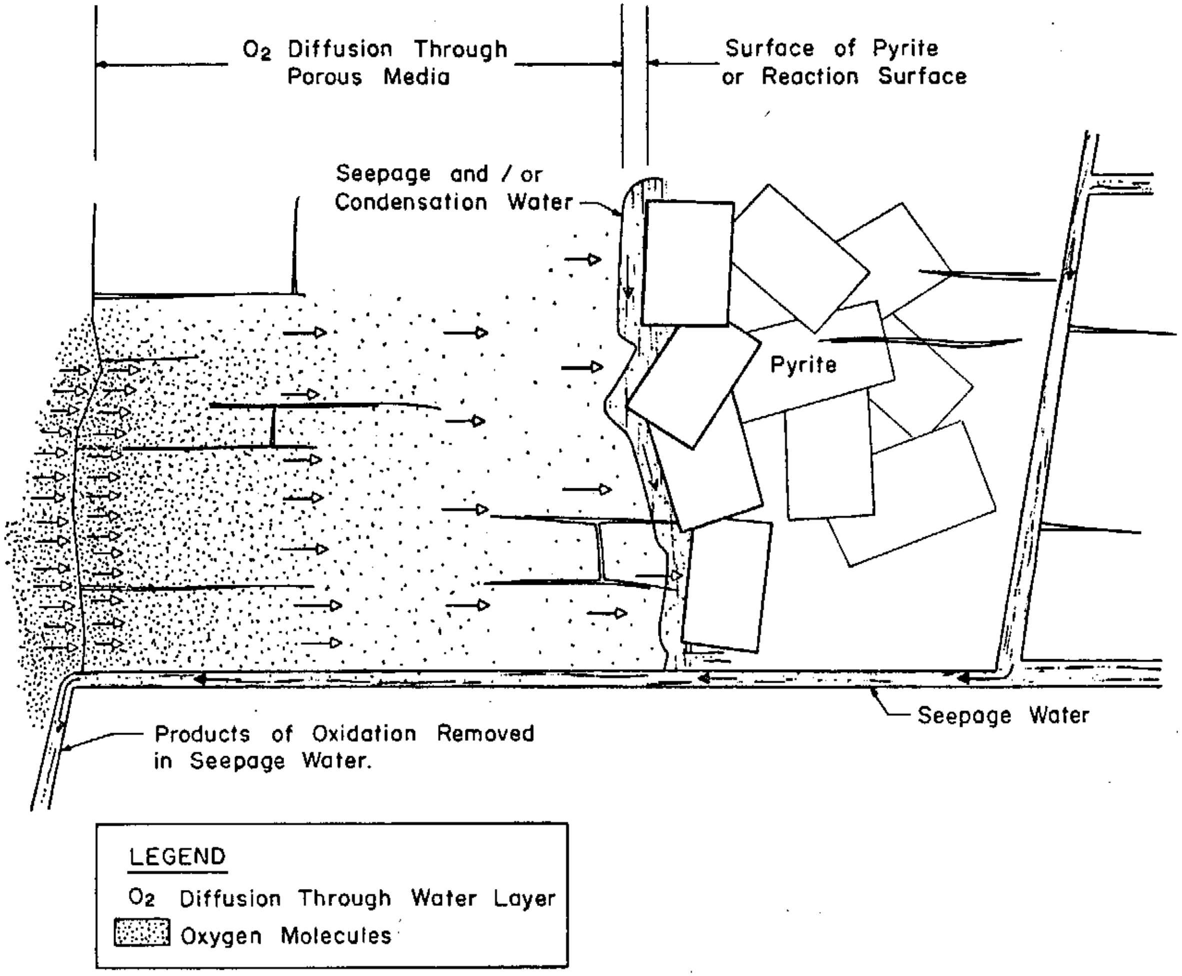


Figure 1. Steps of Pyrite Oxidation in the Formation of Acid Mine Water (25)

the pyrite surface, the oxygen must also diffuse through this layer. Since the diffusivity of oxygen in water is low, a water film of thickness greater than one or two centimeters effectively seals off the pyrite from any type of oxidation.

B. Factors Affecting Waste Quality

1. Mode of Occurrence of Pyrite

The sulfur content of a coal sample can be broken into three types: (1) organic sulfur, (2) pyritic sulfur, and (3) sulfate sulfur. Organic sulfur is usually not chemically reactive. Pyritic sulfur is that component which is found in the disulfide phase. Sulfate sulfur represents the weathering products of the disulfide phase. Mansfield and Spackman (26) have shown that, in bituminous coal samples collected in coal fields of Western Pennsylvania, the pyritic sulfur content varied with coal seam position.

Carrucio (27) studied samples from strip mine areas in Central Pennsylvania; one area containing acid producing mines, the other non-acid drainages. In the samples collected from the acid producing regions, the pyrite occurred in clusters of spheres approximately 25.0 μm in diameter. Each sphere contained an agglomeration of smaller crystals approximately 0.25 μm in diameter. This type of pyrite was studied by Gray, Shapiro and Coe (28), and was identified as framboidal pyrite.

Carrucio (29,30) also showed that framboidal pyrite is much more reactive than other types. Later studies by Carrucio (31) indicated that the acid producing potential of a coal seam can be measured by the percentage of framboidal pyrite multiplied by the total sulfur content in a sample from the seam.

2. Type of Mines

There are two types of natural pyritic systems: (1) pyrite is left in place but exposed to an oxidizing environment as encountered in underground mines, and (2) relocated pyrite materials, such as are found in strip mines, spoil piles and refuse piles. Both are the subject of a review by Shumate and Brant (25).

Underground mines are the most complex of the pyritic systems. The quality and volume of drainage produced are dependent upon the amount and type of pyrite available, the degree to which the pyrite is exposed, the rate at which the pyrite surfaces are refreshed, the location and flow of underground water and the location of the air entrance into the mine. Underground mines are particularly susceptible to seasonal variations in climactic conditions.

Fluid (air and water) transport in an underground mine is an important factor in the occurrence of acid mine drainage. The permeability and porosity of the overburden allows for both air and water transport. Water transport through the mine is a gravity phenomenon. Infiltrating water may move horizontally at times, but its course is basically downward. The path of natural drainage through a mine is a function of its geologic structure and gravity.

In strip mines the oxygen transport is restricted to the pyrite relatively close to the surface of the high wall. However, during strip mining the major source of pollution is the spoil pile. The physical characteristics of the spoil pile provide easy air (oxygen) access and susceptibility to flushings during periodic precipitation.

Refuse piles are similar to spoil piles with the exception that the pyrite content is often higher. Pyritic materials are distributed throughout the pile; however, the reaction zone is limited to a narrow region near the surface.

3. Calcareous Material in the Surrounding Strata

The acidic quality of the drainage emanating from a particular mine is a strong function of the potential for the overlying strata to produce alkalinity. At a certain partial pressure of CO_2 in the infiltrating water, reaction can occur between the water and the calcareous material ($CaCO_3$) as given by Garrels and Christ (32),

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- \tag{6}$$

$$HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^- \tag{7}$$

The amount of alkalinity (H_2CO_3) produced is limited by the solubility of calcium carbonate in water at the pH of the water. In general, if the acidity is less than the alkalinity that can be produced, the drainage will be neutral; if the amount of acidity is greater, the resulting drainage will be acidic.

4. Biological Effects

The rate of iron oxidation, Equations (1)-(4), under normal conditions is quite slow; however, certain Autrotrophic microorganisms known as iron bacteria, can increase the rate of these reactions by a factor as large as 10^6, (24). <u>Thiobaccillus-Ferrobacillus</u>, iron bacteria, are a group of autotrophic chemosynthetic microbes that can survive in an acid water, pH <5.5, with only minimal amounts of nutrients available.

Oxidation of iron by the Ferrobacillus bacteria proceeds as follows:

$$Fe^{2+} \rightarrow Fe^{3+} + \text{electron} \qquad (8)$$

The ferric ion produced by this reaction can react with sulfide nonbiologically as follows:

$$8Fe^{3+} + S^{2-} + 4H_2O \rightarrow 8Fe^{2+} + SO_4{}^{2-} + 8H^+ \qquad (9)$$

The ferric ion is reduced back to the ferrous ion, making it again available for oxidation by the bacteria.

Acid can also be produced by the microbiological oxidation of sulfur compounds. A review showing the production of H^+ and $SO_4{}^{2-}$ resulting from bacterial metabolism of reduced sulfur compounds is given by Dugan and Randles (25).

5. Seasonal Variation

During an infiltrating rainfall or a spring thaw, water passes over various rock types and rinses the weathering products from the surface. The water retained by capillary forces in contact with the rock surfaces creates an environment conducive to the formation of acidity and alkalinity. This environment of chemical reactivity remains intact until flushed by a new water front and replaced by fresh water. Geidel and Carrucio (33) have shown that the interval between each successive flushing of the rock surfaces is a determining factor in the quality of the resulting drainage.

Since the productions of acidity and alkalinity are strong functions of the time between successive flushings of the respective sites, the drainage from a single mine can be expected to change with climactic changes. During seasons with recurrent rainfall, the drainage may be less acidic. At the end of a long period of negligible precipitation, the drainage may be very acidic. Typical seasonal variations in drainage quality is shown in Table 2 (11).

C. Expected Waste Quality

The cation exchange capacity of the materials in the overburden, the dissolution of clay minerals and heavy metals content of the coal and surrounding strata determine the metal content of the drainage. Geidel (34) has found that during the weathering process, aluminum silicate minerals dissolve liberating hydroxides to produce alkalinity as follows:

$$Al_2Si_2O_5(OH)_4 + 5H_2O \rightleftarrows 2Al^{3+} + 2H_4SiO_4(aq) + 6OH^- \qquad (10)$$

TABLE 2

Typical Seasonal Variations of Acid Mine Water Quality (11)

Season	pH	Acidity, mg/l as $CaCO_3$	Al, mg/l	Ca mg/l	Total Fe mg/l	Fe^{2+} mg/l	Mg mg/l	$SO_4{}^{2-}$ mg/l	TDS* mg/l
Winter	2.86	732	32	114	146	6.6	33	1040	1604
Spring	2.98	372	16	54	73	1.5	19	600	875
Summer	2.7	644	38.5	115	153	<1	38	936	--
Fall	2.8	357	26	72	74	<1	25	610	--

*Total Dissolved Solids

The aluminum remains in solution to add to the metal content of the drainage. The alkalinity produced during this process is available to neutralize the acidity in the drainage. The clay minerals in the shale overburden can exchange cations with cations (including H^+) in the drainage. Cations, such as calcium, sodium, potassium, iron and aluminum, are exchanged with the hydrogen ions from the drainage.

There is no "typical" acid mine drainage; however, all acid mine drainage has certain characteristics - high acidity (>400 mg/l as $CaCO_3$), iron (>100 mg/l), calcium (>200 mg/l), magnesium (>100 mg/l), manganese (>10 mg/l), aluminum (>40 mg/l), sulfate (>500 mg/l) and heavy metals such as copper, cadmium and zinc (<20 mg/l). The conductivity of the waste is usually greater than 800 µmho/cm and has a pH between 2.5 and 4.0. The iron in acid mine drainage is usually present in various Fe^{2+}/Fe^{3+} ratios. The EPA (35) has divided acid mine drainage into four classes according to their chemical makeup. These classes appear in Table 3.

TABLE 3

Mine Drainage Classes (35)

Component	Acid Discharges	Partially Oxidized and/or Neutralized	Oxidized and Neutralized and/or Alkaline	Neutralized and not Oxidized
pH	2-4.5	3.5-6.6	6.5-8.5	6.5-8.5
Acidity, mg/l as $CaCO_3$	1,000-15,000	0-1,000	0	0
Fe^{2+}, mg/l	500-10,000	0-500	0	50-1,000
Fe^{3+}, mg/l	0	0-1,000	0	0
Al^{3+}, mg/l	0-2,000	0-20	0	0
$SO_4{}^{2-}$, mg/l	1,000-20,000	500-10,000	500-10,000	500-10,000

IV. CHEMICAL PRECIPITATION

A. Theory

The removal of metals (Fe^{3+}, Fe^{2+}, Al^{3+}, heavy metals, etc.) and acidity neutralization from industrial wastewaters are often accomplished by hydroxide (lime) precipitation and subsequent settling. The principle behind this method of treatment is related to the solubility of precipitated metal hydroxide (or carbonate) in solution, which is a function of pH. With hydroxide addition to a solution, the metal ions undergo the following general reactions:

$$M^{2+} + OH^- \rightleftarrows M(OH)^+ \qquad (11)$$

$$M^{2+} + 2OH^- \rightleftarrows M(OH)_2(s) \qquad (12)$$

where M represents a metal. Some metal ions can also form polynuclear hydroxide species containing several metal atoms. This causes the equilibrium relationships for the above reactions to be non-linear. The hydroxide precipitates of many metals are amphoteric in nature and tend to dissolve at certain pH values because of the reaction

$$M(OH)_2(s) + OH^- \rightleftarrows M(OH)_3^- \qquad (13)$$

The specific pH value at which the precipitates dissolve varies with each metal. Baes and Mesmer have presented an excellent discussion on the hydrolysis of cations (36).

Figure 2 represents the pH dependence of the solubility of several metal hydroxide precipitates pertinent to acid mine drainage. Initially, for each metal, as the pH is raised, the metal ion concentration decreases, indicating precipitation. However, the curves representing Al^{3+}, Fe^{2+}, and Fe^{3+} go through a minimum. This is due to the amphoteric nature of the precipitates. For the most effective separation of the metals from the solution, the pH should be adjusted to the point where the distribution curve is at its minimum. Since all of the curves do not reach a minimum at the same pH, a compromise must be reached as to the operating pH. For acid mine drainage work, the operating pH may be determined by comparing the amount of metal in the solution to the amount allowed by the discharge standards and selecting an optimum pH where concentrations of all the species are within acceptable limits. It should also be noted that the overall separation of metals is not only dictated by solubility phenomena but also by the effectiveness of a precipitation (such as settling basins) process.

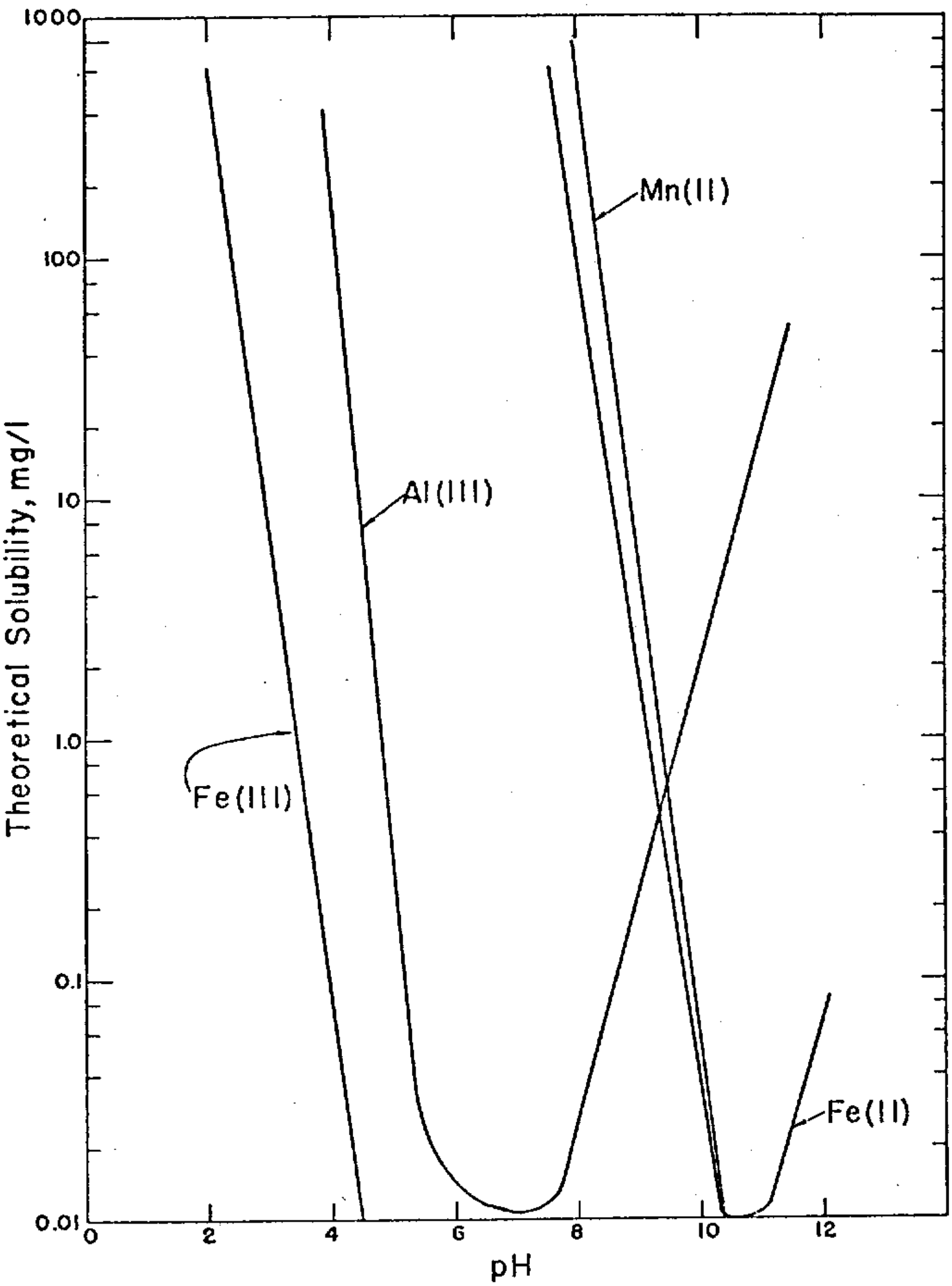


Figure 2. Theoretical Solubilities of Metals as a Function of pH

B. Literature Review on Acid Mine Waste Treatment

The treatment of acid mine wastes require neutralization of the acidity and subsequent precipitation of metals. Hence alkali requirement will be directly related to the influent waste acidity.

1. Lime and Limestone Process

Lime is by far the most common reagent used for neutralization of acid mine drainage. Wilmoth, *et al*. (2, 3, 4) have extensively studied lime and limestone treatment of both ferric and ferrous iron drainages. The processes have been evaluated in terms of reaction time, amount of sludge produced and product water quality. The lime and limestone precipitation behavior of both ferric and ferrous type wastes are discussed.

a. Ferric Acid Mine Waste

An extensive field study utilizing lime and limestone neutralization was conducted at the Norton, West Virginia site (2). The drainage was taken from Grassy Run, a small stream in which 90 percent of the flow is from abandoned coal mines. Typical qualities of the Grassy Run water appear in Table 4.

Initially tests were made to determine the time required for reaction for lime and limestone. Figure 3

TABLE 4

Typical Grassy Run Waste Quality (2)*

Component	Concentration
pH	2.8
Conductivity	1190 μmho/cm
Acidity	466 mg/l as $CaCO_3$
Ca	211 mg/l
Mg	93
Hardness	304
Total Fe	93
Al	31
SO_4^{2-}	612

*Norton, West Virginia

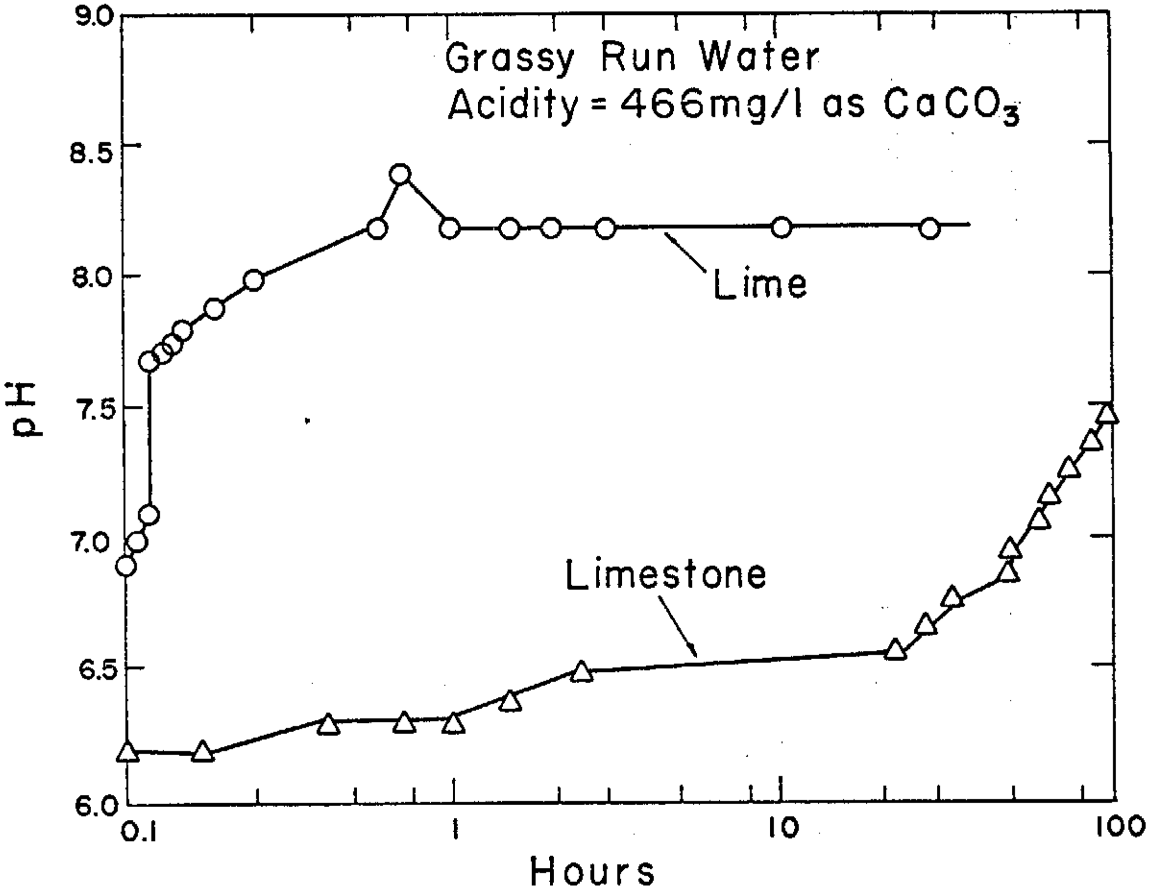


Figure 3. pH Change After Neutralization of the

Figure 3. pH Changes After Neutralization of the Norton, West Virginia Water (2)

shows the pH of identical samples of the drainage after treatment with each of the two reagents as a function of time. The high reactivity of lime is evident from this figure. The reaction was complete and the pH had stabilized within a half hour. In contrast, the pH of the sample treated with limestone had not stabilized even after 96 hours. This can also be seen from Figure 4, which shows that a pH of 10 can easily be reached with lime; whereas, with limestone the maximum pH that can be obtained is 7.0. This is due to the lower solubility of carbonate in water. Since limestone cannot raise the pH above 7.0, it would not be applicable for treatment of ferric iron drainage containing manganese, which must have a pH of 9.0 or greater to be adequately precipitated (refer to Figure 2).

In terms of settling characteristics the subsidence settling rate of the lime sludge (7 cm/min) was considerably higher than that obtained with the limestone sludge (0.5 cm/min). The final sludge volume was about 6 percent of the total volume. Table 5 shows the percent removal of various components obtained by neutralization and subsequent settling of the Grassy Run water (see Table 4). Both reagents reduced the acidity by more than 99 percent, but as expected the sulfate removal was negligible. The

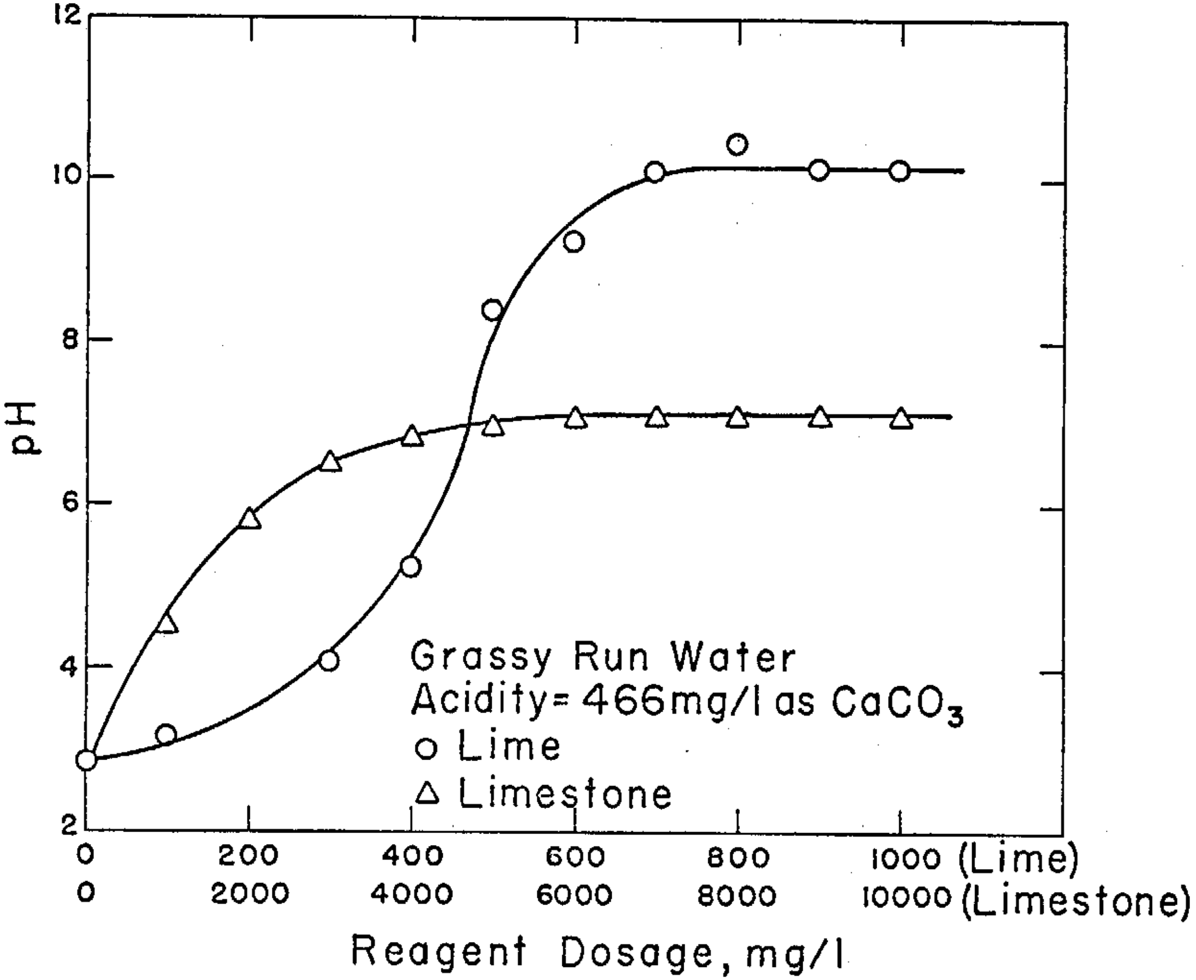


Figure 4. Comparison of Lime and Limestone Reactivities (2)

TABLE 5

Effects of Neutralization of Ferric Mine Waste with Lime and Limestone on Effluent Water Quality (2)

Grassy Run Waste: Acidity = 466 mg/l as $CaCO_3$

	% Removal	
Component	Lime pH 6.9	Limestone pH 6.6
Conductivity	0	<10
Acidity	99.7	100
Al	97.3	94.2
Ca	-240*	-310
Fe	99	96.2
Mg	0	0
SO_4^{2-}	3	14

*Negative removal indicates that the effluent concentration was higher than the feed concentration due to added lime.

calcium concentration would be expected to increase after treatment.

Wilmoth (2) also reported that the limestone utilization efficiency was drastically lower than that for lime. Limestone utilization efficiency was only 31 percent, therefore a large amount of reagent would be wasted and would have to be disposed of. The lime utilization efficiency was 100 percent.

b. Ferrous Acid Mine Waste

Acid mine wastes containing iron in the ferrous state (Fe^{2+}) usually require aeration (to oxidize Fe^{2+} to Fe^{3+}) during the neutralization process to precipitate Fe as $Fe(OH)_3$ (37) or require the use of $pH > 9.0$ to precipitate Fe as $Fe(OH)_2$ (3).

Morgantown, West Virginia (Crown site) (3) was the site for neutralization studies involving ferrous iron acid mine drainage. Typical water qualities appear in Table 6.

Effluent concentrations obtained with lime and limestone neutralizations at two pH values are shown in Table 7, which shows that limestone precipitation cannot be used to remove Fe^{2+} or Mn^{2+} from mine drainage.

TABLE 6

Typical Crown Waste Quality (3)*

Component	Concentration
pH	5.04
Conductivity	3760 μmho/cm
Acidity	640 mg/l as $CaCO_3$
Al	15 mg/l
Ca	370
Total Fe	300
Fe^{2+}	270
Mg	110
Mn	6
SO_4^{2-}	3040
TDS	4320

*Morgantown, West Virginia

TABLE 7

Effect of Neutralization of Ferrous Mine Waste with Lime and Limestone on Effluent Water Quality (3)

Crown Mine Waste: Acidity = 640 mg/l as $CaCO_3$

	% Removal			
	Lime		Limestone	
Component	pH 6.5	pH 9.5	pH 6.5	pH 9.5**
Conductivity	-108**	-105	0	--
Acidity	--	100	34	--
Al	93.8	92.4	93.0	--
Ca	-176	-227	-158	--
Total Fe	35	99.9	11	--
Fe^{2+}	10	99.9	11	--
Mg	0	0	0	--
Mn	0	97	0	--
SO_4^{2-}	7	9	3	--

*With limestone, the pH cannot be raised to 9.5

**Negative removal indicates that the effluent concentration was higher than the feed concentration due to added lime.

2. Other Precipitation Processes

Although lime is the most commonly used reagent for the treatment of acid mine drainage, many other chemicals have been evaluated for neutralization and precipitation. The use of a combination limestone and lime treatment of ferrous or ferric mine waste resulted in a 30 percent reduction in reagent usage compared to a single-stage treatment of the same water. Effluent waste quality parameters from lime and limestone-lime processes are comparable (3, 4).

Soda ash (sodium carbonate) has been effective in producing effluent waters low in hardness, but high in sodium (2). A combination lime-soda process has been evaluated and found to produce potable water when the influent waste is quite dilute. During the process the pH is raised to 11 to remove magnesium; soda ash is then added to precipitate calcium and a final pH adjustment is made to neutrality (7).

A sodium hydroxide treatment scheme has proven effective in removing acidity, iron and aluminum from mine drainages. However, the effluent water was high in sodium. Although the process investigated has promising applications in the area of acid mine drainage, the applicability is restricted to small isolated discharges (6).

The alumina-lime-soda process (8) is capable of producing potable water from acid mine drainages with sulfate concentrations ranging from 400 to 1200 mg/l. The sulfate concentration can be reduced to less than 100 mg/l. The sludge generated from the process is a mixture of solids containing calcium sulfoaluminate, sulfoferrite and carbonate; is microsynthetic in structure and could be readily dewatered for ease in handling.

V. MEMBRANE PROCESSES

A. Definition of Terms

A process schematic showing the basic membrane variables appears in Figure 5. Various parameters employed in describing membrane performance are defined below:

Δp = transmembrane pressure
= $(P_i+P_o)/2$ (14)

$\Delta\Pi$ = osmotic pressure difference
= $\Pi_i-\Pi_f$ = iCRR'T (Van't Hoff Eq.) (15)

J_w = membrane water flux
= Fu/A (16)

r = ultrafiltrate (permeate) water recovery
= 1-Fu/Fi = 1-JwA/Fi (17)

R = solute rejection
= $1-C_f/C_i$ at $r \simeq 0$ (18)

R^* = solute removal
= $1-C_f/C_i$ at $r>0$ (19)

B. Theory

Pressure activated membrane processes (reverse osmosis and ultrafiltration) require the use of an anisotropic (500-2000 A° thin skin supported by a thick porous substructure) membrane substructure. Charged membrane ultrafiltration is a unique low-pressure separation

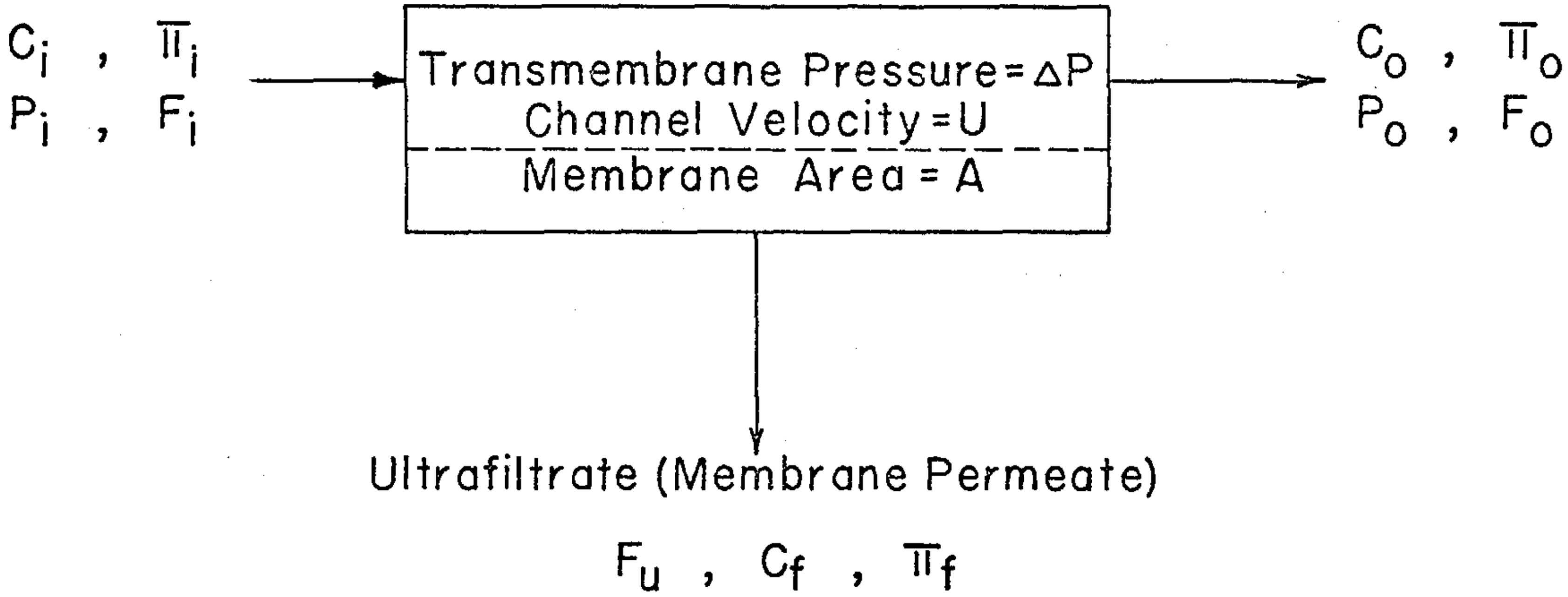


Figure 5. Membrane Process Variables

technique that has proven effective in separating and concentrating inorganic salts present in aqueous solutions. The relatively low pressures ($3.0\text{x}10^5 N/m^2$ to $7.0\text{x}10^5 N/m^2$) employed during operation is the reason the process is termed ultrafiltration. Reverse osmosis is a process in which the natural process of osmosis is reversed by the application of high pressures (greater than the osmotic pressure) to the concentrated stream. Although most commercial reverse osmosis membranes are of the cellulosic type, the charged ultrafiltration membranes have non-cellulosic skins containing fixed ion exchange charged groups.

1. Membrane Water Flux Behavior

Water transport through high pressure reverse osmosis membranes is a diffusion transport mechanism; whereas, charged ultrafiltration membranes follow a viscous flow mechanism. For solute-free water (distilled water) the steady state water flux, J_w, is related to Δp by:

$$J_w = \frac{\Delta p}{R_m} \tag{20}$$

For feed streams containing dissolved solutes the effect of osmotic pressure and surface fouling (or concentration polarization) resistance must be taken into account:

$$J_w = \frac{\Delta p - \Delta \Pi}{R_m + R_f} \tag{21}$$

Since surface fouling and concentration polarization are related to mass transfer behavior at the membrane surface, J_w is generally a strong function of the channel velocity, U. With high pressure reverse osmosis J_w also decreases with operational time, due to membrane compaction phenomena.

Although for acid mine water, a typical $\Delta\Pi$ would be less than $0.5\text{x}10^5 \text{N/m}^2$, but for applications involving sea water desalination, the osmotic pressure would be greater than $1.8\text{x}10^6 \text{N/m}^2$. Since charged membrane ultrafiltration is typically operated at $\Delta p \leq 7.0\text{x}10^5 \text{N/m}^2$, concentrated feed solutions with high osmotic pressures cannot be processed. Low to moderate flux reverse osmosis membranes at pressures above $4.0\text{x}10^6 \text{N/m}^2$ are used for water desalination and/or for waste streams of high osmotic pressures for which very high removals of organic ions are desired.

The average water flux that can be obtained during operation is dependent on the extent of water recovery, r. Water recovery can be limited by several factors: the nature of the feed solution, concentration polarization, and the membrane operational limitations. A membrane may become fouled when the concentration in the brine solution reaches the limit of solubility and precipitation occurs. These precipitates may cake on the membrane surface creating significant resistance to flow through the membrane. As the concentration of the feed is increased, the potential for precipitation is increased. The higher the operating pressure, the greater the percent recovery. However, the operating pressure is limited by the strength of membrane. Elevated pressures cause the pores of the membrane to collapse which decreases water flow through the membrane, thus limiting recovery.

2. Rejection Mechanisms

Rejection, R, is a measure of a membrane's ability to effect a separation with respect to a particular solute. Thus, R = 0 indicates no solute removal by the membrane and R = 1.0 indicates complete solute removal.

a. High Pressure Reverse Osmosis Membranes

The model commonly used to describe solute rejection in a reverse osmosis membrane is the solution diffusion model (38, 39, 40). According to this model, the components dissolve in the membrane and diffuse through the membrane as a result of concentration differences. Rejection occurs because the distribution coefficient and partition coefficient are different for the solute and solvent.

Assuming dilute solutions, that the diffusion coefficients are independent of concentration and that membrane properties are constant, the solution diffusion model is given by the following equations:

$$J_w = \frac{D_w \quad (\Delta p-\Delta \Pi)}{R'T\lambda} = A'(\Delta p-\Delta \Pi) \qquad (22)$$

$$J_s = D_s K_1 \frac{\Delta C}{\lambda} = B\Delta C \qquad (23)$$

In cases where the rejection is high, the osmotic pressure of the product stream is low and $\Delta \Pi = \Pi_1$.

According to the solution diffusion model, solute flow through the membrane is independent of water flow resulting in an increase in rejection with an increase in the net pressure difference ($\Delta p-\Delta \Pi$). Since solute transport through the membrane is dependent upon membrane intrinsic properties (Equation 23), the solute rejections would be dependent on membrane polymer type and structure.

b. Charged Membrane Ultrafiltration

The rejections of the solutes is primarily due to the well known Donnan exclusion mechanism which states that membranes carrying fixed charged groups on the pore walls can exclude salts by the establishment of a Donnan equilibrium between the membrane and aqueous phases.

When a membrane is immersed in a salt solution, as occurs in membrane ultrafiltration, a dynamic equilibrium is substantially maintained (41, 42). While the membrane is immersed in the solution, the salt dissolves in the membrane according to a distribution law and as a result, the counterion concentration is higher in the bulk solution than inside the membrane. The coion concentration is considerably lower in the membrane phase than in the bulk phase due to the fact that the coions are repelled by the fixed charges in the membrane phase. An electric field called the Donnan equilibrium potential is established between the bulk solution and the membrane phase that retards diffusion of the counterions back into the bulk solution. A similar situation occurs when water is caused to flow through the membrane by the application of a pressure gradient as occurs in charged membrane ultrafiltration. In this case the water flow through the membrane prevents the charge separation present when the membrane is just immersed in the solution. If the membrane contains fixed negative charges, as do the membranes used for charged membrane ultrafiltration, the effect of the Donnan potential is to repel anions (coions) and because of the electroneutrality requirement, the counterions are also rejected, resulting in solute rejection.

The overall flux of an ion through the membrane is given by a summation of fluxes due to convection, diffusion and electric potential and is given by the extended Nernst-Planck equation (43),

$$(J_s)_j = J_w C_{j(m)} - D_j \frac{dC_{j(m)}}{dy} - Z_j C_{j(m)} D_j \frac{F}{R'T} \frac{d\psi}{dy} \qquad (24)$$

Bhattacharyya, et al. (44) in their studies with various single-salt systems observed that rejection increased to an asymptotic value at $\Delta p \geq 5.6 \times 10^5 N/m^2$ as a result of negligible influence of diffusion at higher water fluxes. Other models have been developed for the flux of an ion through the membrane; they include the fixed charge model (45, 46), and the ion association model (47, 48).

The dependence of solute rejection upon concentration is indicated by all the above models. In cases where there is no concentration polarization and the transmembrane pressure is held constant, the ultrafiltrate quality (C_f) for negligible water recovery situations in which the operation is a continuous flow, steady state situation can be related to the influent concentration by relationships of the form (49, 50):

$$C_f = KC_i^{n'} \qquad (25)$$

$$R = 1-KC_i^{n'-1} = 1-KC_i^{n} \qquad (26)$$

where K and n' are constants that depend upon the solute type, membrane charge density and possibly membrane-solute interactions.

C. Literature Review of Reverse Osmosis Applications to Acid Mine Waste Treatment

The ability to obtain a high degree of separation of dissolved salts from a concentrated solution has made reverse osmosis a promising technique for the treatment of acid mine drainage (10-19). In the past decade, many investigations have been conducted with the ultimate production of potable or near potable water from the drainage.

The use of cellulose acetate and polyamide membranes has been extensively reported because of their commercial availability in modular form (51). The flux from a cellulose acetate membrane is usually around 6.0×10^{-4} cm/sec (12 gal/ft^2-day) at 6×10^6N/m^2. Typical metal rejections are presented in Table 8 (38).

Polyamide membranes are among the newer types of membranes available. They are usually a crosslinked polymer of either aromatic polyamide or aromatic polyamide hydrazide (51). The flux obtained from this type membrane is around 4.0×10^{-4} cm/sec at 5×10^6N/m^2. To make up for the lower water throughput per unit area, polyamide membranes are usually employed in the hollow-fiber form to maximize

TABLE 8

Typical Rejections for Reverse Osmosis Membranes (38, 39)

Component	Rejection Cellulose Acetate	 Polyamide Hollow Fiber
Aluminum	0.995	---
Calcium	0.99	0.979
Iron (III)	0.998	0.70
Iron (II)	0.99	---
Manganese	0.995	---
Magnesium	0.99	0.983
Potassium	0.92	0.87
Sodium	0.94	0.89
Chloride	0.93	0.57
Boron	0.53	0
Sulfate	0.99	.974
Nitrate	0.79	0.21
Flouride	0.95	>0.50
TDS	0.95	0.905

surface area. The hollow fibers are typically 0.005 cm in outer diameter with a 0.001 cm wall. Rejections are generally lower with polyamide membranes. Typical rejections are given in Table 8 (39). Polyamide membranes are more pH tolerant (pH 2-9) and have higher chemical and physical stabilities than cellulose acetate and therefore have longer operating lives.

All high pressure reverse osmosis system studies with acid mine wastes were conducted at various drainage sites utilizing spiral-wound and tubular cellulose acetate or polyamide hollow-fiber membrane modules. Gulf Environmental Systems, Inc. (10, 11, 13, 14) conducted several tests at the Norton, West Virginia site to study the reverse osmosis treatment of ferric iron acid mine drainage. Rex Chainbelt, Inc., Gulf Environmental Systmes, Inc., and the EPA conducted studies at Morgantown, West Virginia (10), Mocanaqua, Pennsylvania (10, 13), and Ebensburg, Pennsylvania (10) to investigate the reverse osmosis treatment of ferrous iron acid mine drainage. The raw wastewater qualities for each site appear in Table 9.

In all cases prior to reverse osmosis treatment, the pH of the waste was adjusted to 3.0 (to eliminate ferric hydroxide precipitation) and the water was filtered with 10μm filters to remove suspended solids. In general,

TABLE 9

Raw Waste Quality at Reverse Osmosis Test Sites

	Concentration			
Component	Norton, WV (10,11,13,14)	Morgantown, WV (10)	Mocanaqua, PA (10,13)	Ebensburg, PA (10)
pH	2.8	2.2	3.4	3.6
Fe, mg/l	93	2,960	80	135
Ca, mg/l	211	530	120	190
SO_4, mg/l	612	11,000	800	1,640
Conductivity, µmho/cm	1,190	7,000	1,100	1,500

the spiral-wound module performance was superior to the tubular and hollow-fiber systems. A summary of performance data (using spiral-wound modules) from the four sites appears in Table 10. These data were collected and summarized from the individual reports for each investigation. The Morgantown waste was extremely concentrated and therefore high water recovery would not be feasible. In each case, with exception of the Morgantown water, the permeate quality was excellent.

At all sites the flux declined with time due to membrane compaction and iron and calcium sulfate fouling problems. An example of the flux decline with time at 91% recovery is shown in Figure 6 (10). It is noted that the flux did not decline sharply. After 100 hours of operation, the flux had dropped only 21%. An extensive study of various types of flushes was conducted on the Grassy Run water at the Norton site (10). From Figure 7 (10) it is noted that combination flushes (flush with acidified product or a low recovery flush followed by a unit shutdown) are most effective in restoring the flux. In each case, immediately following the combination flush, the initial water flux was almost completely regained, keeping the average water flux relatively high. The overall unit flux was held at

TABLE 10

Reverse Osmosis Performance Parameters
(Spiral-Wound Modules)

	Parameter Values			
Parameter	Norton, WV	Morgantown, WV	Mocanaqua, PA	Ebensburg, PA
Transmembrane Pressure, N/m^2	$4.2x10^6$	$4.2x10^6$	$4.2x10^6$	$4.2x10^6$
Average Water flux, cm/sec	$8.6x10^{-4}$	$6.4x10^{-4}$	$9.2x10^{-4}$	$6.5x10^{-4}$
Water Recovery, %	75	50	75	84
Hours of Operation	3000	112	1672	191
Permeate Concentration, mg/l:				
Fe	1.1	39	0.4	1.7
Ca	1.1	9.6	0.4	1.2
SO_4	1.2	190	0.9	14
Conductivity, μmho/cm	77	420	17	92

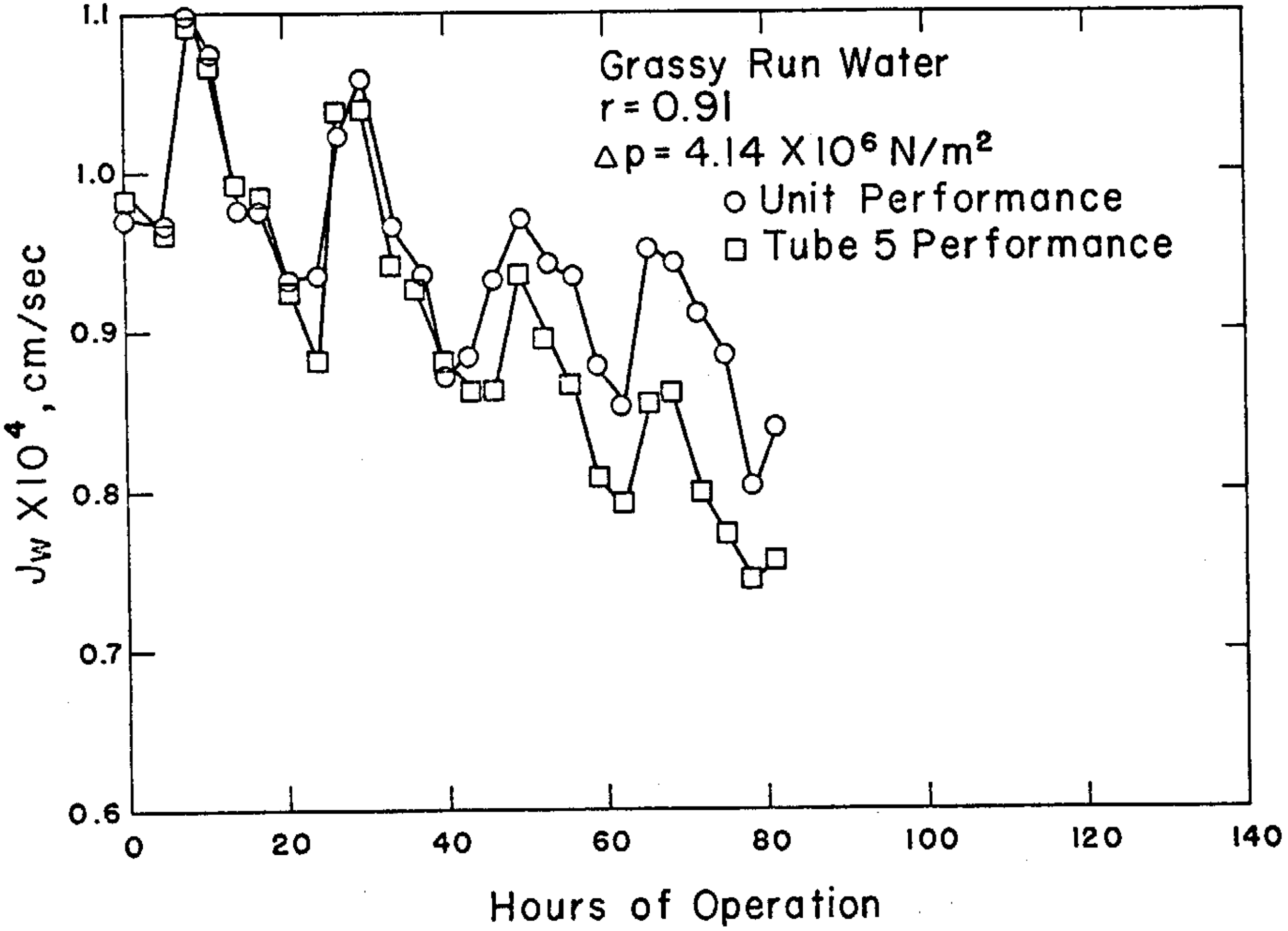
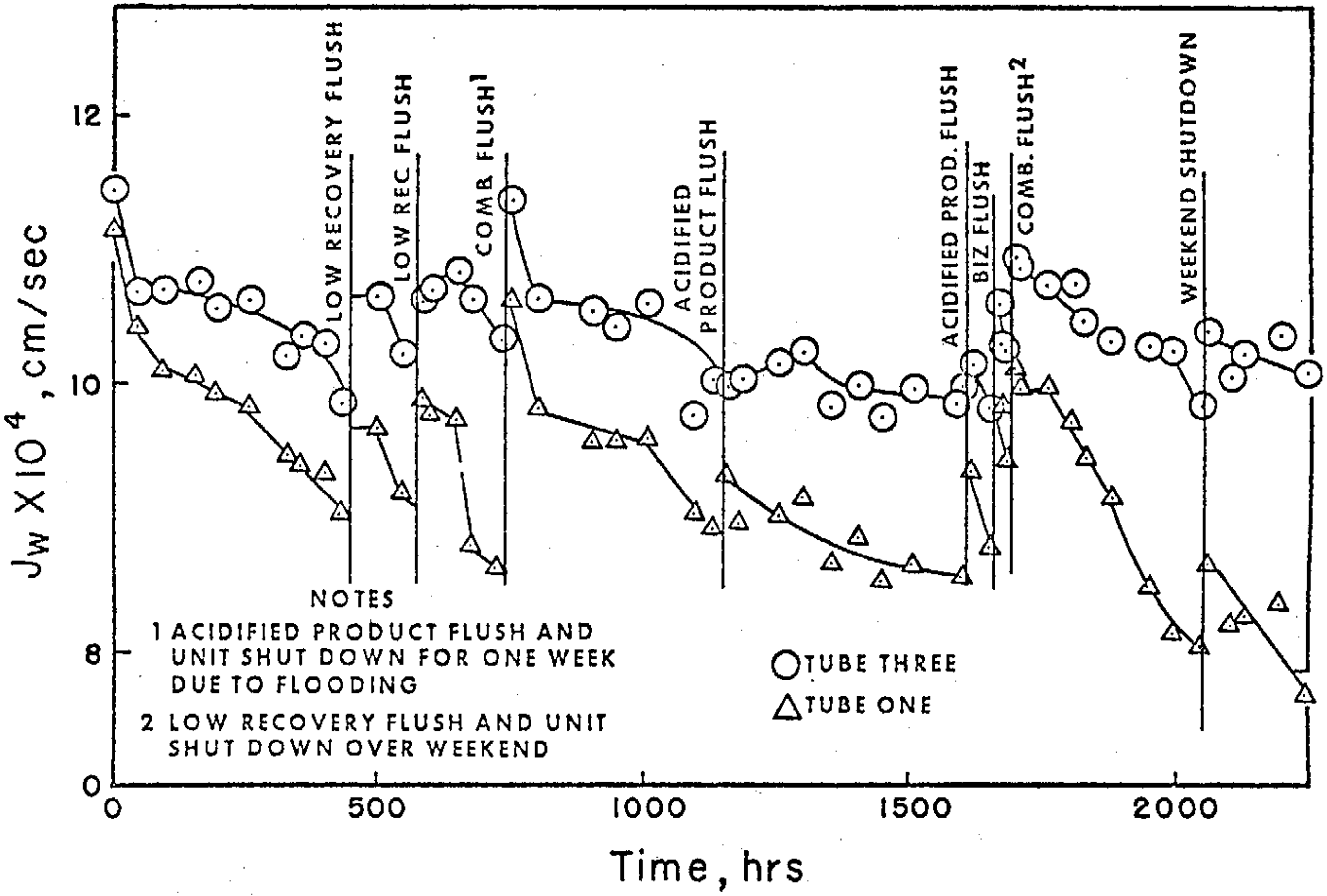


Figure 6. Membrane Flux Behavior with Reverse Osmosis Test made at Norton, West Virginia (10)



NOTES

1 ACIDIFIED PRODUCT FLUSH AND UNIT SHUT DOWN FOR ONE WEEK DUE TO FLOODING

2 LOW RECOVERY FLUSH AND UNIT SHUT DOWN OVER WEEKEND

Figure 7. Long Term Reverse Osmosis Membrane Performance at Norton, West Virginia (10)

approximately $9.2 \times 10^5 N/m^2$ a drop of only 20% for 3000 hours of operation compared to a 21% drop for the 100 hour run with no flushing (Figure 6).

Calcium sulfate fouling was a problem at each site where the water recovery was high. Several precipitation inhibitors were investigated, but all failed to correct the problem (18, 19). A method was developed to predict calcium sulfate precipitation (11). The method states that precipitation occurs when the ratio $\sqrt{Pmc/Ksp}$, where Pmc is the product molar concentration of calcium and sulfate is the concentrate and Ksp is the solubility product of calcium sulfate in distilled water, is in the range of 3.0 to 4.0. The method was later reevaluated and modified to account for the ionic strength of the solution. Data from all the sites were considered and it was determined that a limit of 2.0 for the ratio $\sqrt{Pmc/Ksp}$ dictated precipitation and a limit of 1.2 for the ratio $\sqrt{Pmc/Ksp_C}$, where Ksp_C is the solubility product corrected for ionic strength. Using the value of 2.0, the maximum recovery can be predicted by

$$r = 100-0.55\sqrt{(Ca)x(SO_4)} \tag{27}$$

where (Ca) is the acid mine drainage feed calcium concentration in mg/l and (SO_4) is the concentration of sulfate in the feed in mg/l. This method is predicted to be accurate within ±5 percent recovery (10). For example, the Norton, West Virginia waste (Table 9) contained 211 mg/l Ca^{+2}, and 612 mg/l $SO_4{}^{2-}$, thus Equation 27 would predict a maximum recovery of 80%. This value can be compared to the actual value of 75% (Table 10) obtained during the 3000 hours test run.

D. Literature Review of Applications of Charged Membrane Ultrafiltration

Although no report independent of this investigation (52) is made in the literature of charged membrane ultrafiltration being used to treat acid mine drainage, several reports have been made of the effective application of this treatment process to various industrial wastewaters. Since rejection of metals by negatively charged ultrafiltration membranes is dependent upon the type of anion present in the water, salts of multivalent (di-, tri-) anions would always be rejected better than monovalent anions. Thus at a fixed feed concentration $R_{Na_3PO_4} > R_{Na_2SO_4} > R_{Nacl}$. Typical rejections of some metal salts reported in the literature are reported in Table 11 (23, 56). Rejections of salts (primarily salts of monovalent anions)

TABLE 11

Typical Rejections of Inorganic Salts by a Negatively Charged Ultrafiltration Membrane (23, 56)

C_i = 3mM
$\Delta p = 5.6x10^5 N/m^2$

Salt	Rejection
Na_3PO_4	0.99
Na_2SO_4	0.95
$MgSO_4$	0.93
$CdSO_4$	0.92
$ZnSO_4$	0.90
NaCl	0.52
$MgCl_2$	0.79
$CdCl_2$	0.81
$ZnCl_2$	0.82

decreased with increasing inlet concentration, as preducted by the Donnan exclusion model.

Bhattacharyya, et al. have evaluated the applicability of charged membrane ultrafiltration to plating rinse waters (49), photographic wastes (23), wastewaters from nonferrous metal manufacturing processes (22), laundry wastes (53, 54) and dissolved solids reduction (55). The use of charged non-cellulosic membranes provided a broadly applicable technique for the separation and concentration of various ionic solutes present in aqueous solutions. The membranes provide good water fluxes at low pressures and adequate to excellent rejections of various inorganic salts, depending on the process application. The aspects of reusing industrial wastewaters by ultrafiltration has also been reported (22, 49). For example, for a copper smelting plant utilizing 2.2×10^6 l/day of scrubber water, 95% water recovery under multiple-pass water recycle operation could be achieved with $2.9 \times 10^3 m^2$ of membrane area.

VI. EXPERIMENTAL METHODS

A. Waste Preparation

Although the occurrence of specific metals and their concentrations are dependent on the environment in which the drainage was formed, in studying literature it was noticed that certain metals are present in almost every acid mine drainage. The synthetic 1X waste used in this study was prepared with Reagent Grade metal sulfate salts. These concentrations and other waste characteristics appear in Table 12. The concentrations of other synthetic wastes used in the study, such as 5X and 10X, are five times and ten times, respectively, the 1X concentrations. The method of preparing the waste consisted of first dissolving the proper amounts of the salts of Mn^{2+}, Mg^{2+}, and Ca^{2+} in approximately 26 l of tap water in the feed tank, adjusting the pH with 6mM H_2SO_4 to 2.5, dissolving the salts of Al^{3+} and iron in the feed tank and filling the tank to 30 l with tap water. Most of the experiments were made with iron in the ferric state; however, several runs were made with iron in the ferrous state. The pH was adjusted with lime slurry to the desired level.

Studies were also made with actual acid mine drainage

TABLE 12

Composition of Acid Mine Wastes

Component	Synthetic (1X)	Actual*
pH	2.5	3.1
Conductivity	3020 μmho/cm	1050 μmho/cm
Acidity	570 mg/l as $CaCO_3$	320 mg/l as $CaCO_3$
Al^{3+}	30 mg/l	5 mg/l
Ca^{2+}	200	50
Fe^{3+}	100	35
Mg^{2+}	30	---
Mn^{2+}	10	2.5
SO_4^{2-}	1350	280
Total Solids	2050	650
Suspended Solids	75	150

*Western Kentucky

obtained from a strip mine located in Western Kentucky. The metal concentrations and waste characteristics appear in Table 12. Since the metal concentrations in the waste were so low, Reagent Grade metal sulfate salts were added until the concentrations were approximately equal to those in the synthetic 1X waste. This was done to aid in the analysis of the waste. Again, all pH adjustments were made with lime slurry.

B. Settling Equipment and Procedures

Various settling studies were conducted with 1X to 20X wastes at pH 4-9 by pH adjustment with lime. The waste was allowed to settle in a column (180 cm height, 10 cm diameter) equipped with sampling ports. The sludge height was monitored as a function of time. Samples were taken of the raw feed and the settled supernatant from the sampling port located 45 cm below the top of the column. The effects of pH on the suspended solids, metal removal, and settling rates were studied. Ultrafiltration runs were also made with settled waste. After sixty minutes of settling time the entire volume of the supernatant was removed and immediately ultrafiltered.

C. Ultrafiltration Equipment and Procedures

The general procedure followed in the ultrafiltration studies involved continuous pumping of an acid mine waste feed solution (1X to 20X) after pH adjustment with lime slurry through a membrane unit. The ultrafiltration cell (0.08 cm height, 1.3 cm width) contained 50.3 cm^2 of membrane area. For most ultrafiltration experiments both the ultrafiltrate and the concentrate streams were returned to the feed tank to maintain constant feed tank concentration throughout the entire run. Periodically, small samples were taken of the ultrafiltrate for various analyses. A detailed schematic of the apparatus is shown in Figure 8. Each ultrafiltration run was conducted for 5 to 6 hours at 25± 1°C to ensure steady state operation, during which the flux was measured every hour.

Two types of negatively charged ultrafiltration membranes were used in the study; Millipore PSAL (non-cellulosic skin on cellulosic backing) and Millipore PTAL (non-cellulosic skin and backing). Their intrinsic characteristics appear in Table 13. During the initial phase of the study the membranes were cut from several commercially available sheets with different water flux characteristics. In the latter phases of the study the membranes were cut from the same sheet to ensure consistency in the flux and rejection data. After being cut

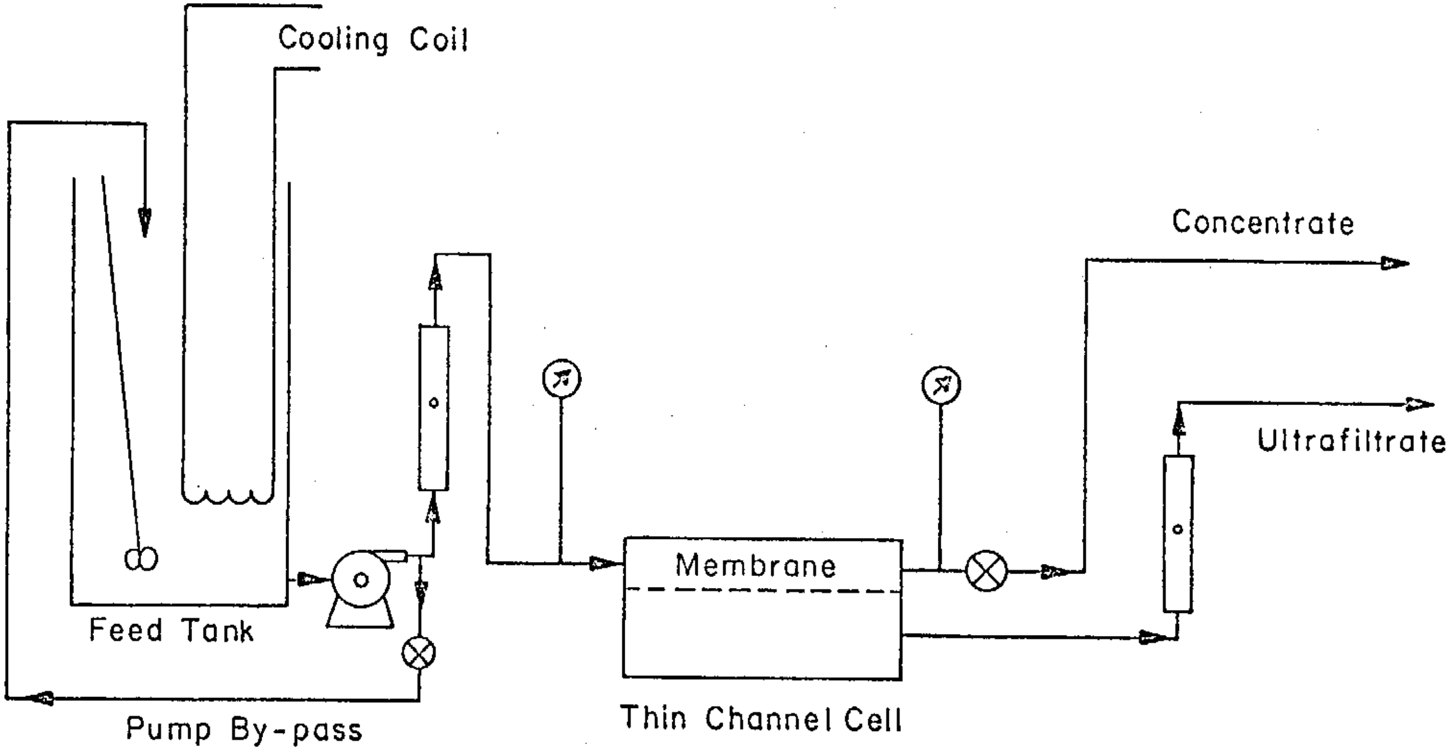


Figure 8. Schematic Diagram of Experimental Ultrafiltration Unit

TABLE 13

Properties of PSAL and PTAL Membranes

Property	Membrane PSAL	 PTAL
Composition	Non-cellulosic skin on cellulosic backing	Non-cellulosic skin on non-cellulosic backing
Membrane Thickness	150 μm	240 μm
Operating pH	3.0-11.0	1.0-12.5
Temperature Limit	35°C	70°C
Pressure Limit	$9.0\text{x}10^5\text{N/m}^2$	$9.0\text{x}10^5\text{N/m}^2$
Fixed Charge	Negative sulfonate group	Negative sulfonate group
Typical Water Flux at $5.6\text{x}10^5\text{N/m}^2$	$8.2\text{x}10^{-4}\text{cm/sec}$	$17.3\text{x}10^{-4}\text{cm/sec}$
Typical Na_2SO_4 Rejection	0.92	0.80-0.92

from the dry sheet, the membranes were allowed to soak in distilled water and then cut to the correct size and installed in the cells. Distilled water was then passed through the unit and the flux was checked for linearity at $2.8\text{x}10^5 \text{N/m}^2$ and $5.6\text{x}10^5 \text{N/m}^2$. Nonlinearity would indicate that the O-ring seal in the cell was leaking and the feed solution was contaminating the ultrafiltrate stream. This procedure was also performed before and after each acid mine waste ultrafiltration run. Periodically, the membrane deterioration was evaluated by making an ultrafiltration run using a 3mM feed solution of $CaCl_2$ or Na_2SO_4.

Ultrafiltration studies were made on synthetic (1X) and actual acid mine wastes. The effects of transmembrane pressure and channel velocity on the ultrafiltrate flux were evaluated by varying the channel velocity from 40 cm/sec (Re = 1200) to 430 cm/sec (Re = 13,000) at transmembrane pressures ranging from $2.8\text{x}10^5 \text{N/m}^2$ to $5.6\text{x}10^5 \text{N/m}^2$. Studies were also made to determine the effect of feed pH on metal rejections. Synthetic 5X and 10X wastes were ultrafiltered to simulate high recovery conditions. To incorporate the possibility of very concentrated raw wastes that could not be ultrafiltered directly, settled waste was used as the feed solution.

D. Analysis

Total solids, dissolved solids, and suspended solids determinations were made on feed and ultrafiltrate samples and feed and supernatant samples. The total solids measurement was made by evaporating the moisture from a known volume of sample and determining the weight of the residue per unit volume of the original sample. The dissolved solids measurement was made in the same manner using a filtered sample of known volume. Determination of suspended solids was made by subtracting the dissolved solids from the total solids concentration. Conductivity measurements were made on feed and ultrafiltrate samples. Since the samples were multi-salt systems, conductivity could only be used as a gross rejection parameter to monitor membrane performance. Specific metal rejections were determined by measuring each metal concentration using atomic absorption techniques. The instrument used was the Varian 375 ABQ atomic absorption unit giving analytical accuracy of ±2%. Table 14 lists the principal absorption wavelengths, flame type and sensitivity used for each metal analysis.

TABLE 14

Atomic Absorption Characteristics

Metal	Wavelength, nm	Flame Type	Sensivity, mg/l
Al	309.3	acetylene-N_2O	0.6
Ca	239.9	acetylene-N_2O	4.0
Fe	248.3	air-acetylene	0.05
Mn	279.5	air-acetylene	0.05

VII. RESULTS AND DISCUSSION

A. Waste Characteristics

1. Waste Composition

Most of the experiments in this investigation were conducted with the synthetic (1X) waste defined previously (Refer to Table 12). The results were substantiated with an actual acid mine waste (Refer to Table 12) collected from a strip mine in Western Kentucky. Since the actual waste was relatively dilute, Reagent Grade sulfate salts were added to the raw waste to bring the metal concentrations near those defined in the synthetic (1X) waste. Studies were also made with concentrated synthetic wastes, 5X, 10X, and 20X. The metal concentrations in these wastes were 5, 10, and 20 times those in the 1X waste.

2. Lime Dosage Required

In any treatment process, the feed stream (inlet) pH and the calcium sulfate content are important parameters; therefore, the lime dosage requirements for the synthetic (1X) and actual wastes were determined. They appear in Figures 9 and 10. It is noted from these

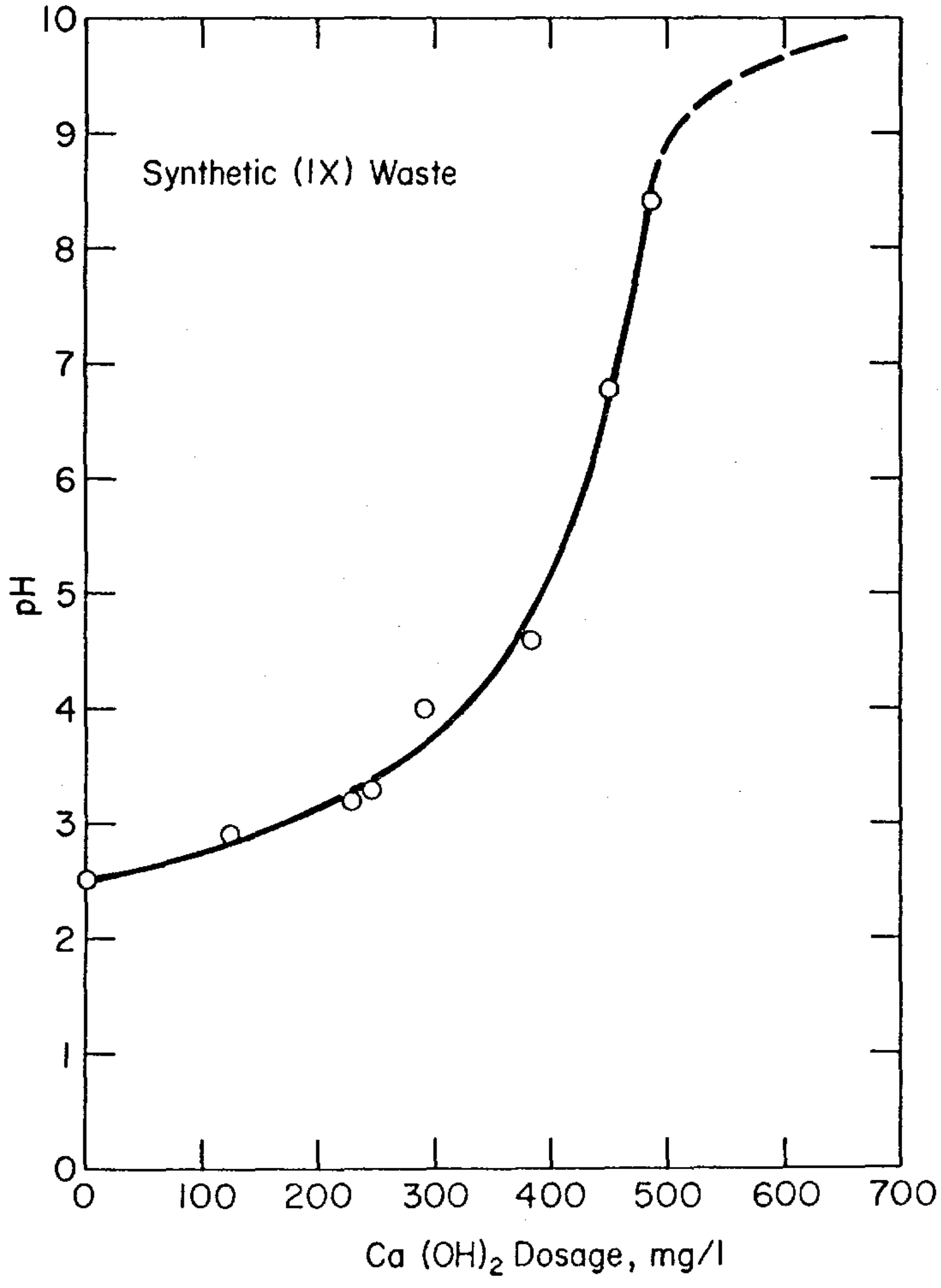


Figure 9. Determination of Lime Dosage as a Function of pH for a Synthetic Waste

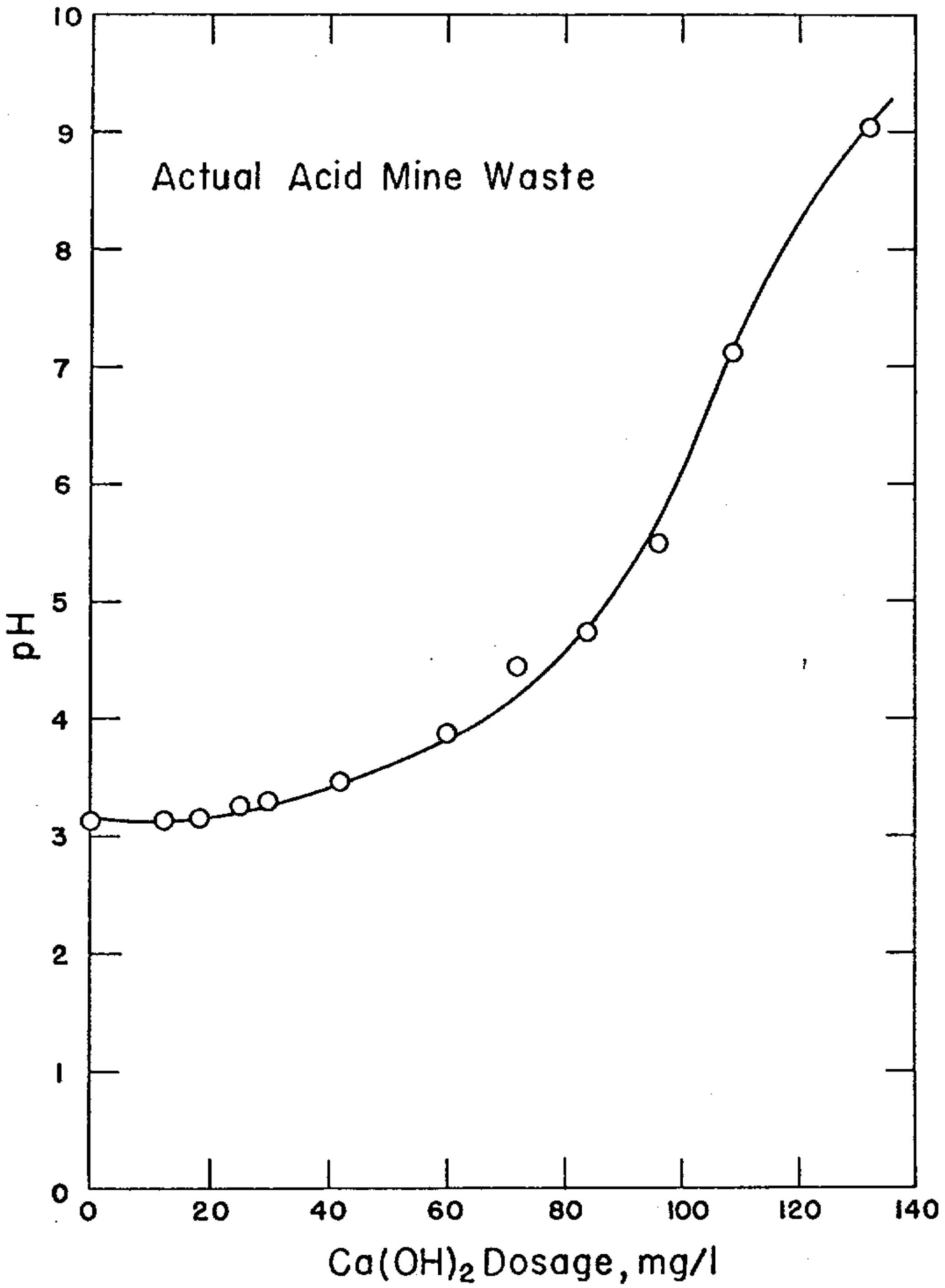


Figure 10. Determination of Lime Dosage as a Function of pH for an Actual Mine Waste

figures that the lime dosages for the synthetic waste is significantly greater than that for the actual waste, due to the higher acidity present in the synthetic waste.

B. Precipitation and Settling Studies

The settling behavior of the synthetic (1X) and the actual mine waste were evaluated in terms of settling rates and clarified water quality. Investigations were also made to study the settling behavior of more concentrated wastes, i.e., synthetic 5X, 10X, and 20X wastes. These experiments were conducted to determine the suitability of a lime precipitation-settling method for the treatment of concentrated mine wastes or the incorporation into a combination precipitation-ultrafiltration treatment scheme.

1. Extent of Separation

The extent to which the metals and solids are removed from the waste by precipitation and settling is a major concern whether the water is to be discharged, reused or subjected to further treatment. Extensive studies were made with the synthetic (1X) waste to determine the effect of pH on the removal of metals by settling and filtration. The concentration of metals obtained by filtration would correspond to 100% removal of solids by a settling operation. The results for Mn and Al appear in Figures 11 and 12, respectively. The iron was effectively precipitated and removed by settling at a pH of 5. The solubility limit of calcium sulfate was not exceeded and it did not precipitate.

For optimum metal removal, if the effluent is to be discharged or reused, operating pH for the precipitation process should be between 8.0 and 8.4. Operation at a lower pH would not effectively remove the Al^{3+} and Mn^{2+} from the solution. Tables 15 and 16 show the effluent metal concentrations from 60 minute settling processes for both the synthetic (1X) and actual acid mine waters. The settling process effectively reduced the metal concentrations in both wastes with the exception of calcium, which was not removed in either case, as expected. The tables also show the soluble concentrations (by filtration) of metals present in both wastes after neutralization. The supernatant concentrations were 2 to 60 times higher than the soluble metal concentrations.

Results from extensive precipitation studies made with the concentrated wastes (5X, 10X, and 20X) show that neutralization to pH 4.0-4.5 and settling for 60 minutes significantly reduced the solids concentration of the wastes. The reduction in the total solids

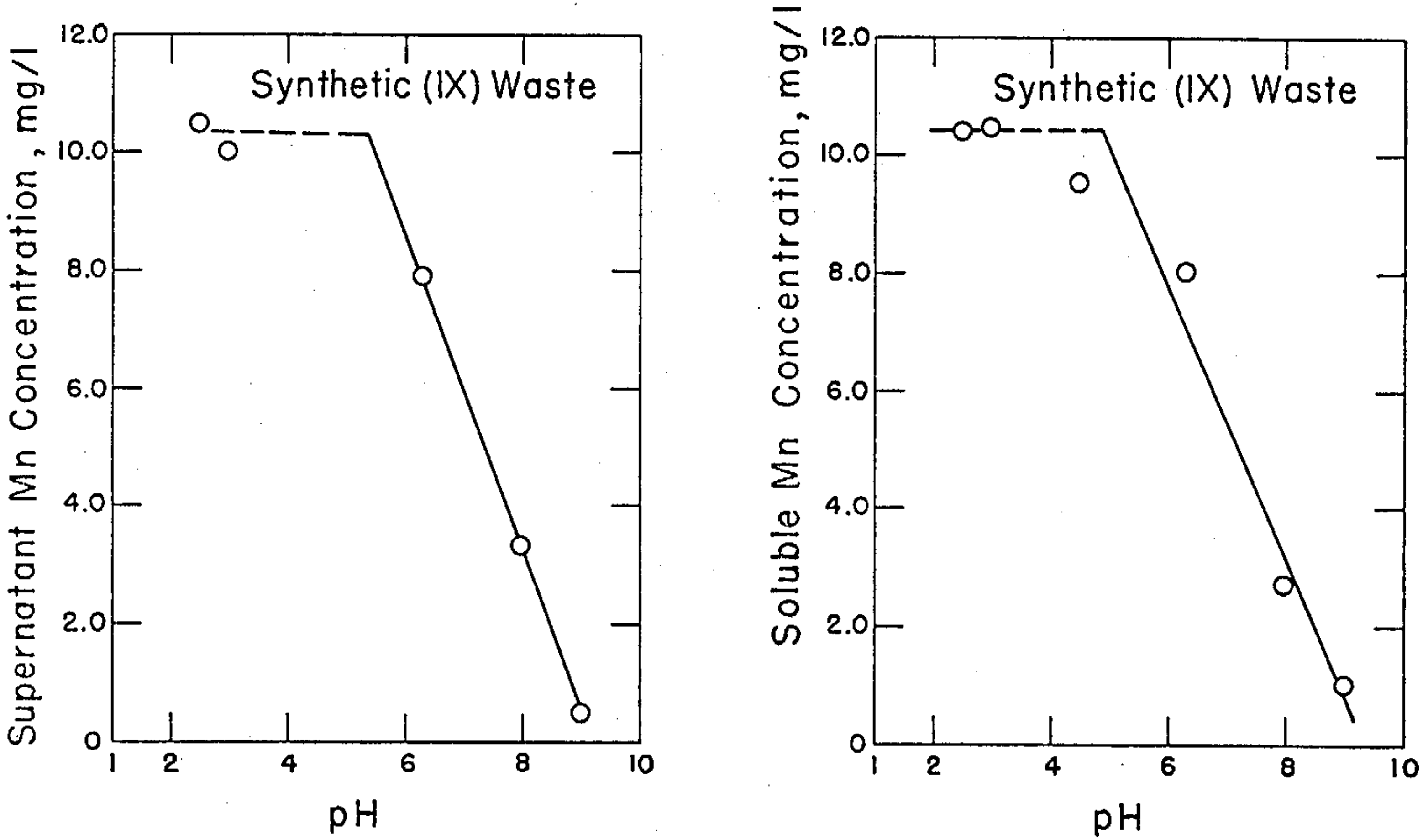


Figure 11. Comparison of Supernatant and Soluble Mn Levels at Various pH Levels

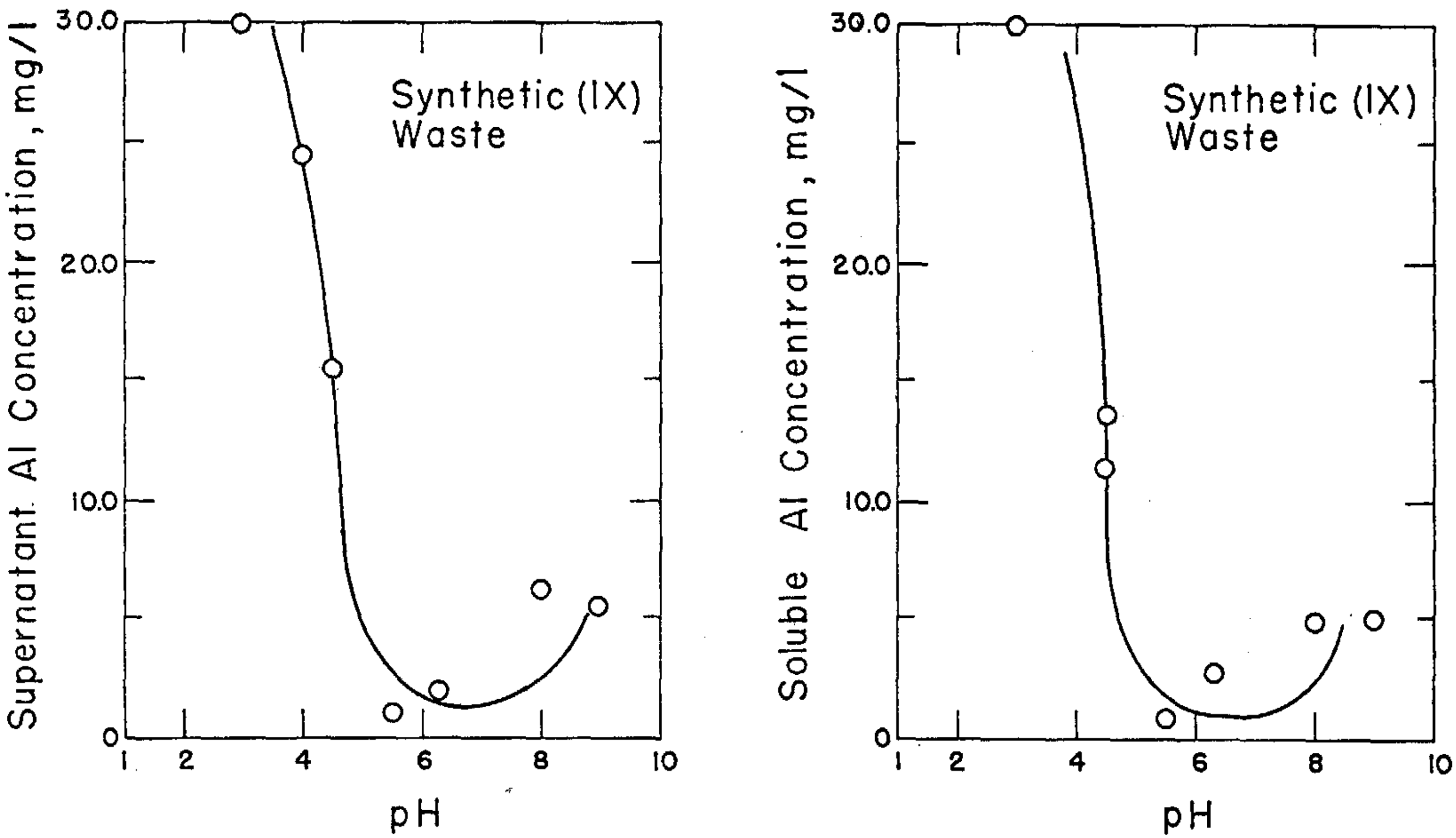


Figure 12. Comparision of Supernatant and Soluble Al Levels at Various pH Levels

TABLE 15

Effect of Settling and Filtration on Effluent Quality of Synthetic (1X) Wastes

pH = 8.0-8.4
Acidity = 570 mg/l as $CaCO_3$

Metal	Concentration, mg/l Supernatant	Soluble
Al	6.4	5.0
Ca	446	446
Fe	3.0	<0.5
Mn	3.2	2.7
Suspended Solids	81	---

TABLE 16

Effect of Settling and Filtration on Effluent Quality of Actual Mine Wastes

pH = 8.0-8.4
Acidity = 320 mg/l as $CaCO_3$

Component	Concentration, mg/l Supernatant	Soluble
Al	9.9	6.1
Ca	385	385
Fe	6.1	.1
Mn	2.3	1.1
Suspended Solids	44	---

concentrations ranged from 52% to 72% (See Figure 13) for concentrations ranging from 5X to 20X. The increase in total solids removal with increasing concentration can be attributed to the higher concentrations of suspended solids in the concentrated wastes (Figure 14), which are removed during settling. In all cases the suspended solids removal was approximately 94%.

As seen previously with the synthetic (1X) waste, the calcium concentration was not reduced during the neutralization-precipitation process. The precipitation of calcium sulfate is a function of the concentrations of calcium and sulfate present in the solution and precipitation will occur only when the product of the molar concentrations of calcium and sulfate significantly exceed the solubility product ($Ksp = 2.4 \times 10^{-4}$). Although the precipitation of calcium sulfate is not a function of pH, the calcium concentration is increased with the addition of lime [$Ca(OH)_2$] for pH adjustment, thus increasing the product of the molar concentrations. The effect of these increases in calcium and sulfate concentrations on the reduction of soluble calcium in the waste at pH4 is shown in Figure 15. For example, for a 10X waste which contains a total Ca^{2+} concentration of 3500 mg/l, 84% of the calcium would be present as $CaSO_4$ precipitate and 16% as

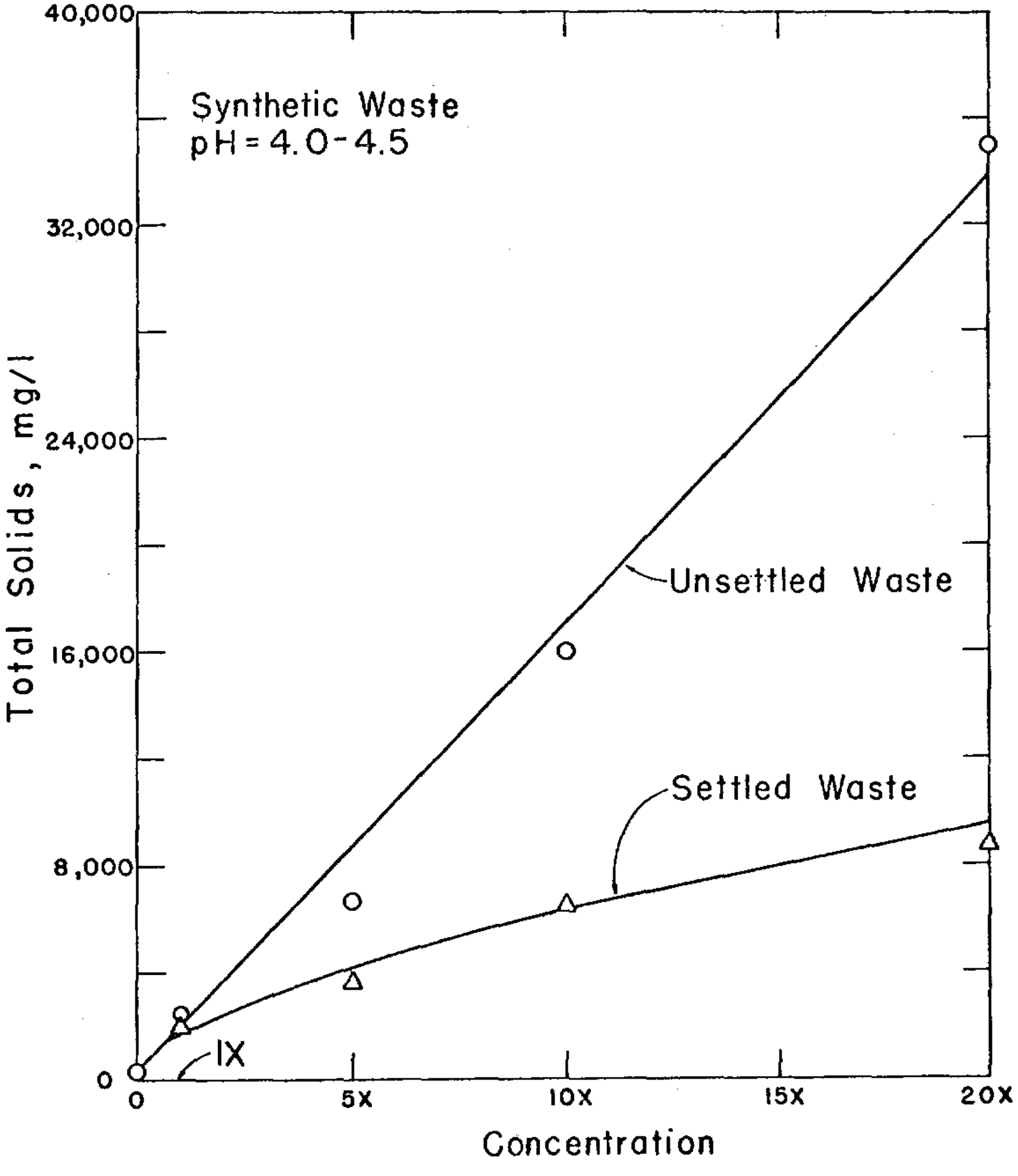


Figure 13. Variations of Total Solids with Waste Concentration

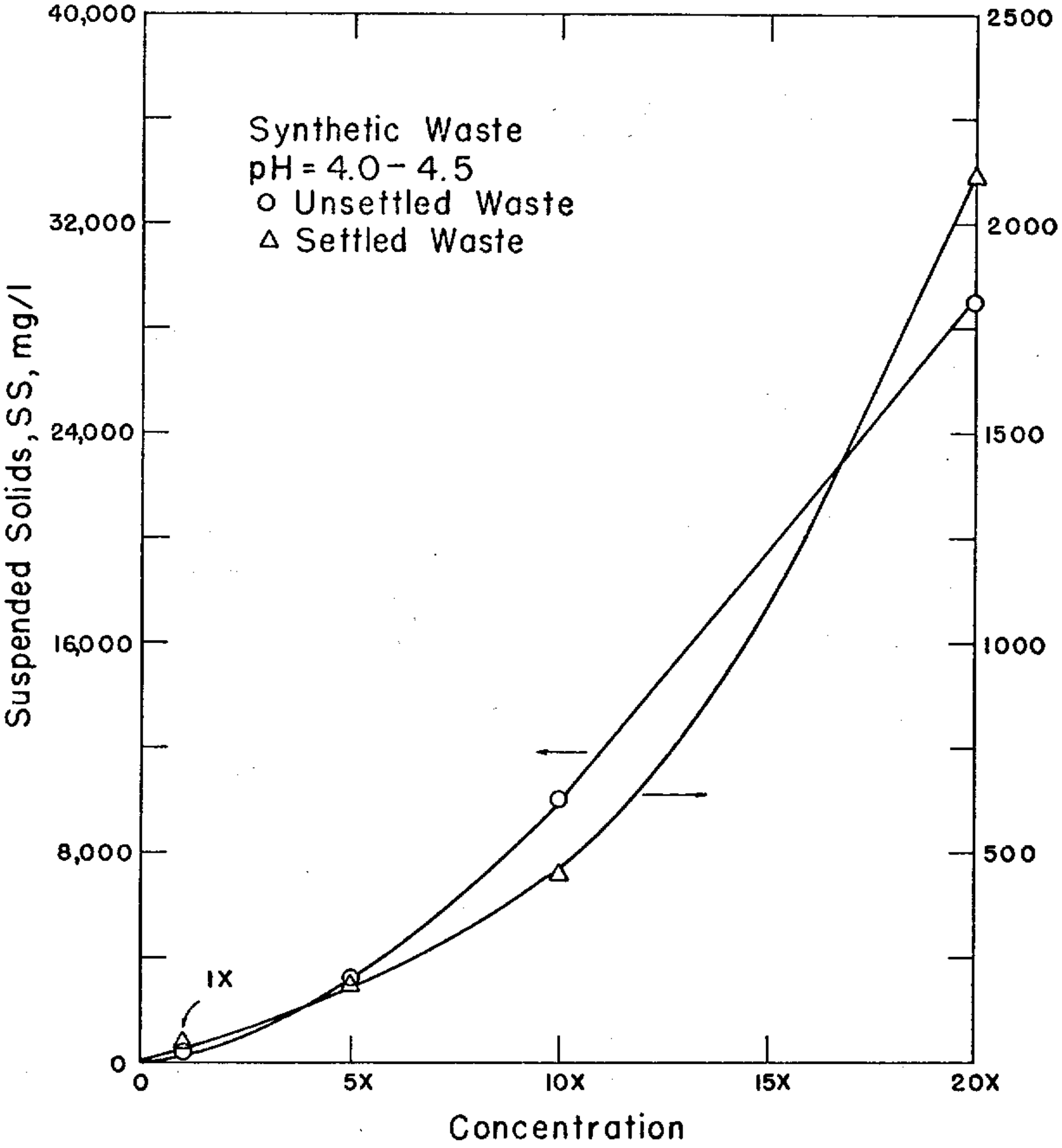


Figure 14. Variations of Suspended Solids with Waste Concentration

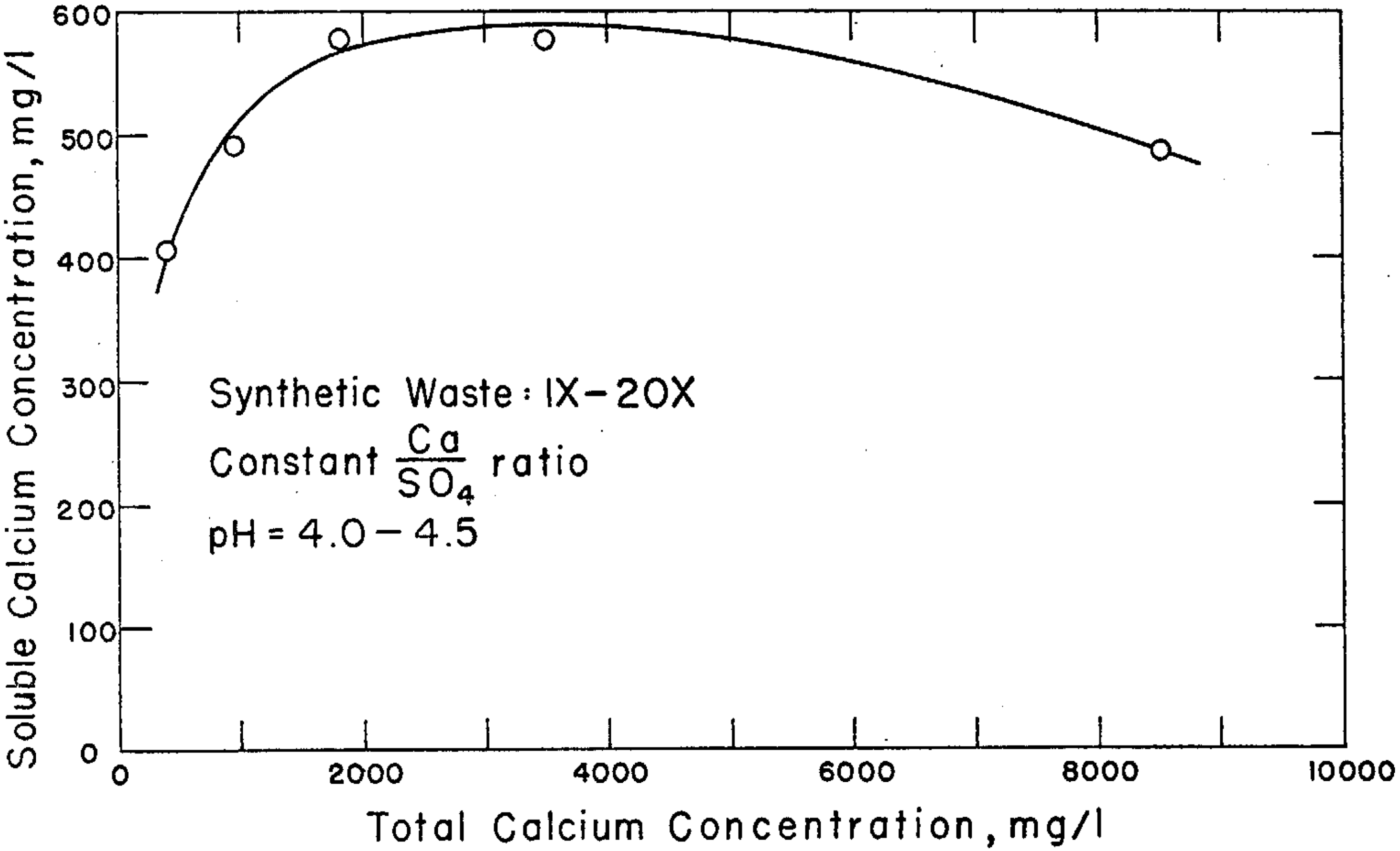


Figure 15. Relationship Between Soluble Calcium Concentration for a for a Constant Ca/SO_4 Ratio of 3.3

soluble $CaSO_4$. With 1X (total Ca^{2+} = 406 mg/l), no $CaSO_4$ precipitation occurs, as shown in the figure. The soluble calcium concentration is equal to the total feed calcium concentration.

The precipitation and settling process also significantly reduced the metal concentrations in the more concentrated wastes at high pH values. As an example, Table 17 shows the metal concentrations that would be present after a lime precipitation-settling (60 minutes) operation at pH4 or pH8. At pH8 reductions of the metal concentrations were greater than 97%. However, at pH4 only Fe^{3+} removal (98%) was significant.

2. Precipitate Settling Rates

Extensive studies were conducted to determine the precipitate settling rates at various operating conditions. Examples of the sludge height versus time relationships at various pH values appear in Figures 16 to 18. From these figures the initial settling rates are computed and are shown in Table 18. The low settling rate exhibited with the 20X waste is due to the presence of extremely high concentrations of suspended solids (29,000 mg/l).

The settling behavior of the synthetic wastes was also evaluated in terms of the amount of sludge produced.

TABLE 17

Supernatant Quality of Synthetic (10X) Wastes

Component	Concentration, mg/l pH 4.0	 pH 8.0
Al	187	1.8
Ca	746	≃900
Fe	18.8	2.7
Mn	102	3.5
Suspended Solids	430	95

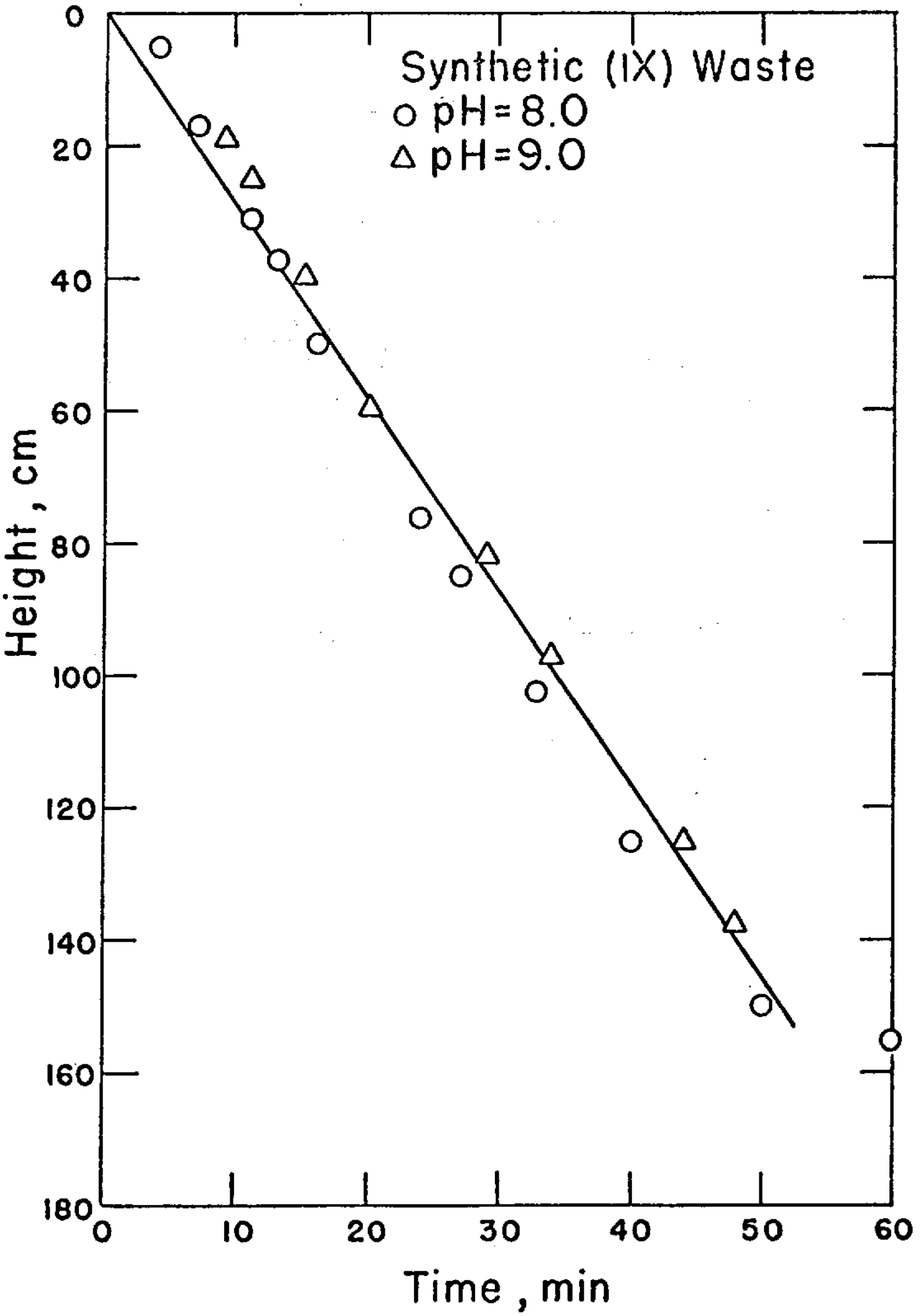


Figure 16. Settling Behavior of Synthetic (1X) Waste After pH Adjustment with Lime

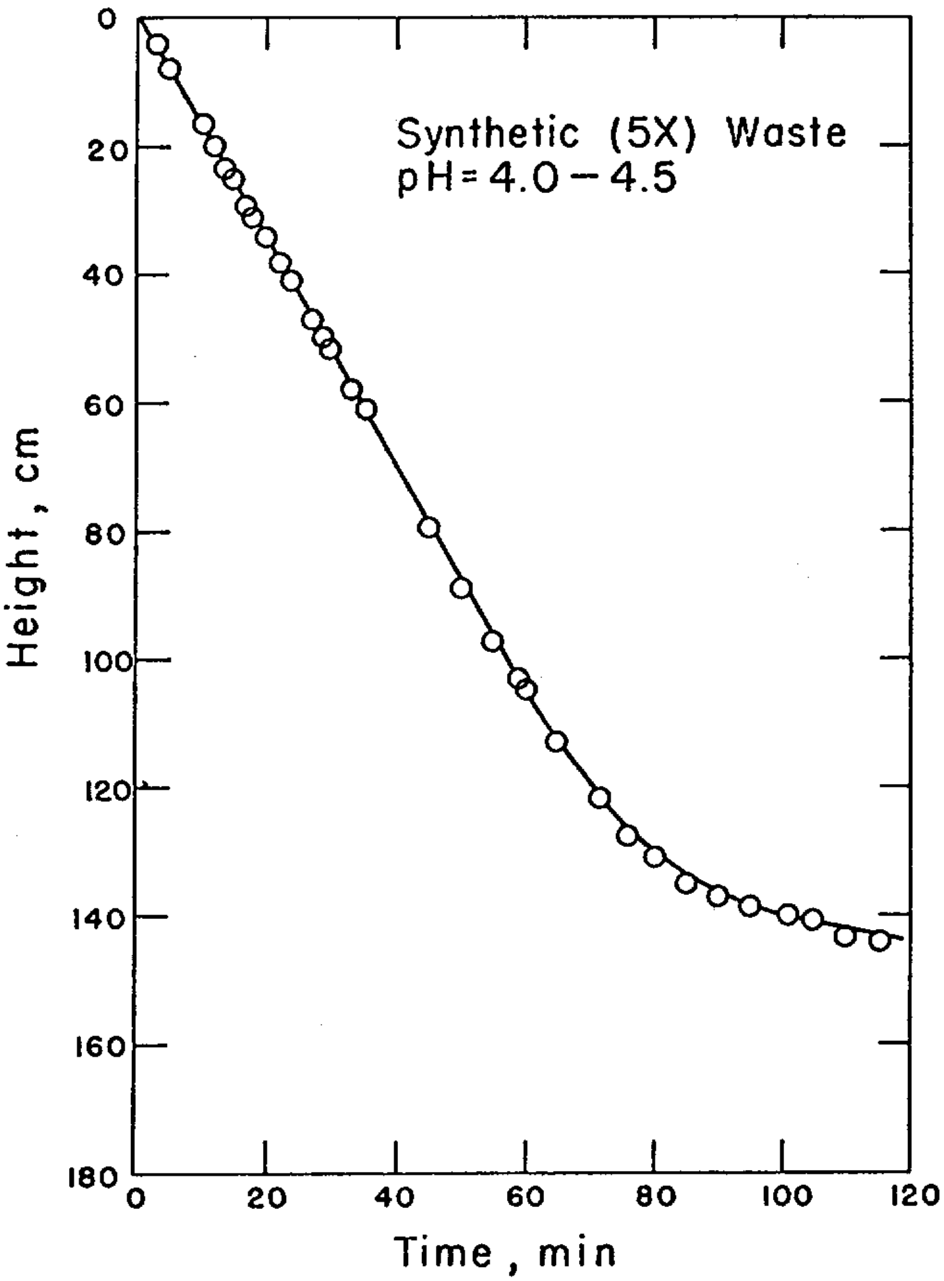


Figure 17. Settling Behavior of Synthetic (5X) Waste After pH Adjustment with Lime

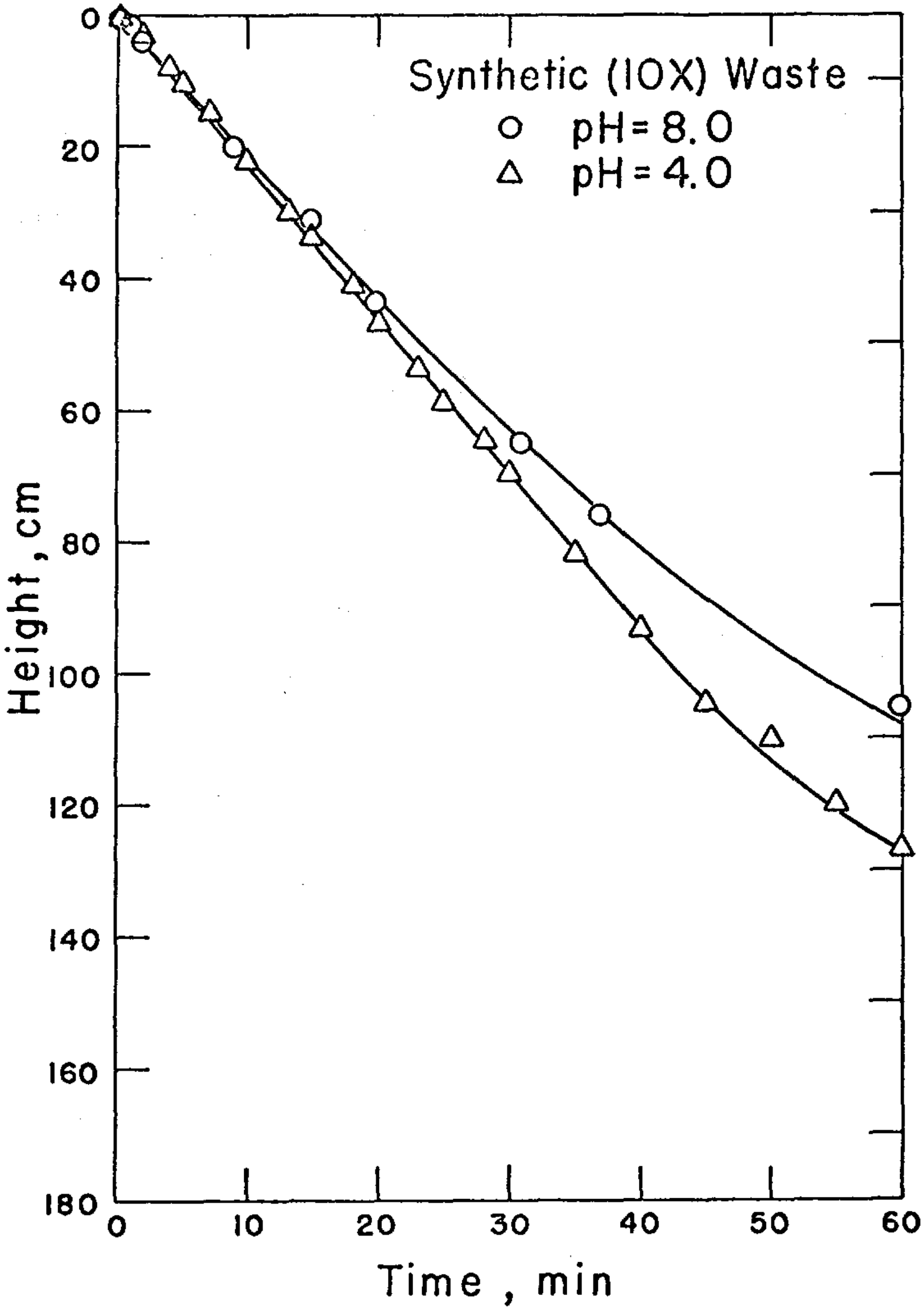


Figure 18. Settling Behavior of Synthetic (10X) Waste After pH Adjustment with Lime

TABLE 18

Settling Rates of Synthetic Wastes

Waste	Settling Rate, cm/min pH 4.0	 pH 8.0
1X	*	2.9
5X	1.8	3.3
10X	2.4	2.2
20X	0.9	---

*No Significant Precipitation

Table 19 summarizes the volume of sludge, produced for each waste at pH4 and 8. The increased sludge volumes at the high pH's are of course due to the presence of metal hydroxide precipitates. It can also be noted that the sludge produced from the synthetic (20X) waste at pH4 was 69% of the total volume of the waste, even after 60 minutes.

C. Charged Membrane Ultrafiltration of Acid Mine Wastes

1. Single Constituents

For a charged membrane ultrafiltration process to be feasible for the treatment of acid mine wastes, the membrane must be capable of totally rejecting suspended solids, adequately rejecting dissolved solids and, in particular, a substantial water flux loss must be avoided. Initially, to determine the approximate rejection behavior of the constituents present in the acid mine waste, experiments were made with single salt systems of Mg^{2+}, Fe^{3+}, Ca^{2+} and Mn^{2+}. The rejections, in general, were greater than 90% (Figure 19) and the flux drop in all cases was less than 15%.

2. Synthetic and Actual Wastes

Extensive studies were conducted with synthetic and actual acid mine wastes to determine the effects of pH,

TABLE 19

Volume of Sludge
(% of Total Volume of Sludge)

Composition	pH	Volume of Sludge Settling Time, Minutes 60	 75	 120
1X	4	--	--	--
1X	8	14	--	--
5X	4	36	29	20
5X	8	--	--	--
10X	4	24	12	--
10X	8	46	--	--
20X	4	69	--	--
20X	8	--	--	--

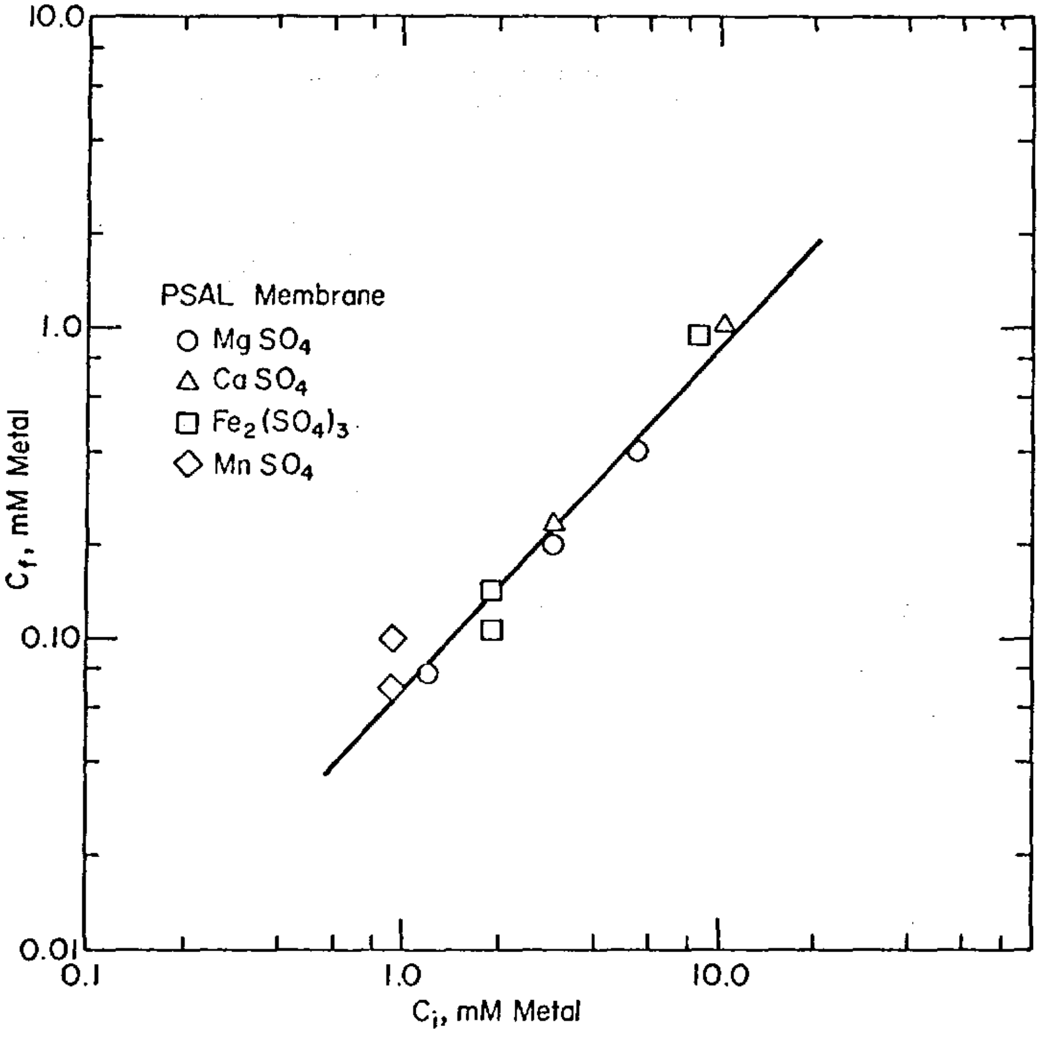


Figure 19. Relationship Between Ultrafiltrate Concentration and Feed Concentration for Single-Salt Systems

waste concentration, transmembrane pressure and channel velocity on the metal rejections and membrane water flux. Because ferrous (Fe^{2+}) iron present in the waste has proven to cause severe fouling problems due to precipitation, several initial experiments were also made with synthetic (1X) acid mine water containing 100 mg/l ferrous iron instead of ferric iron. Table 20 shows that the ferrous iron was adquately rejected by the membrane (92% and 94%). The table also shows the fraction present as precipitate. Although part of the feed Fe^{3+} and Al^{3+} was present as precipitate, considerably higher membrane rejections are due to the concommitant removal of soluble metals. Although Fe^{2+} would not be expected to precipitate at pH4, the partial oxidation of $Fe^{2+} \rightarrow Fe^{3+}$ resulted in $Fe(OH)_3$ precipitation, as shown in Table 20. However, in both cases the flux loss was only 15%, which did not indicate a severe fouling problem. Since no problems were evident with wastes containing ferrous iron and for consistency in the data, the remaining experiments were conducted with wastes containing ferric iron.

Preliminary studies were conducted with several tailored, charged membranes of different "initial" water flux (membrane resistance) values. Since the suspended solids of the feed increased significantly above pH5,

TABLE 20

Rejection of Metals and Fraction Precipitate Present in Ferrous Iron Synthetic (1X) Waste

$\Delta p = 5.6 \times 10^5 N/m^2$
pH = 4.2-4.7

Component	Rejection	Fraction Present as Precipitate
Conductivity	0.80-0.82	---
Al	$0.97-0.99^+$	0.63
Ca	0.86-0.87	0
Fe	0.92-0.94	0.43
Mn	0.90	0

due to iron and aluminum hydroxide precipitation, the majority of the membrane evaluations were conducted at or below pH 4.5 by adjusting the pH with lime (Figure 9).

Figures 20 and 21 show the overall rejection behavior and the flux characteristics as a function of the initial water flux (solute-free water). The initial water flux corresponds to the case where $\Delta\Pi$ and R_f in Equation 21 are zero. In every case the rejection of suspended solids was 100%; however, membranes with initial water flux greater than 25×10^{-4}cm/sec showed a drastic decline in the rejection of total solids (suspended solids plus dissolved solids). Also, membranes of initial water flux greater than 25×10^{-4}cm/sec (at $\Delta p = 5.6 \times 10^{5} N/m^{2}$) exhibited a greater loss in flux during operation with synthetic (1X) waste. Membranes with initial flux below 25×10^{-4}cm/sec exhibited a flux drop of only 10% to 15%. In light of these results, two types of membranes were chosen for extensive studies with acid mine wastes. The PSAL membrane chosen exhibited an initial water flux of 8.2×10^{-4}cm/sec at $\Delta p = 5.6 \times 10^{5} N/m^{2}$ and the PTAL membrane had an initial water flux of 17.3×10^{-4}cm/sec at $\Delta p = 5.6 \times 10^{5} N/m^{2}$. The PSAL and PTAL membranes had pore widths of approximately 12×10^{-8}cm and 18×10^{-8} cm, respectively.

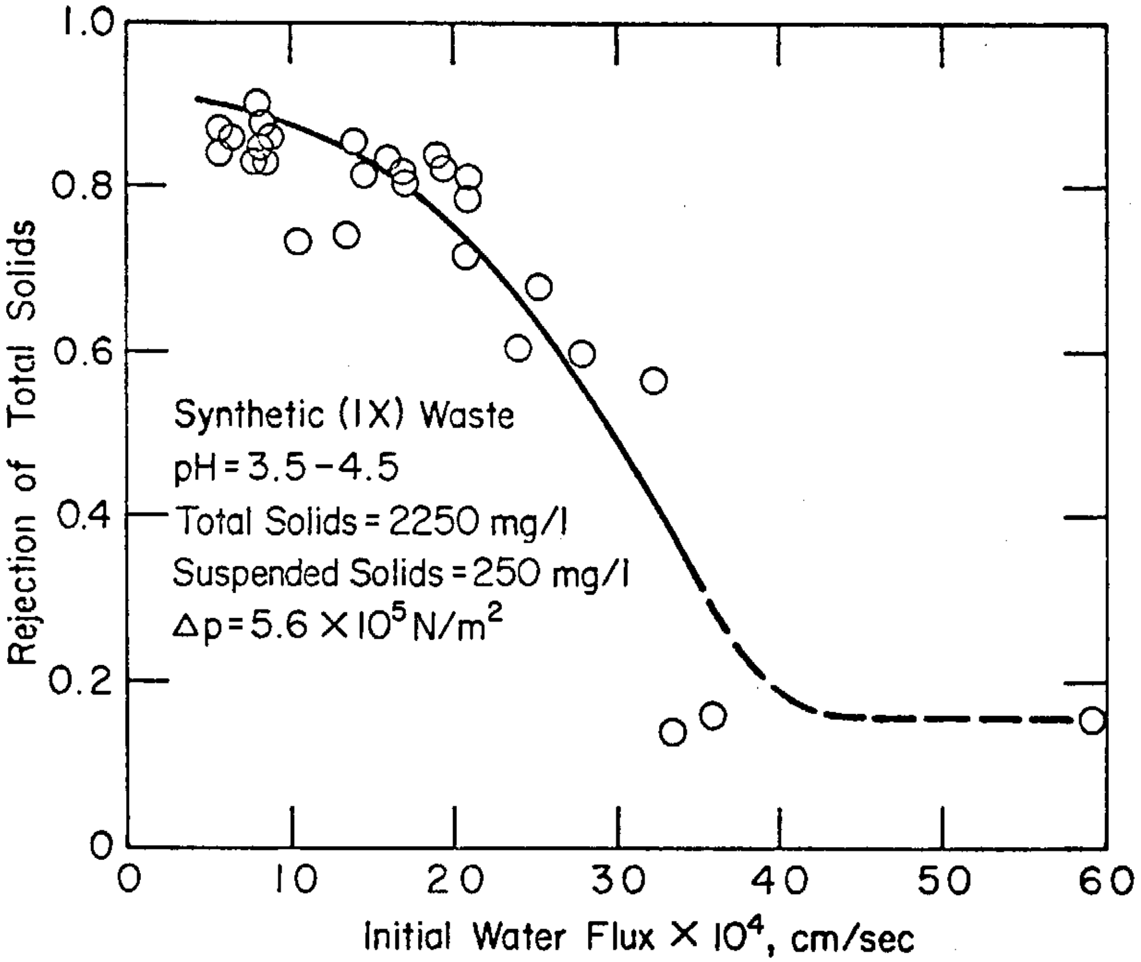


Figure 20. Dependence of Total Solids Rejection on Initial Water Flux

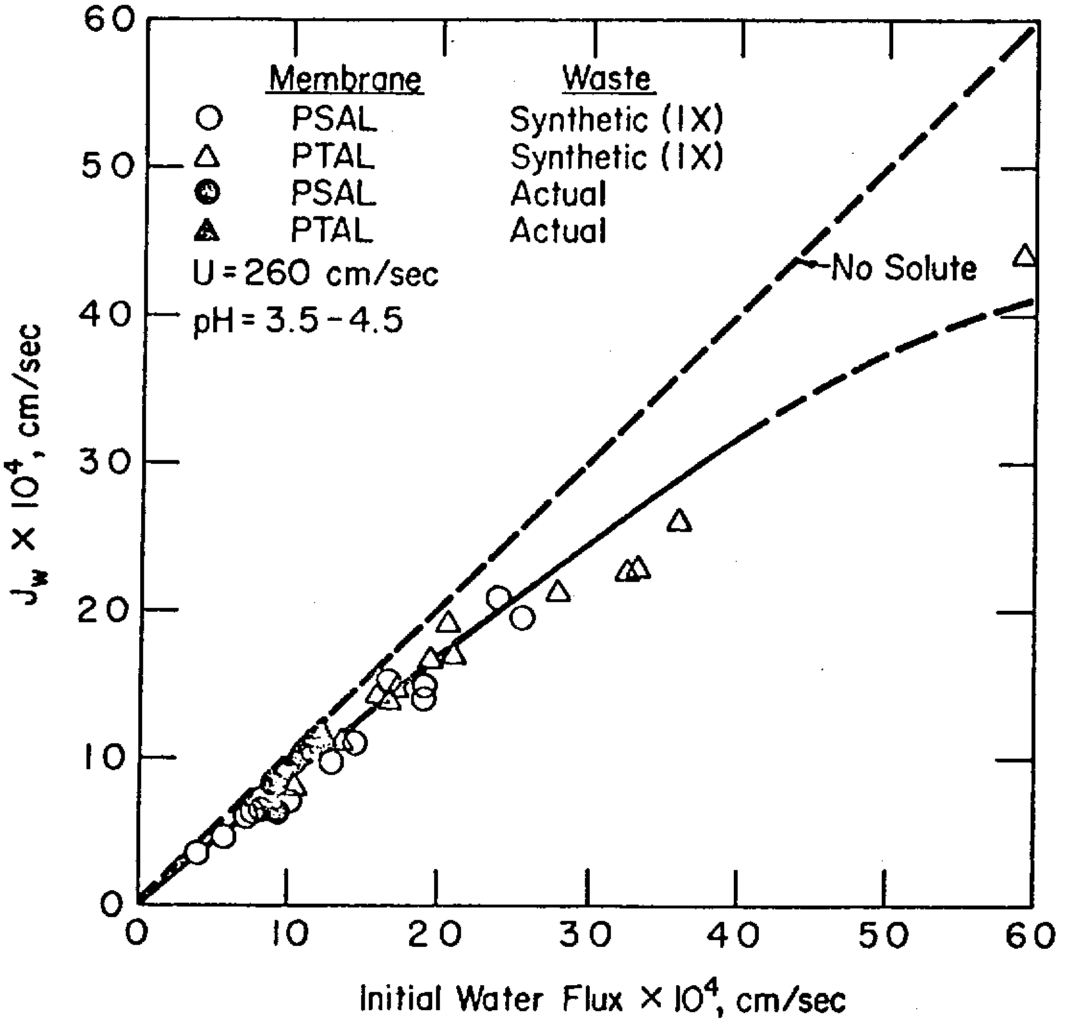


Figure 21. Dependence of Steady State Water Flux on Initial Water Flux

Evaluations were made with these membranes using the synthetic (1X) waste to determine the optimum operating transmembrane pressure and channel velocity. The effects of pressure at a high channel velocity is shown in Figure 22. The linear increase in flux with transmembrane pressure indicates insignificant membrane fouling. Because of possible membrane compaction problems, a pressure of $5.6\text{x}10^5 \text{N/m}^2$ (80 psi) was selected as an optimum. Figure 23 shows the effect of channel velocity at a constant pressure. Below a channel velocity of 80 cm/sec the flux loss is significant for both membranes due to membrane fouling and above 250 cm/sec the flux gain is insignificant. Because of this a channel velocity of 250 cm/sec (Re = 7500) was chosen. The flux drop at U = 250 cm/sec and $\Delta p = 5.6\text{x}10^5 \text{N/m}^2$ was only 13%.

In depth studies were made with each waste to determine the flux behavior as a function of time and waste concentration. The results for the studies with both PSAL and PTAL membranes for synthetic (1X), actual and synthetic (10X) wastes appear in Figures 24 to 27. In all cases the water flux reached a steady state value within 2 hours. The flux behavior exhibited with the synthetic (1X) waste was evaluated with several types of PSAL and PTAL

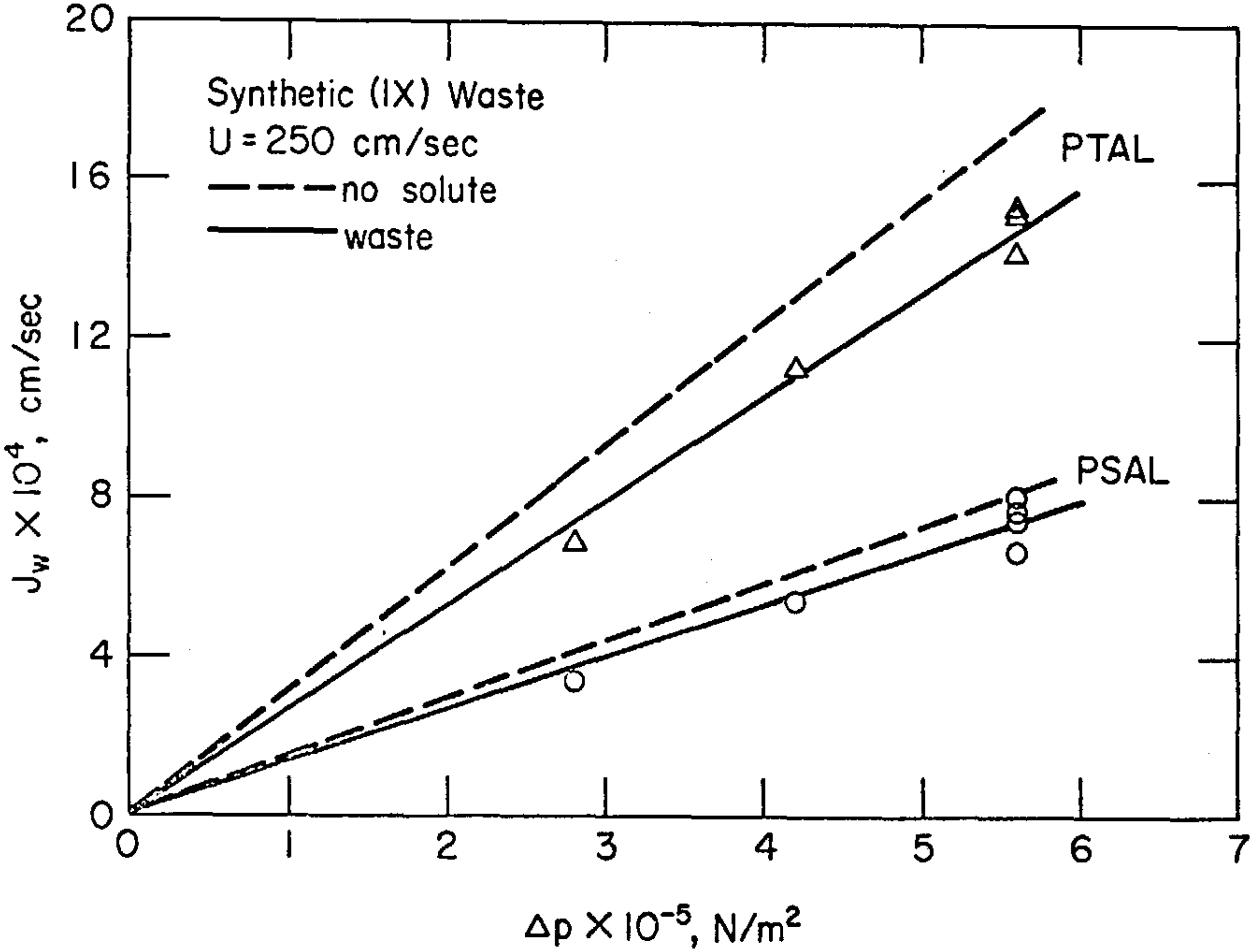


Figure 22. Effect of Transmembrane Pressure on Steady State Water Flux

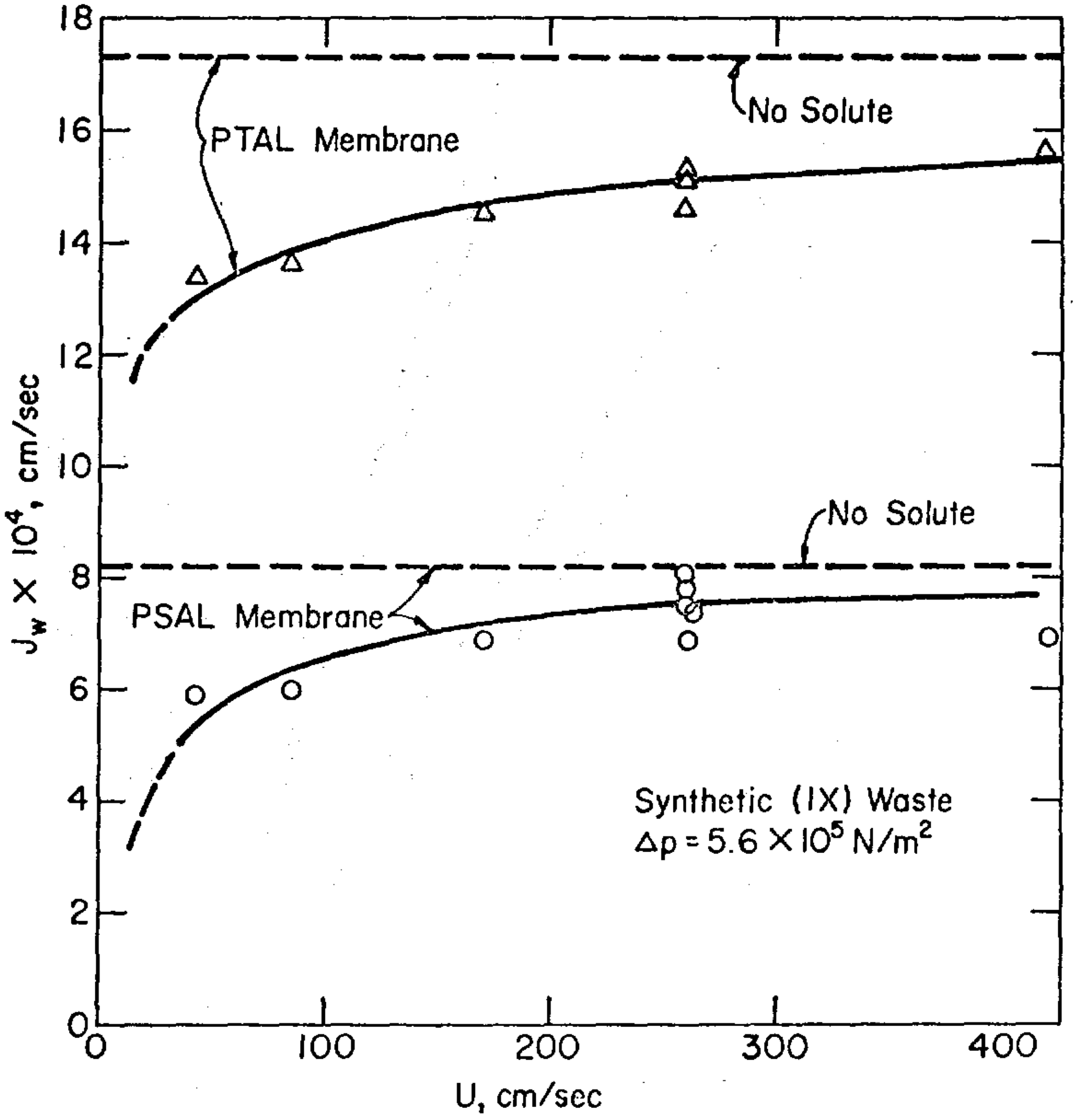


Figure 23. Effect of Average Channel Velocity on Steady State Water Flux

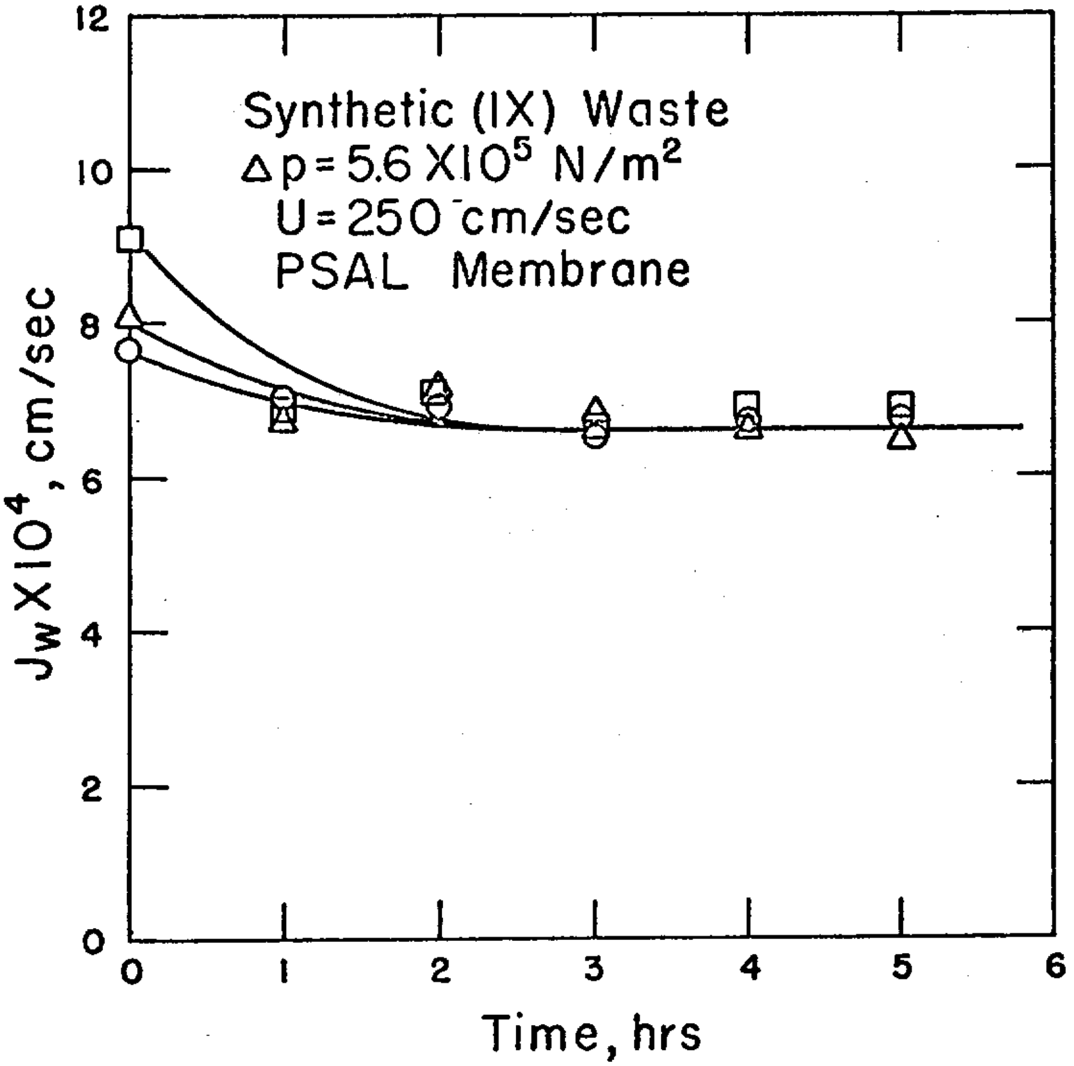


Figure 24. Variation of Water Flux with Time for a Synthetic (1X) Waste with a PSAL Membrane

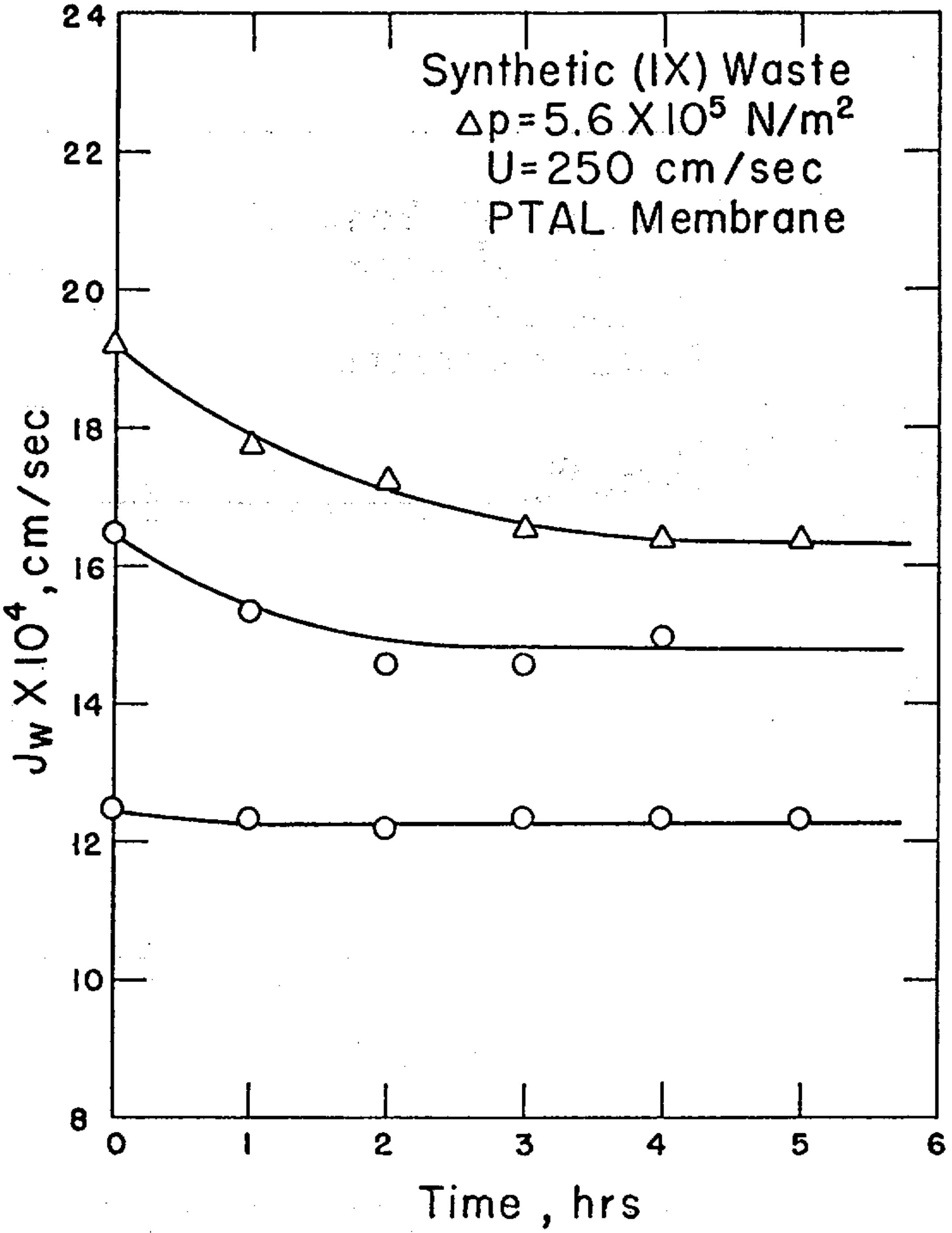


Figure 25. Variation of Water Flux with Time for a Synthetic(1X) Waste with a PTAL Membrane

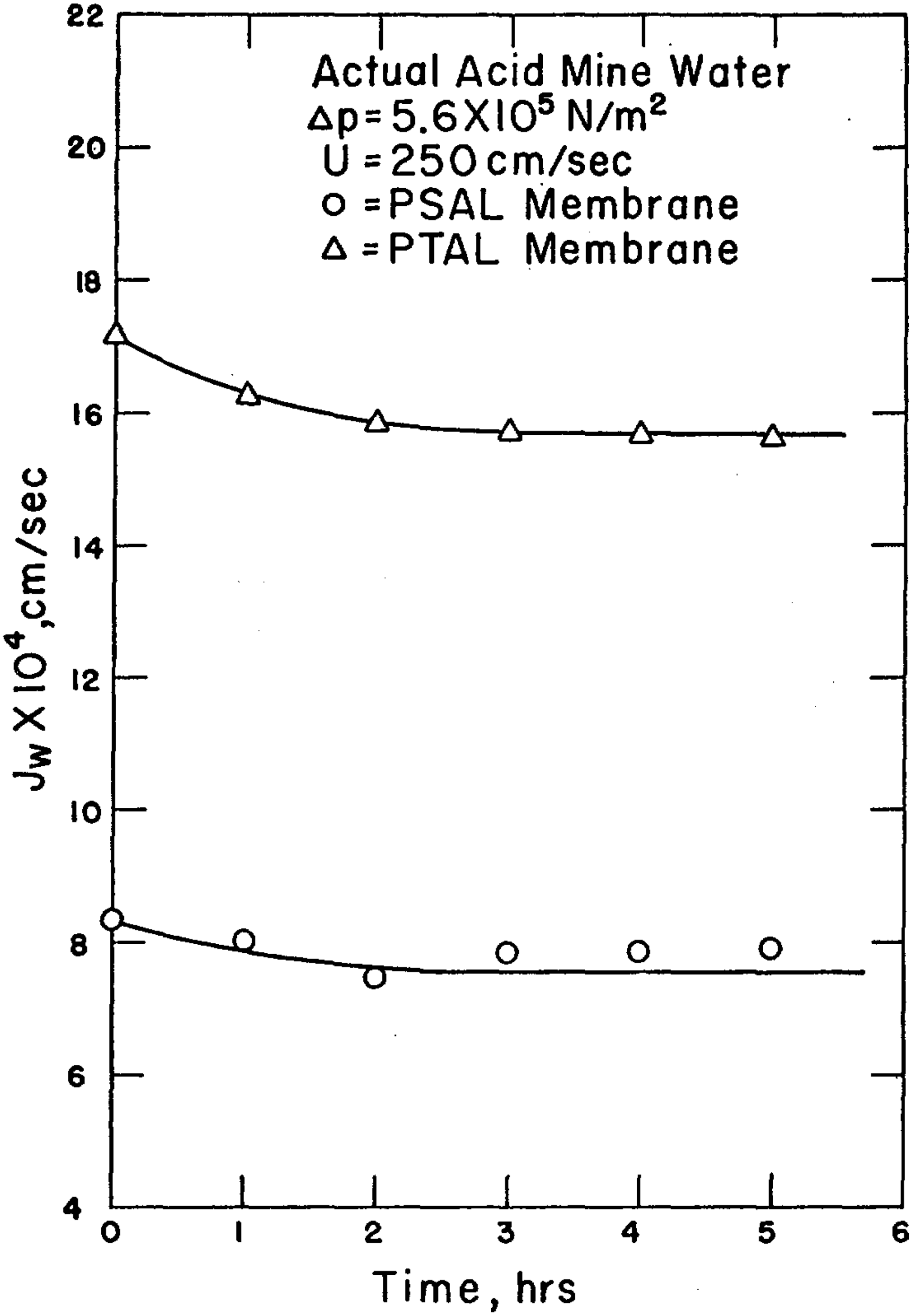


Figure 26. Variation of Water Flux with Time for an Actual Acid Mine Waste

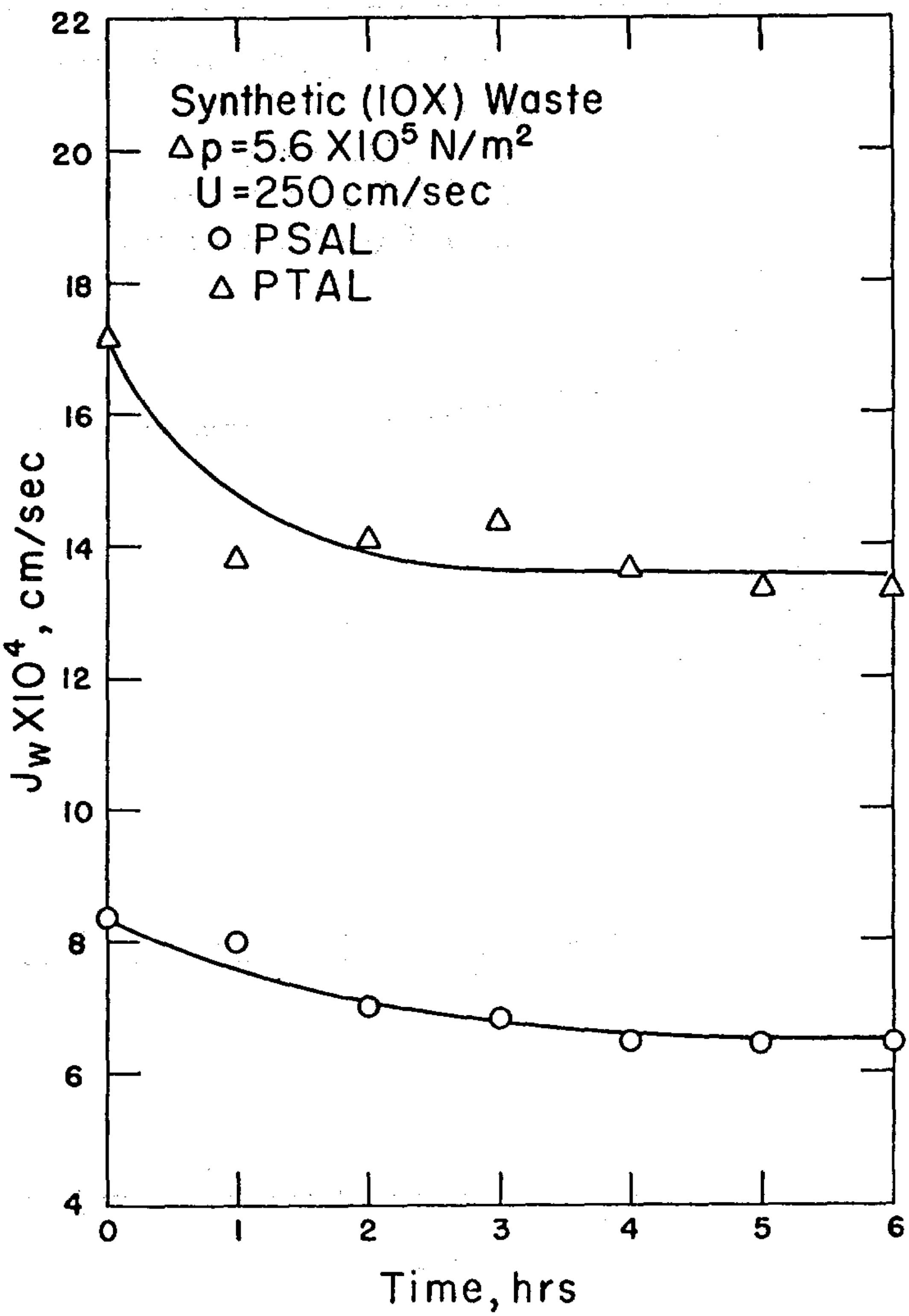


Figure 27. Variation of Water Flux with Time for a Synthetic (10X) Waste

membranes. The PSAL membranes (Figure 24), even though each had a different initial water flux, exhibited the same water flux value at steady state. The PTAL membranes (Figure 25) were more porous and therefore were more susceptible to fouling. This was evident since the flux drop increased as the initial water flux increased. Increase in initial water flux corresponds to decrease in membrane resistance. The flux drop increased from 2% to 14% as the initial water flux increased from 12.5 cm/sec to 19.2 cm/sec at $5.6\times10^5 N/m^2$. The actual mine waste (Figure 26) exhibited, with both membranes, a flux loss of only 10% which was comparable to that of the synthetic (1X) waste. Because of the high concentrations of suspended solids, the flux drops exhibited by the more concentrated wastes were higher. For example, the drops in flux with the 10X waste (Figure 27) were 22% for each membrane. The data obtained from these studies were combined to determine a relationship between the total solids concentration of the waste and the expected steady state water flux and to simulate effects of high water recovery. This relationship appears in Figure 28. It is noted from this figure that the water flux declines as the concentration of total solids increases; however, for a total solids concentration of approximately 10,000 mg/l (10x waste)

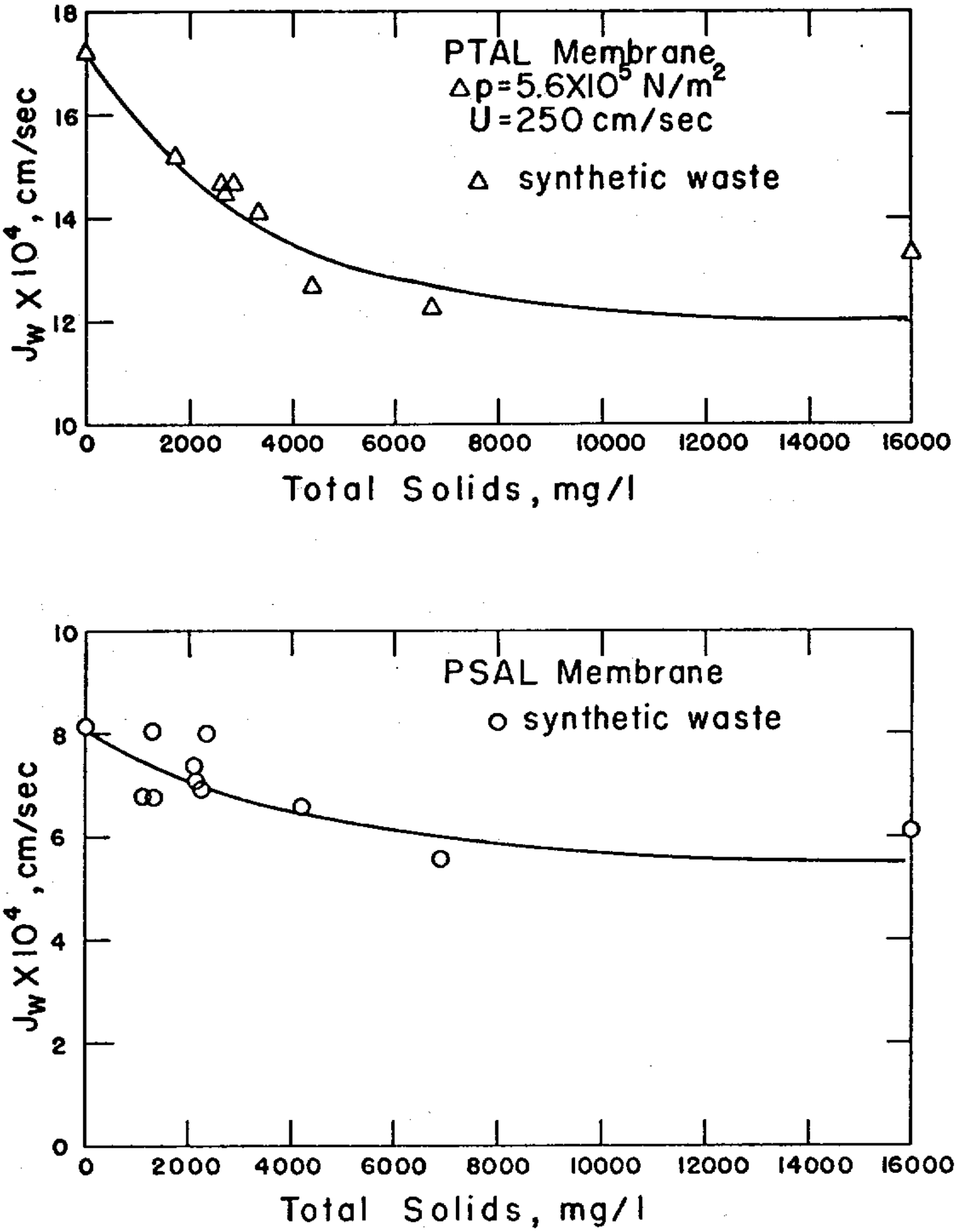


Figure 28. Dependence of Steady State Water Flux on Feed Stream Total Solids Concentration

the flux becomes relatively constant. This is due to the abrasive action of the precipitates flowing across the membrane surface, which can scour deposits from the surface.

Studies were made with the synthetic 1X and 5X wastes to determine the flux behavior over long periods of operation. Both membranes exhibited good water flux stability even after several operating days (Figures 29 and 30). The drop in flux was less than 17% with both membranes.

The membrane rejection behavior of the various metals in the synthetic 1x wastes as a function of pH appears in Figure 31 for the PSAL membrane. At pH 3.0 no metal hydroxide precipitates were present, and the figure shows excellent soluble metal rejections. At pH 4.0-4.5, 95% of the Fe and 30% of the Al in the feed were present as precipitates, and thus simultaneous removals of dissolved metal ions and metals were obtained. With the PTAL membrane, rejections (Table 21) of Fe^{3+} and Al^{2+} were similar to those with PSAL; whereas, Mn^{2+} and Ca^{2+} rejections were somewhat lower. The membrane rejections obtained with the actual mine water (Figure 32) are slightly lower than those obtained with the synthetic waters. Good metal

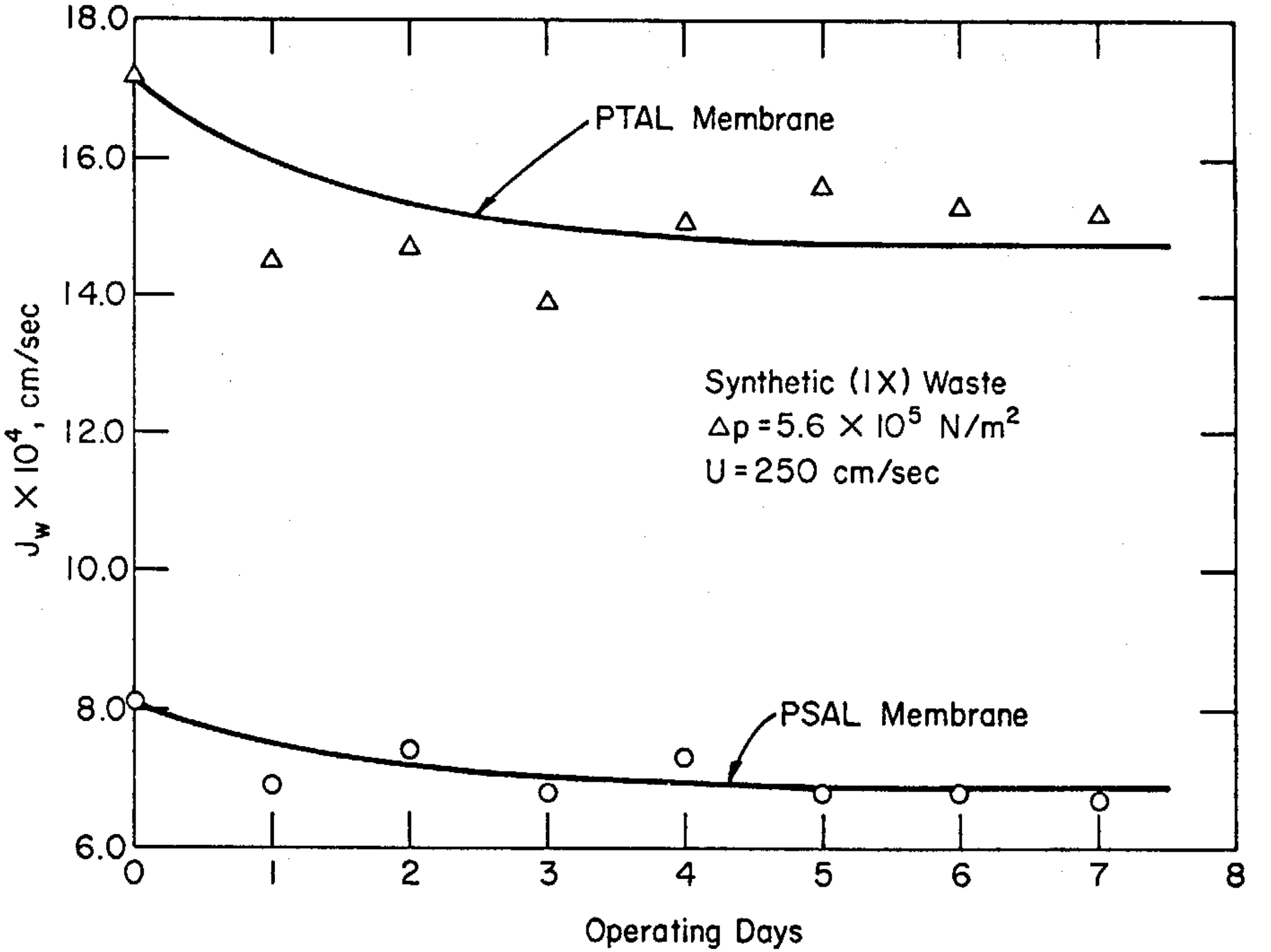


Figure 29. Long Term Water Flux Behavior with Synthetic (1X) Waste

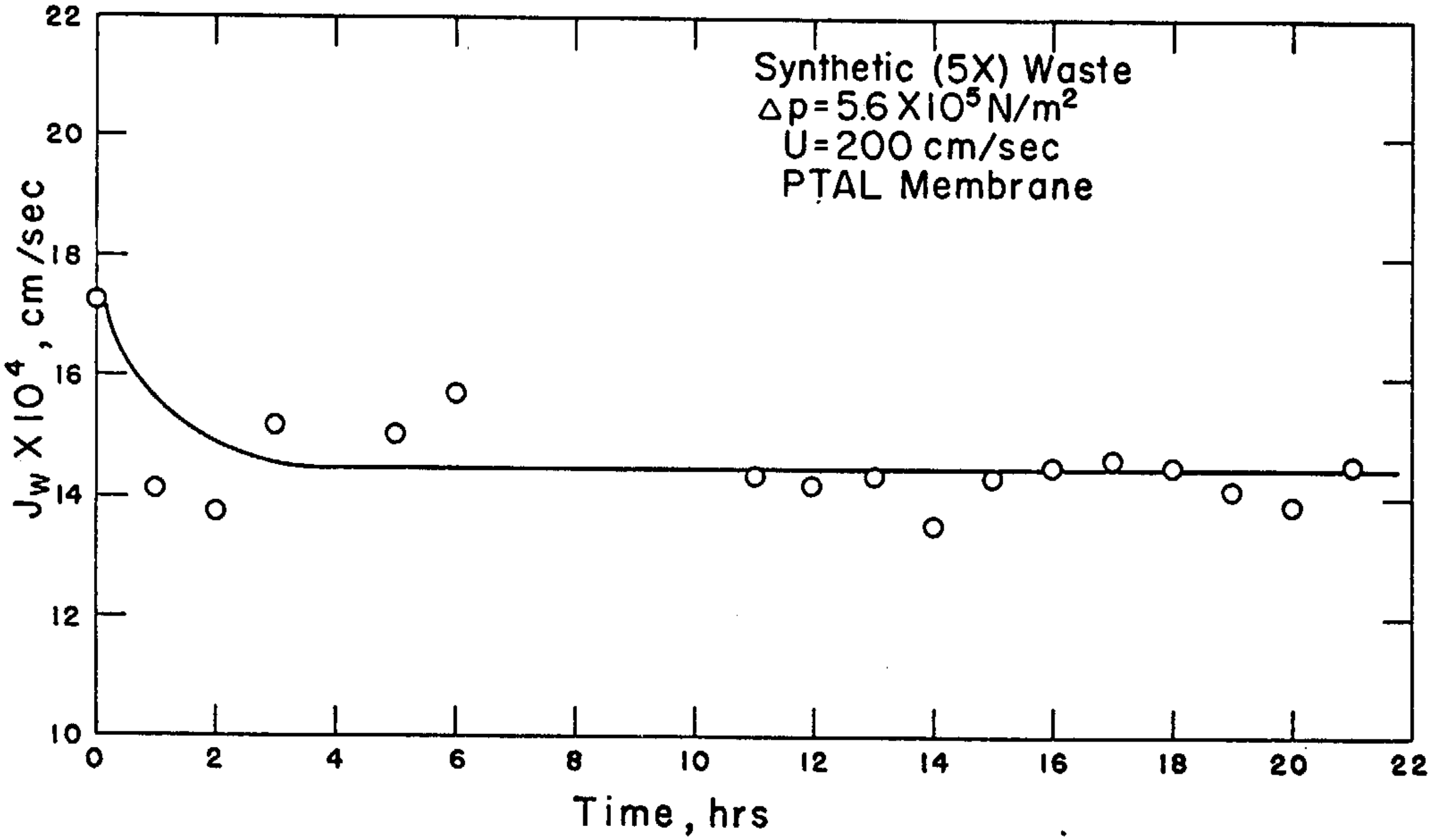


Figure 30. Long Term Water Flux Behavior with Synthetic (5X) Waste

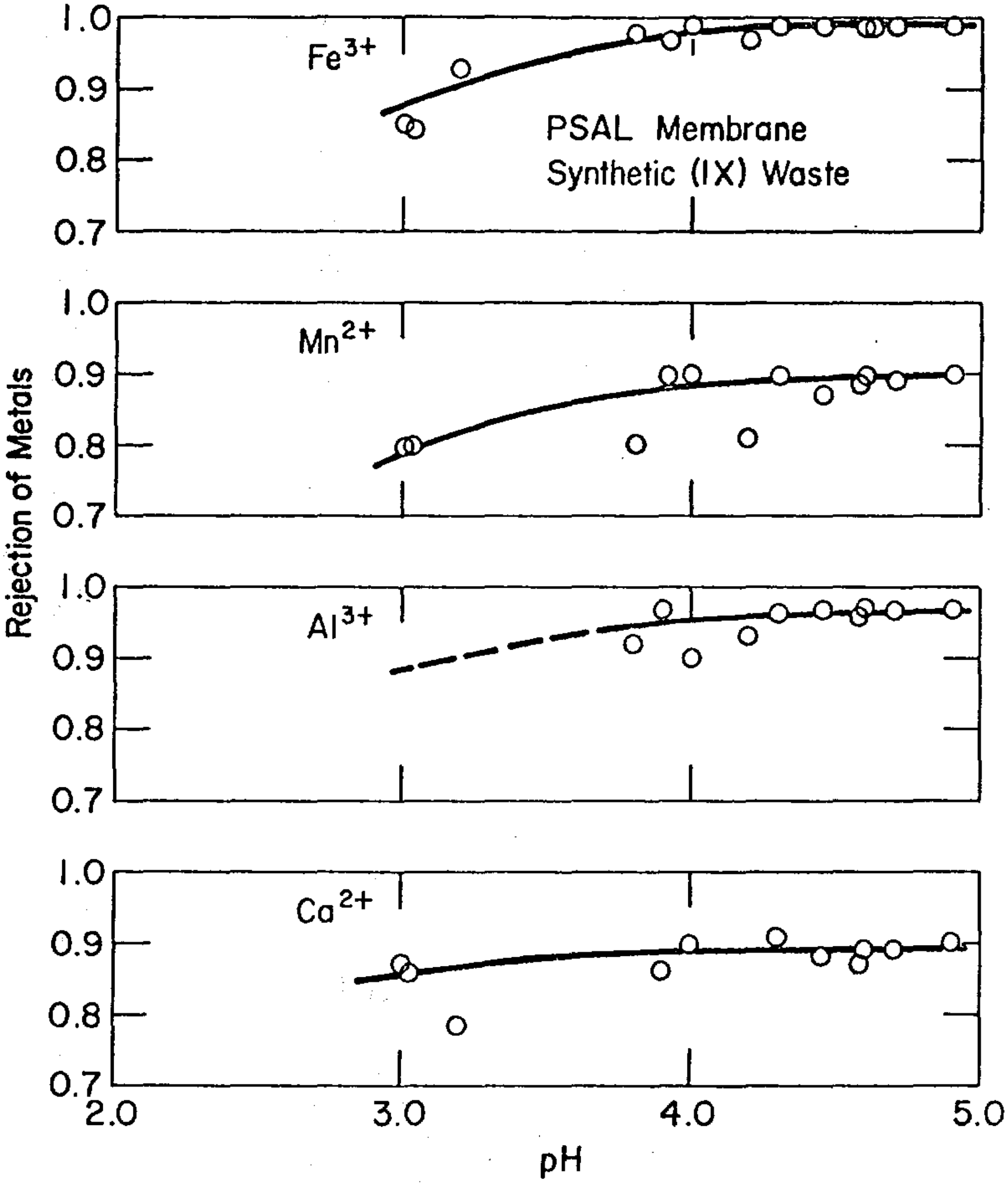


Figure 31. Effect of pH on Rejection of Metals with Synthetic (1x) Waste

TABLE 21

Rejection of Metals from Synthetic (1X) Wastes

$\Delta p = 5.6 \times 10^5 N/m^2$
pH = 4.0-4.5

Membrane	Rejection			
	Al	Ca	Fe	Mn
PSAL	0.95	0.88	0.99	0.86
PTAL	0.95	0.79	0.99	0.80

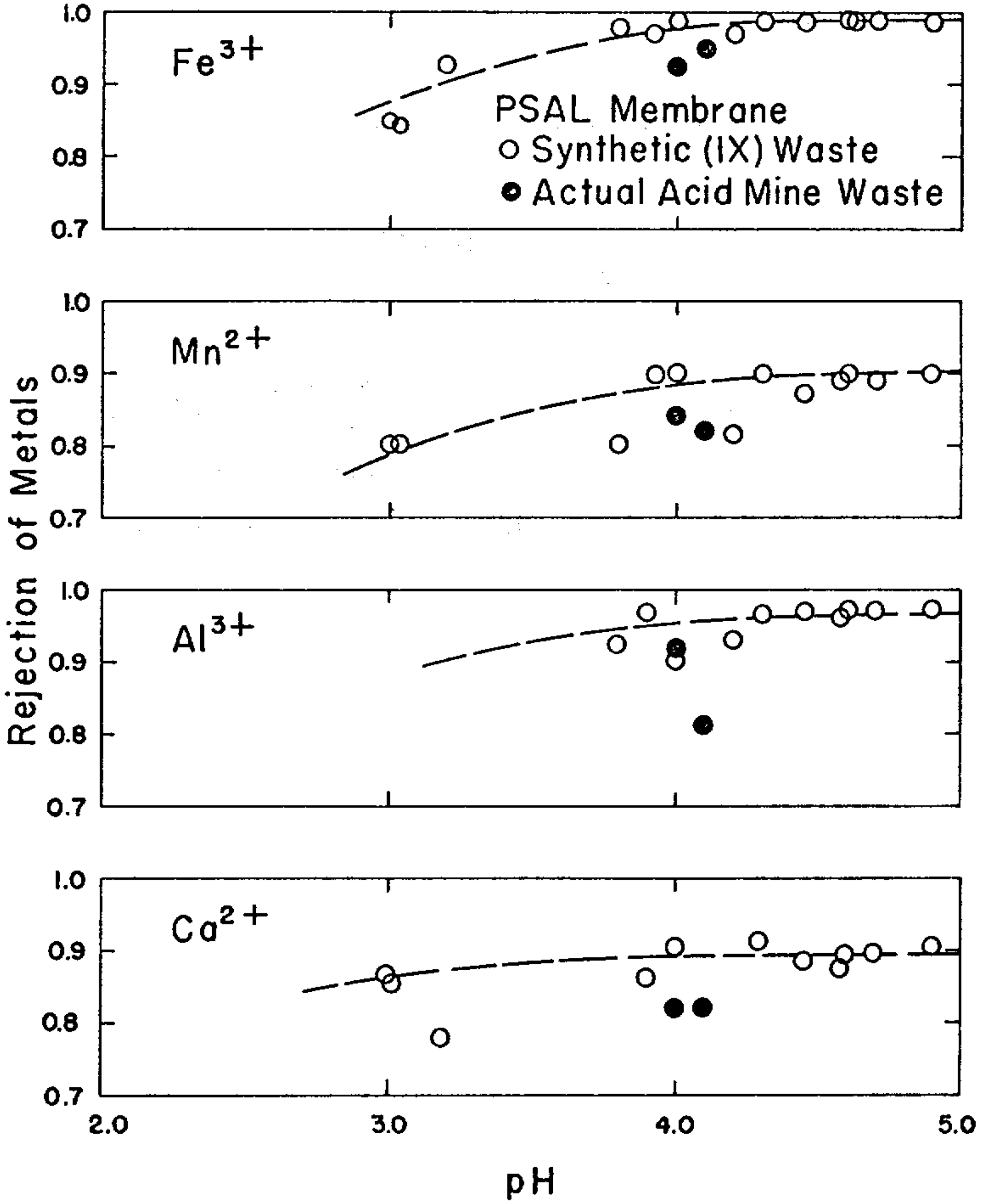


Figure 32. Comparison of Metal Rejection Behavior with Synthetic (1X) and Actual Wastes

rejections were also obtained with the PTAL membranes (Table 22). Metal rejections obtained with the 5X and 10X wastes appear in Table 23. In all cases the Fe was removed in excess of 99% because of precipitation.

For the experiments discussed above, the membrane system was operated at insignificant water recovery. With any waste systems, if rejection of metals is a function of waste concentrations, the overall metal removal would depend on the extent of water (ultrafiltrate) recovery.

A series of experiments were conducted to determine the effect of water recovery on the rejections of metals. As seen in Figures 33 and 34, the PSAL membrane more effectively removed the metals. In both cases the Fe rejection was approximately 99% even at 90% recovery. The removal of Mn was markedly affected by the extent of water recovery. Although the Ca removal initially was similar to that of Mn, it was not as strong a function of recovery and therefore the Ca removal stayed relatively constant over the range of recovery levels.

3. Settled Synthetic Wastes

A series of ultrafiltration studies were conducted with settled wastes (at pH 4.0-4.5) to determine if a pretreatment scheme of lime precipitation-settling would

TABLE 22

Rejections of Metals from Actual Mine Wastes

PTAL Membrane
pH = 4.0-4.5
$\Delta p = 5.6 \times 10^5 N/m^2$

Component	Rejection
Al	0.93
Ca	0.75
Fe	0.95
Mn	0.77

TABLE 23

Rejections of Metals from Concentrated Wastes

$\Delta p = 5.6 \times 10^5 N/m^2$
pH = 4.0-4.5

Waste	Membrane	Rejection			
		Al	Ca	Fe	Mn
5X	PSAL	0.90	0.88	>0.99	0.77
10X	PSAL	0.86	0.91	>0.99	--
5X	PTAL	0.95	0.87	>0.99	0.72
10X	PTAL	0.96	--	>0.99	0.70

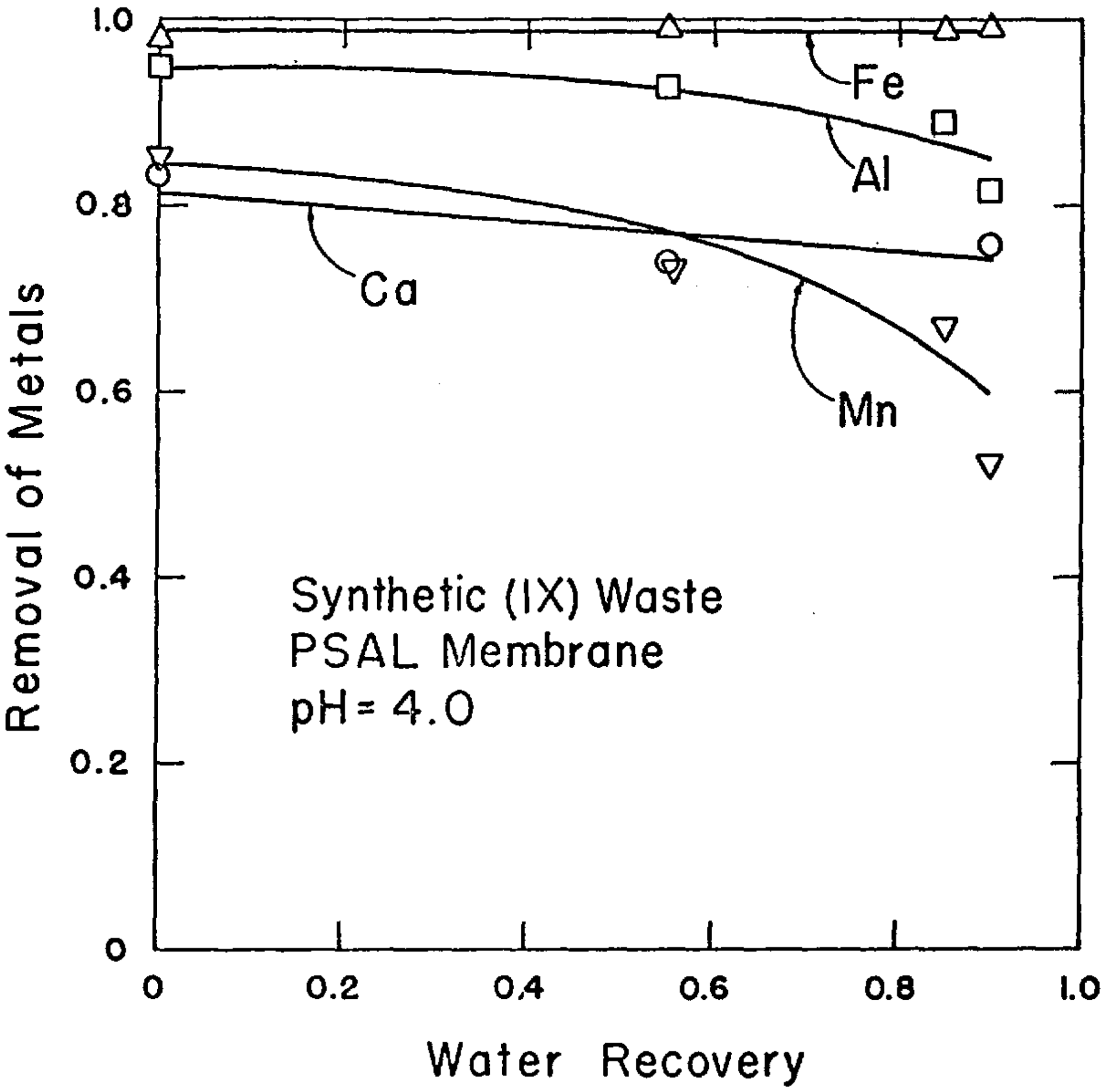


Figure 33. Dependence of Metal Removals on Water Recovery with PSAL Membranes

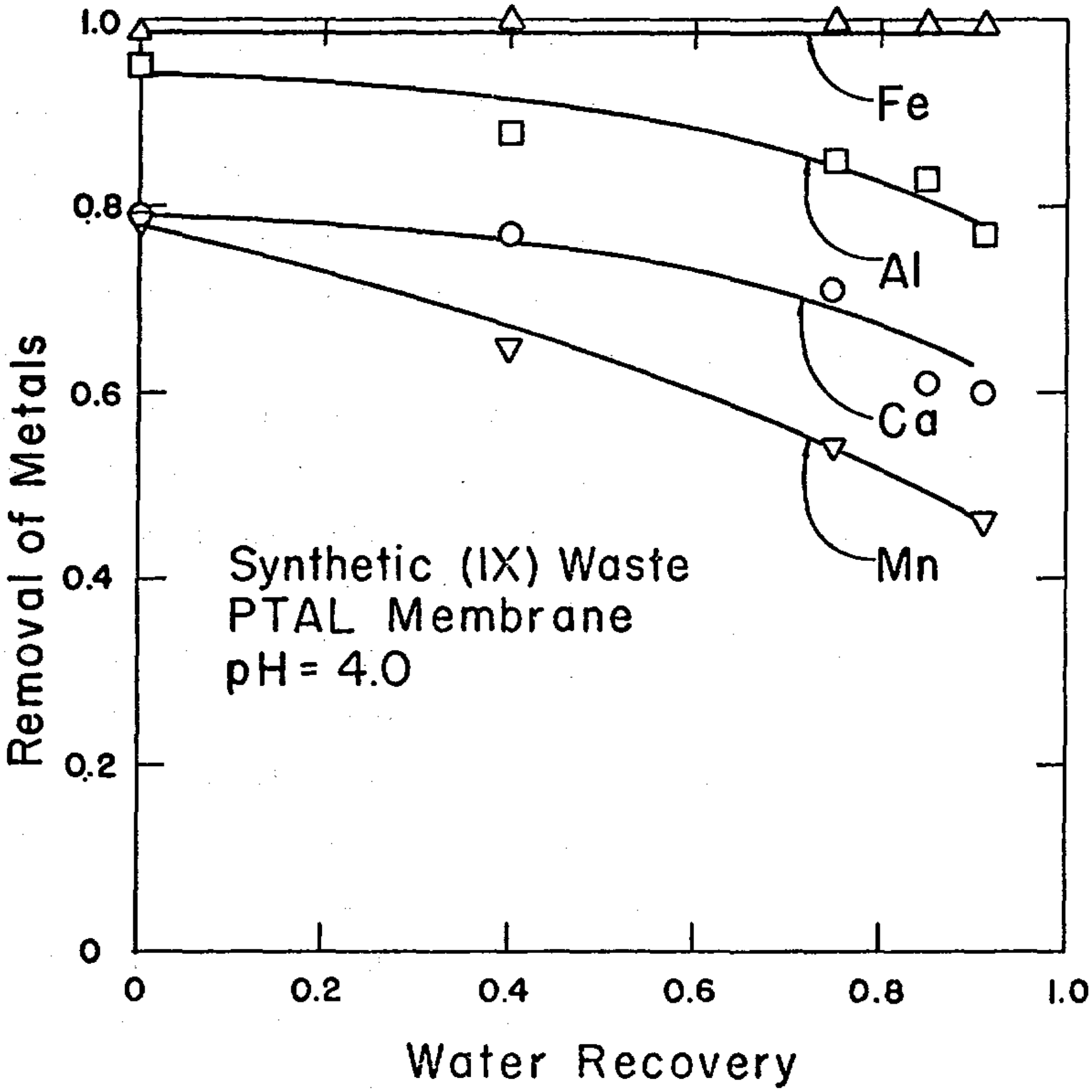


Figure 34. Dependence of Metal Removals on Water Recovery with PTAL Membranes

reduce membrane fouling problems caused by metal hydroxide precipitates and $CaSO_4$, and would improve ultrafiltrate quality by reducing the inlet concentrations to the ultrafiltration unit. The extent of metal separations and reduction of suspended solids that could be obtained with various wastes (1X to 20X) were discussed in Section B.1. Examples of the water flux as a function of time for settled 5X, 10X, and 20X waste appear in Figures 35 to 37. With each membrane the flux drop increased as the waste concentration increased; however, the flux drop obtained with the settled wastes were greater than those exhibited with the unsettled wastes. With the PSAL membrane, for example, the flux drop obtained with an unsettled 10X waste was 22% (Figure 27), but with the settled waste the drop increased to 29%. The flux obtained with the PTAL membrane with the settled and unsettled wastes (Figure 36 and Figure 27) were similar. A pretreatment scheme also allows the ultrafiltration of 20X waste without extensive membrane fouling due to suspended solids. The flux drops with the PSAL and PTAL membranes were 27% and 17%, respectively. Flux behavior of both unsettled and settled wastes are compared in Figure 38. The flux drop with the PSAL membranes was higher with settled wastes. The differences in flux drop behavior

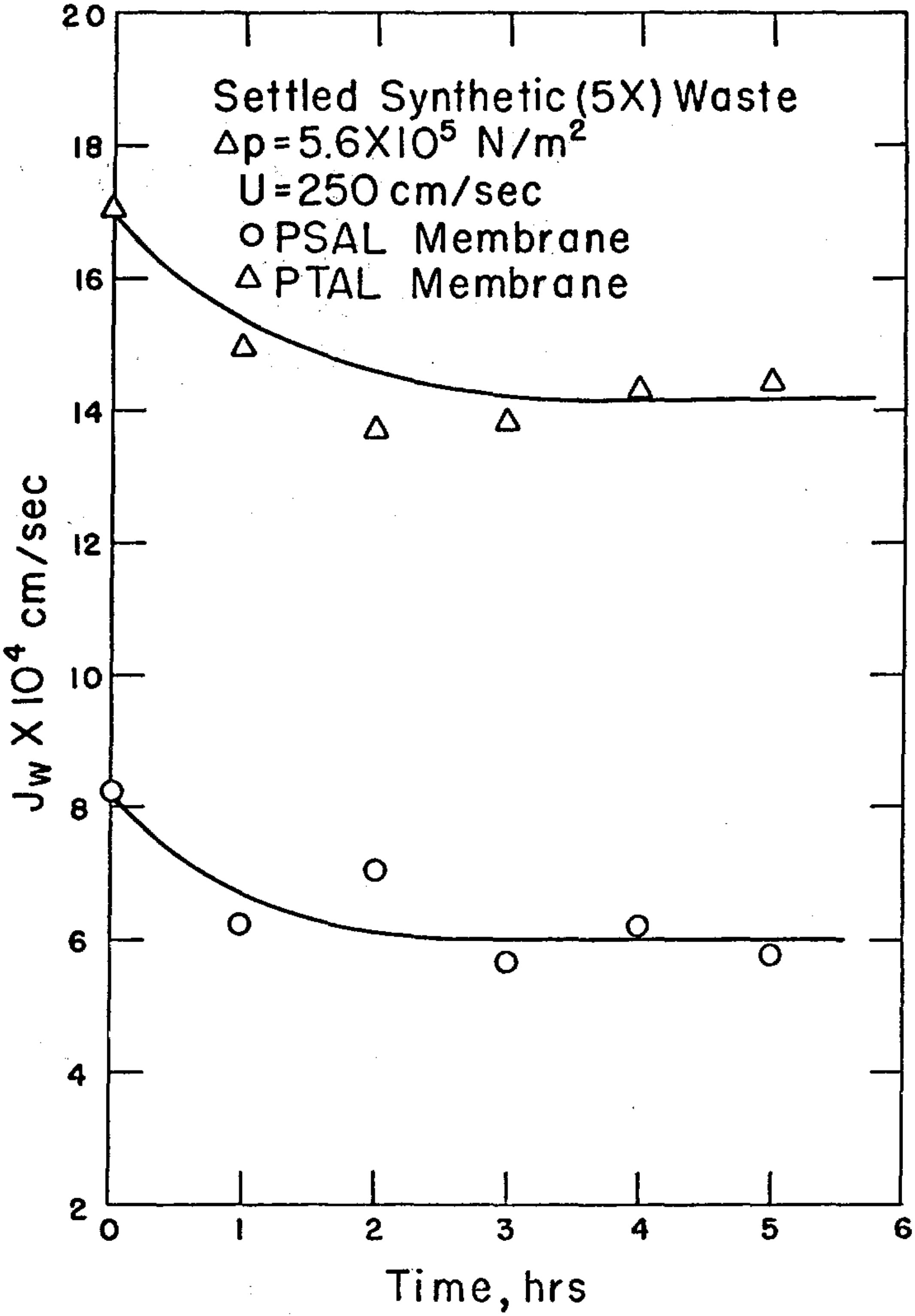


Figure 35. Ultrafiltrate Water Flux Behavior with Settled Synthetic (5X) Waste

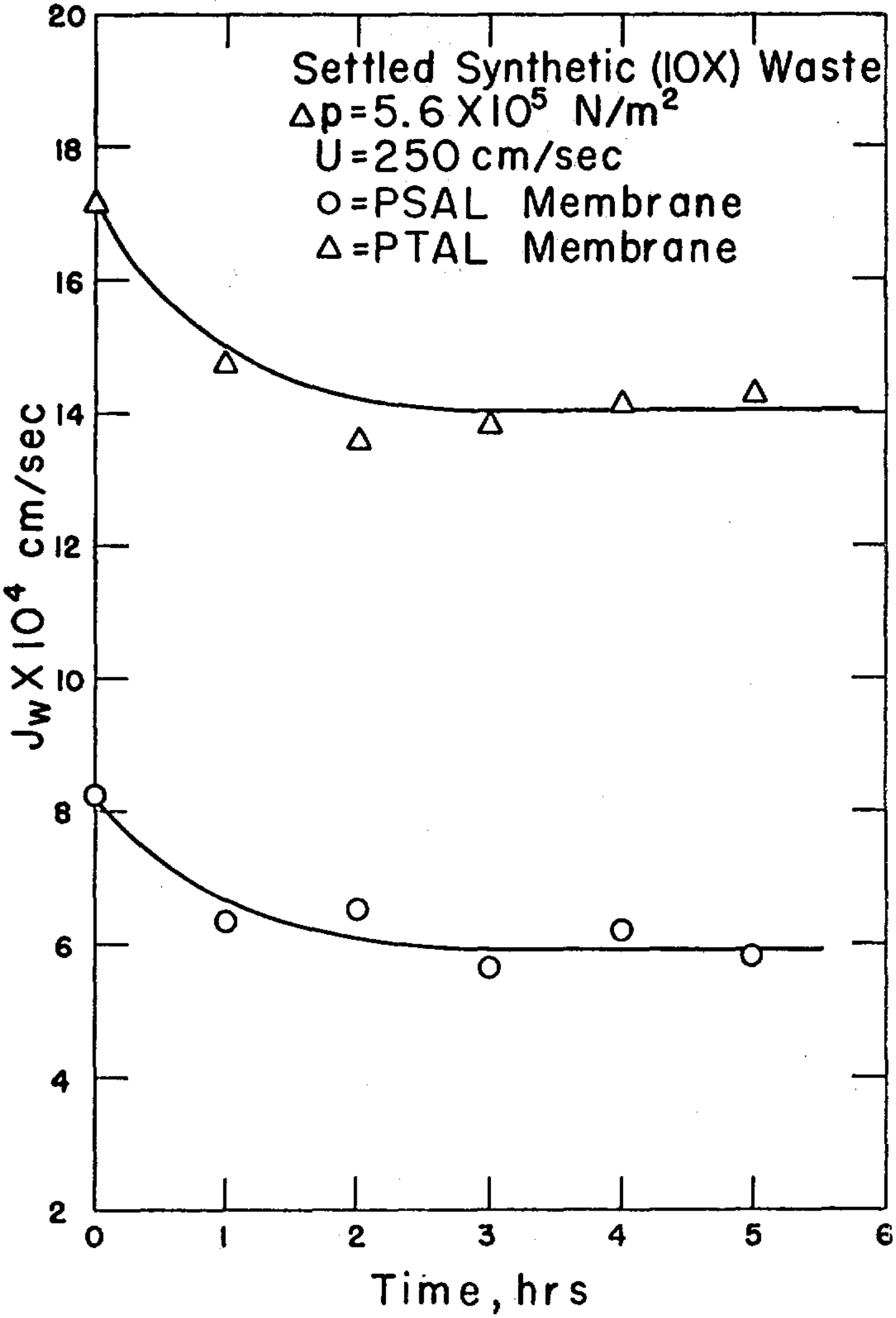


Figure 36. Ultrafiltrate Water Flux Behavior with Settled Synthetic (10X) Waste

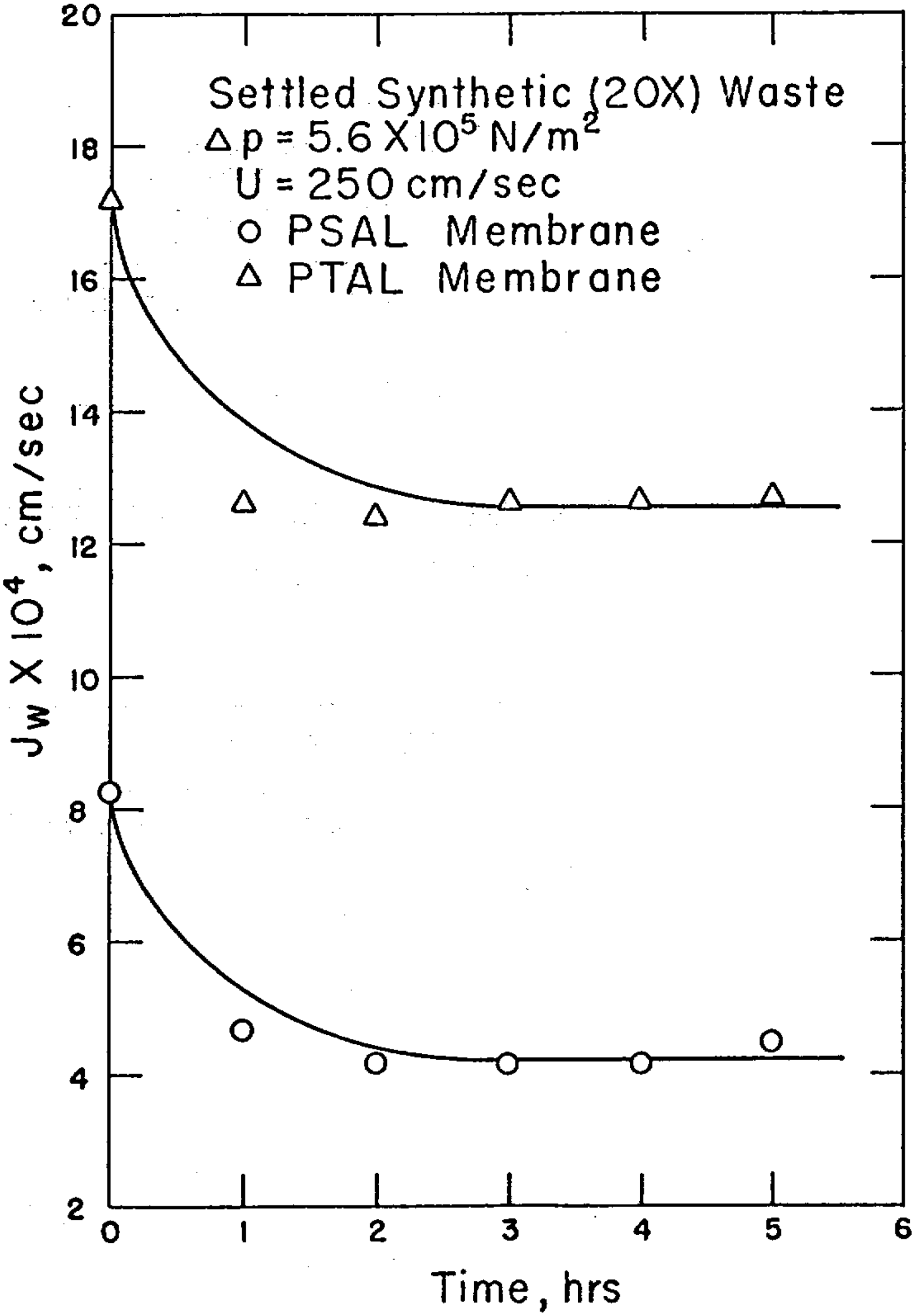


Figure 37. Ultrafiltrate Water Flux Behavior with Settled Synthetic (20X) Waste

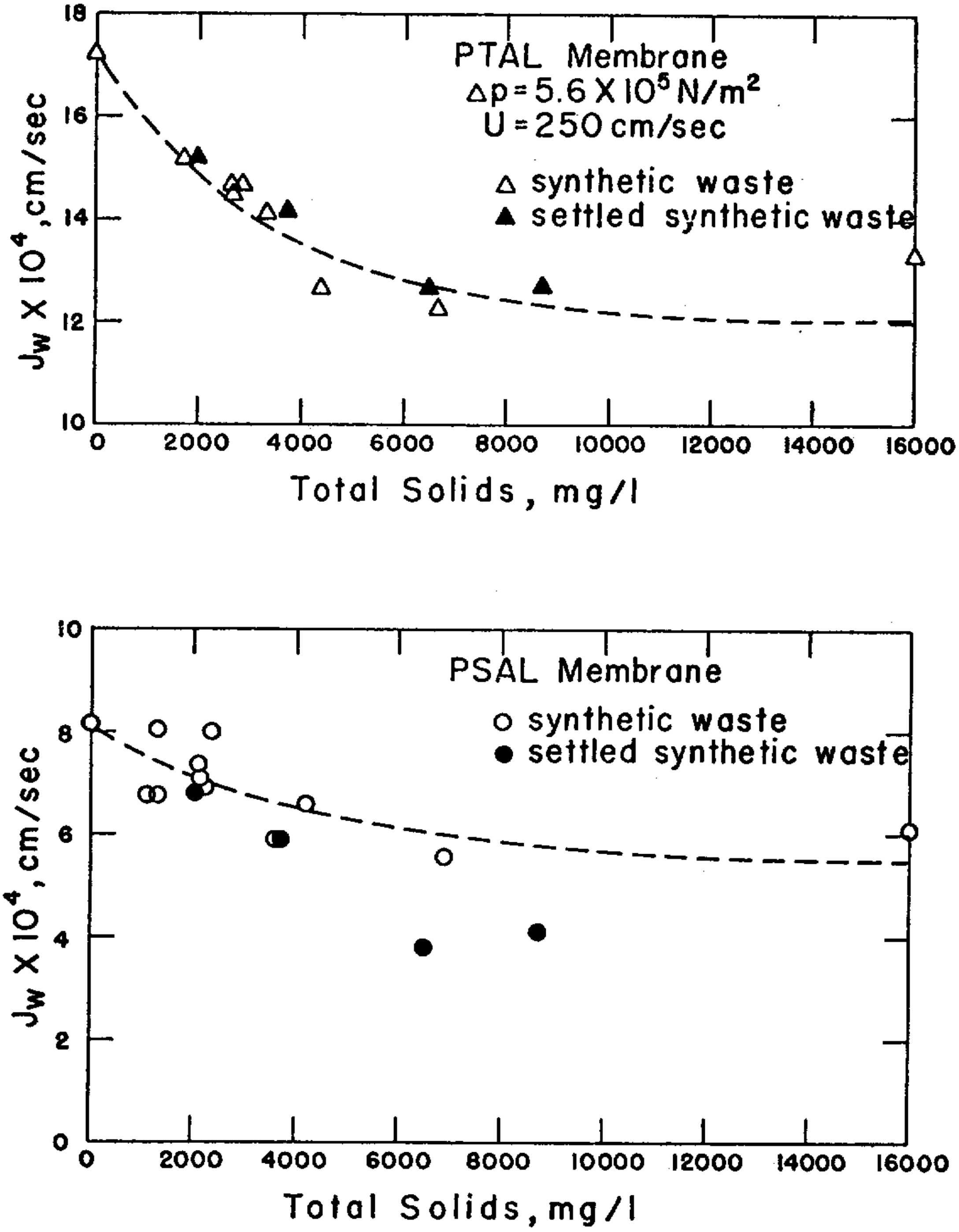


Figure 38. Comparison of Steady State Water Flux with Settled and Unsettled Synthetic Wastes

between PSAL and PTAL membranes may have been caused by the chemical nature of each membrane.

In addition to establishing flux behavior with settled wastes, the ultrafiltrate water quality for combination precipitation-ultrafiltration was determined. The effluent concentrations from the combination process with 5X and 10X wastes appear in Table 24. The Fe concentration in the effluent was less than 1 mg/l in all cases, as expected. With exception of the Fe rejection, the rejections were greater than 83%. The average rejections obtained from the settled 20X waste were less (0.74 for Ca and 0.78 for Mn) than those obtained with the less concentrated wastes. And in every case the rejections with the PSAL membrane were greater than those with the PTAL membrane.

TABLE 24

Rejection of Metals from Settled Wastes

$\Delta p = 5.6 \times 10^5 N/m^2$
pH = 4.0-4.5

Waste	Component	Inlet Concentration mg/l	Rejection PSAL	Rejection PTAL
5X Settled	Al	96.5	0.99	0.99
	Ca	622	0.89	0.83
	Fe	3.42	>0.99	>0.99
	Mn	50	0.96	0.83
10X Settled	Al	746	0.97	--
	Ca	100	0.92	--
	Fe	18.8	>0.99	>0.99
	Mn	187	0.91	0.86

VIII. DESIGN CONSIDERATIONS

Any membrane process produces two streams (Figure 5); one ultrafiltrate (membrane permeate) stream and a concentrate stream. For the operation of a full-scale ultrafiltration unit to be feasible, a high level of water recovery must be maintained to produce a large volume of ultrafiltrate (permeate) which could be reused or discharged and to produce a concentrate stream of low volume. At this level of recovery the membrane must be capable of adequately rejecting soluble metals and sulfate and completely removing suspended solids without a significant loss in water flux.

A. Membrane Systems

Membrane systems are manufactured in the form of tubular, spiral-wound, or hollow-fiber modules. Depending on the type of systems selected, pretreatment of wastes may be required prior to entering the membrane unit. Tubular membranes are manufactured by casting the membrane material on a porous tube. The material may be cast on either side of the tube, but is usually cast on the inside because of the improved hydrodynamics. This configuration is very tolerant of feed streams with high suspended solids, but the large brine channel leads to high concentration polarization. Spiral-wound modules provide the turbulence required to reduce concentration polarization but, due to thin brine channels, require prefiltration of the feed if high concentrations of suspended solids are present. The hollow-fiber configuration (hollow-fiber inside diameter ≈ 20μm) has a high packing density which allows the system to yield the highest product rate per volume ratio even though they exhibit lower fluxes than other configurations. The narrow feed channels prevent the handling of feed streams containing any suspended solids greater than 10 μm; therefore, a pretreatment technique must be provided. Table 25 shows the membrane packing density and pretreatment requirements for various configurations. The packing density values provide information on waste treatment space requirements. With hollow-fiber modules, membranes of low flux can even be used to provide high permeate water throughput from the system because of the high packing density.

B. Scale-Up of the Ultrafiltration Process

The level of water recovery, r, can be effectively increased by arranging multiple ultrafiltration modules in an optimum tapered array (22, 49, 54) as shown in

TABLE 25

Comparison of Membrane Modules

Module	Packing Density, m^2/m^3	Pretreatment of Feed Waste
Spiral-wound	656	Yes
Tubular (1.3 cm ID)	196	No
Hollow-fiber	9186	Yes

in Figure 39. Bhattacharyya, et al. (49, 53) have developed a simulation technique for determining the effect of water recovery on solute removal at various membrane rejection values. The model is based on the theory that the metal concentration in the ultrafiltrate increases as the concentration of the waste increases (Equations 25 and 26) as occurs when water is recovered from the process. Results from the simulation for various rejection levels (as indicated by values of "n") appear in Figures 40 and 41 for two values of water recovery. The solute removal shown on the ordinate is based on the average ultrafiltrate concentration from all the membrane units in the system and is given by Equation 19. The membrane rejection, R, appearing as the abscissa is the rejection obtained from laboratory-scale experiments conducted at zero water recovery with an inlet feed waste of 1X concentration. For example, the solute removal from an ultrafiltration system operating at 90% recovery (Figure 40) for which the membrane rejection for that solute was 80% and the change of rejection with increasing inlet concentration followed Equation 26 and was a function of the inlet concentration to the power 0.30, was 50%.

As discussed previously, high water recoveries can be simulated in the laboratory by conducting ultrafiltration

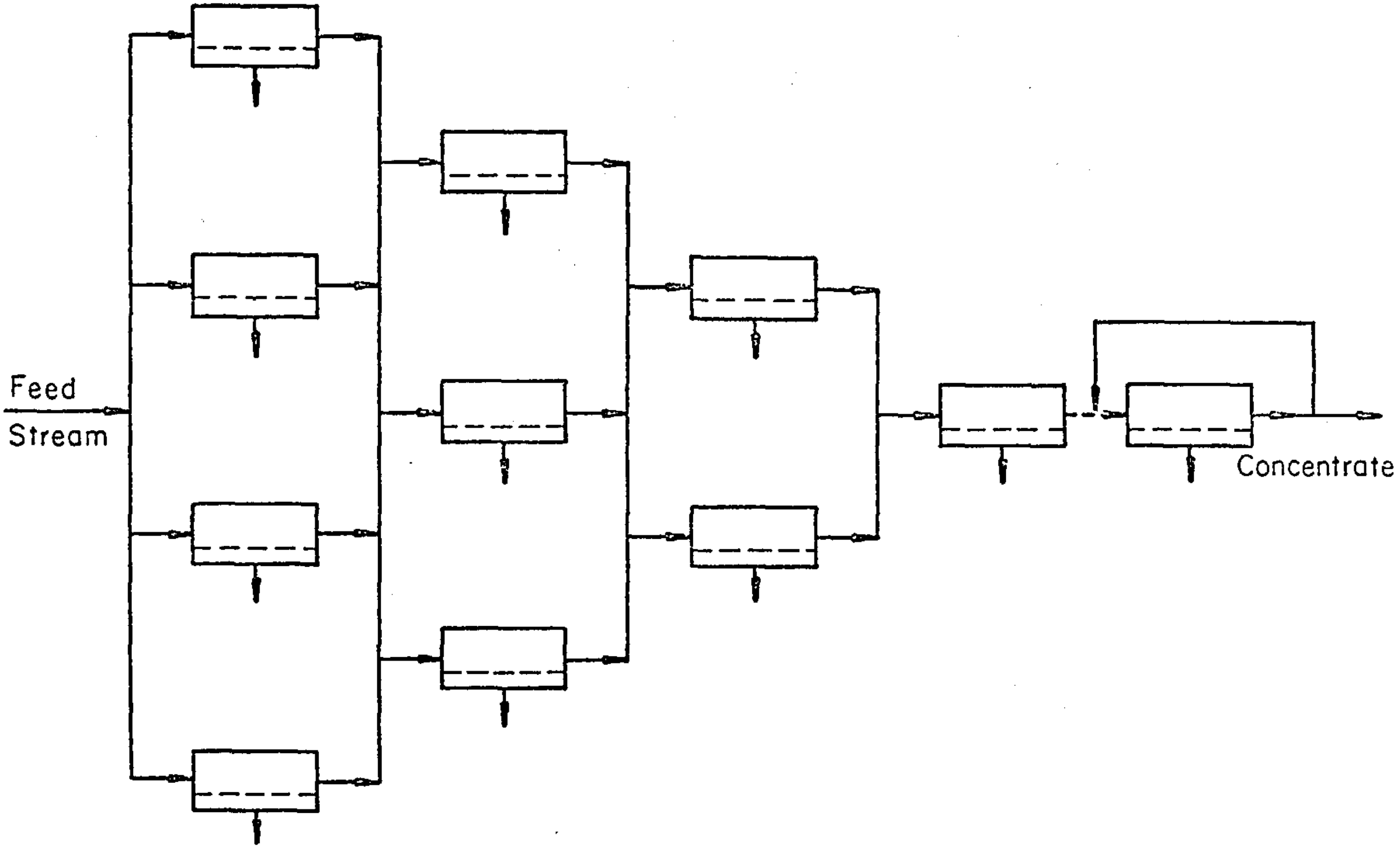


Figure 39. Module in Tapered Configuration

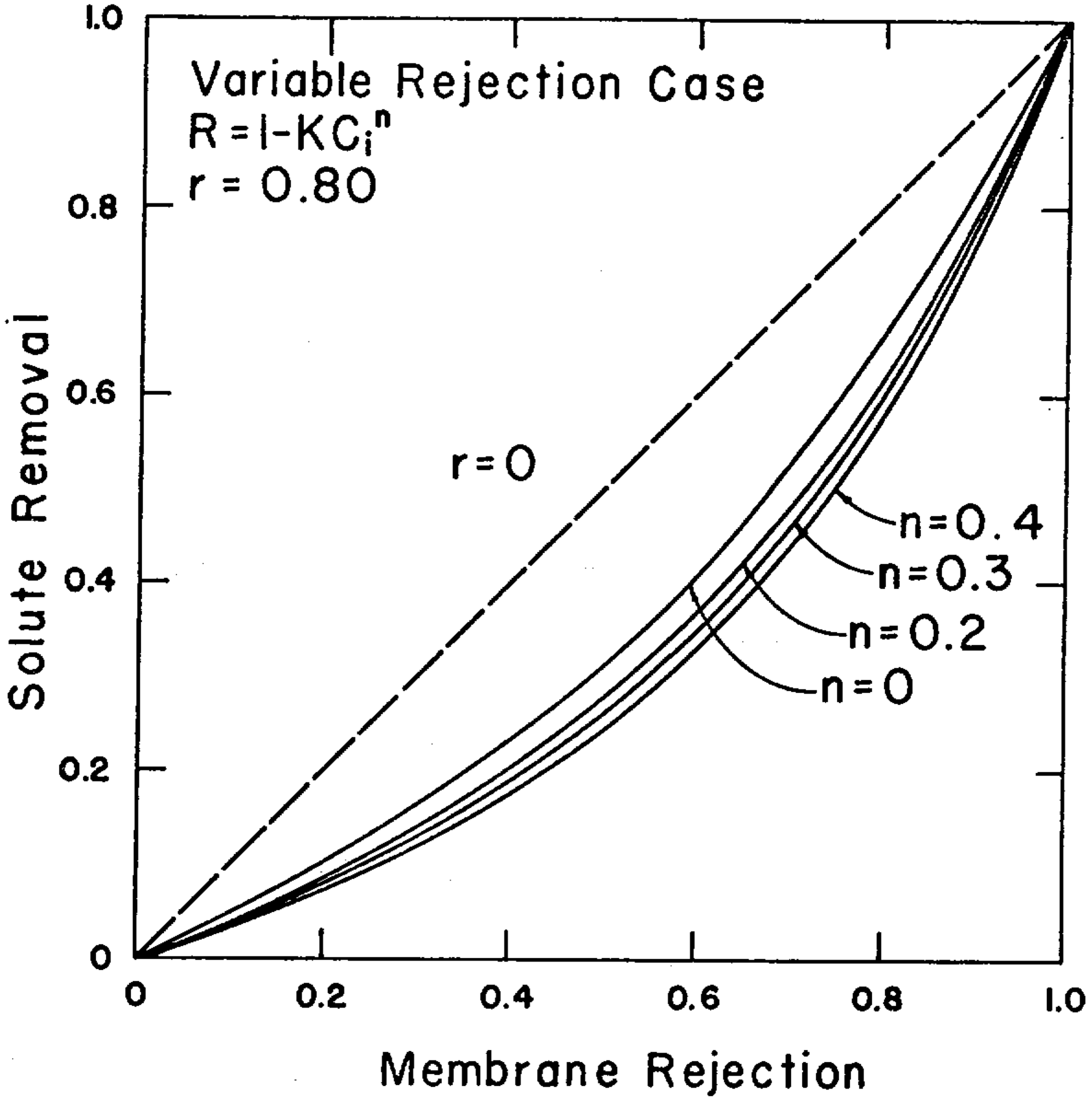


Figure 40. Prediction of Solute Removals as a Function of Membrane Rejections for Various Values of "n" (Equation 26) at r=0.80

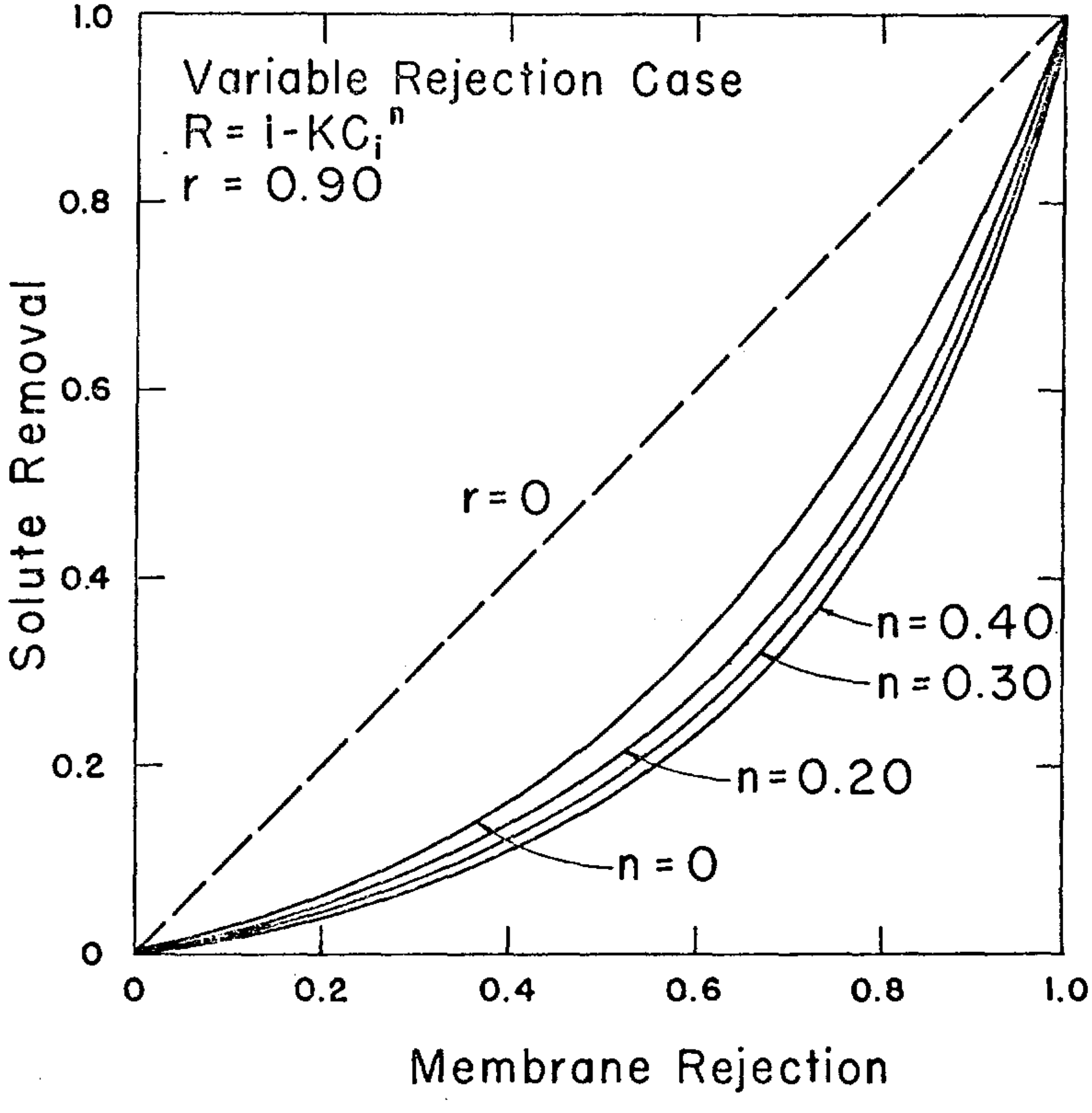


Figure 41. Prediction of Solute Removals as a Function of Membrane Rejection for Various Values of "n" (Equation 26) at r = 0.90

experiments with concentrated wastes. A 5X waste approximately corresponds to the concentration the membrane would be exposed to at 80% water recovery and a 10X waste would simulate 90% water recovery. Therefore, the effect of water recovery on overall metal rejections can be determined by studying the metal rejections obtained with 5X and 10X wastes. Using the metal rejections from the 1X, 5X, and 10X wastes (Tables 21 and 23) the constants, n and K, in Equation 26 were determined and appear in Table 26. The value of n = 0 corresponds to the case where the rejection is not a function of concentration. The values of K were determined from the rejection (Table 21 at pH ≃ 4) data of 1X waste (K = 1-R). For any values of $n \geq o$, the metal removals would decline with increasing feed stream concentration (water recovery) according to Equation 26. Figure 42 shows the results of the simulation for the specific case of acid mine waste with a 1X feed concentration (waste composition shown in Table 12). The graph on the right hand side should be read for Ca and Fe, since the rejections of these metals are not a function of inlet concentration (n = 0). The graph on the left hand side should be read for Mn and Al since the rejections are a function of concentration. For example, the Ca removal from a unit operating at 90% recovery (if

TABLE 26

Values of n and K for the Determination of Solute Removal as a Function of Water Recovery

$pH = 4.0\text{-}4.5$
$\Delta p = 5.6 \times 10^5 N/m^2$

Component	n	K* PSAL Membrane	K* PTAL Membrane
Al	0.2	0.05	0.05
Ca	0	0.12	0.21
Fe	0	0.01	0.01
Mn	0.2	0.14	0.10

*K = 1-R (See Table 21)
where R = rejection with an inlet feed waste (1X)
and $r \approx 0$

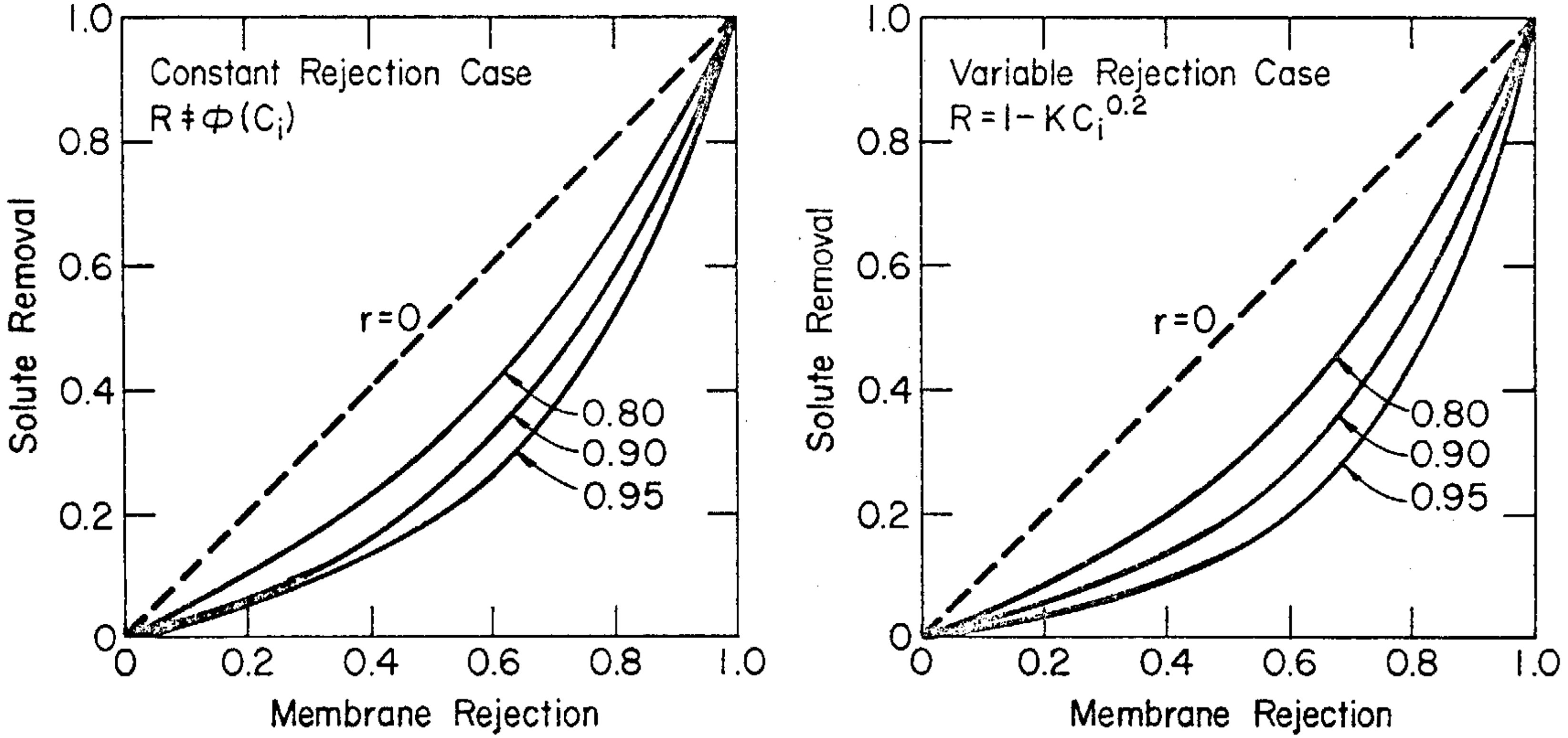


Figure 42. Prediction of Solute Removals as a Function of Membrane Rejection for Specified Water Recoveries

the membrane rejection is 90%) would be approximately 75%. At a water recovery of 80% the removal of Ca would be higher. The removal at a lower water recovery is expected to be greater since the membrane side concentration is lower. This is evident from both cases in Figure 42. Utilizing this figure and Table 26, the removals of the components in acid mine drainage were calculated at 80% and 90% water recoveries. They appear in Table 27. Although the sulfate concentration in the product water was not analyzed, sulfate removals would parallel overall metal removal behavior since the metals are primarily present as sulfates. Figure 43 (top) shows the ultrafiltrate quality at r = 0.90. These values can be compared to those obtained in batch recovery studies made during this investigation (Refer to Figures 33 and 34). With exception of the Mn removal with the PTAL membrane, the removals predicted by the model were similar to those obtained in actual water recovery experiments with a 1X feed waste. It is to be noted, however, that the model was developed for continuous flow systems with water recovery and the water recovery experiments made in this study were under semi-batch operation.

The water recovery and ultrafiltrate quality can also be increased by incorporating an inter-stage settling

TABLE 27

Removal of Metals at High Water Recovery

$\mathrm{pH} = 4.0\text{-}4.5$
$\Delta p = 5.6\mathrm{x}10^5 \mathrm{N/m}^2$

Component	Removal			
	PSAL Membrane		PTAL Membrane	
	r=0.80	r=0.90	r=0.80	r=0.90
Al	0.89	0.85	0.89	0.84
Ca	0.79	0.73	0.65	0.59
Fe	0.98	0.98	0.98	0.98
Mn	0.72	0.65	0.79	0.73
SO_4^{2-}	0.87	0.83	0.78	0.74
Suspended Solids	1.0	1.0	1.0	1.0

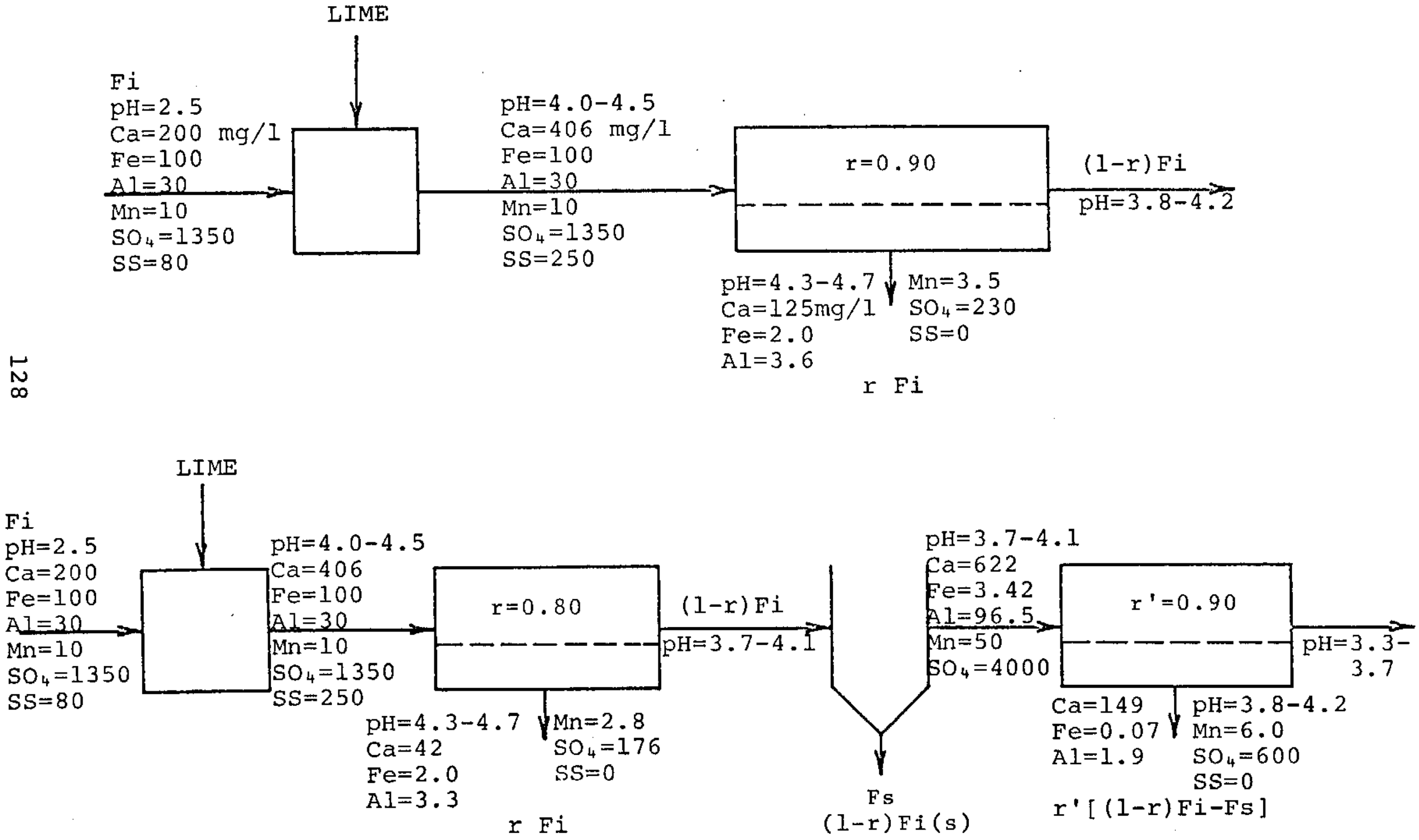


Figure 43. Comparison of Ultrafiltrate Water Quality Obtained with and without Inter-stage Settling

process, as seen in Figure 43 (bottom). The process consists of ultrafiltering a 1X acid mine waste feed solution (pH adjusted to 4.0-4.5) by recovering 80% water in the first stage. After settling the concentrate stream, the supernatant from the settling process is then ultrafiltered again with a unit operating at 90% recovery. By using this treatment scheme the overall water recovery (for the entire process) can be increased to 97% and a better effluent water quality can be obtained. Figure 43 shows the effluent quality obtained from each stage in the combination treatment scheme and a single-stage ultrafiltration process using PSAL membranes. With the exception of Mn, the removals of each metal was significantly increased with the combination treatment process. The overall effluent water qualities (with two types of membranes) for the combination ultrafiltration-interstage settling process are given in Table 28. PTAL membranes gave generally poorer solute removals, but as discussed previously, the PTAL membrane also exhibits substantially higher water fluxes. In both cases for the PSAL membrane the product of the molar concentrations of calcium sulfate in the untrafiltrate were significantly less than the saturation concentration of $CaSO_4$. For example, the values of $[Ca^{2+}][SO_4{}^{2-}] = 7.5x10^{-6}$ $(moles/l)^2$ for the

TABLE 28

Overall Ultrafiltrate Quality with Interstage Settling

$r = 0.97$

	PSAL Membrane		PTAL Membrane	
Component	Concentration mg/l	Removal	Concentration mg/l	Removal
Al	3.0	0.90	3.0	0.90
Ca	61	0.85	155	0.62
Fe	1.6	0.98	1.6	0.98
Mn	3.4	0.65	5.3	0.47
SO_4	250	0.81	382	0.72
Suspended Solids	0	1.0	0	1.0

single-stage process and $[Ca^{2+}][SO_4{}^{2-}] = 4.0x10^{-6}$ (moles/l)^2 for the combination process could be obtained. The values are only 2% to 3% of the saturation concentration.

In addition to ultrafiltration quality, the design of a treatment process requires knowledge of the water flux to be expected at high water recoveries. Laboratory studies conducted over the range of concentrations at negligible water recoveries showed that the steady-state water flux, J_W, declined with an increase in feed waste concentration (Refer to Figures 24 to 28). Utilizing Figure 28 and taking an integrated average at various total solids levels, the average flux values (both PSAL and PTAL membranes) at various recovery levels were calculated and are given in Table 29. For example, at $r = 0.90$ the flux drop (compared to distilled water) is 27% with a PSAL membrane and 24% with a PTAL membrane.

C. Comparisions with Other Acid Mine Waste Treatment Processes

1. Reverse Osmosis

High pressure ($\Delta p=3x10^6$ to $6x10^6 N/m^2$) reverse osmosis processes consistently give superior effluent water qualities as shown in Table 30. With reverse osmosis processes the solute removals are independent of the feed waste

TABLE 29

Calculated Average Water Flux*

Water Recovery	Membrane	
	PSAL	PTAL
0	7.5×10^{-4} cm/sec	15.7×10^{-4} cm/sec
0.50	7.2×10^{-4}	15.0×10^{-4}
0.80	6.5×10^{-4}	14.3×10^{-4}
0.90	6.0×10^{-4}	13.0×10^{-4}
0.97	5.8×10^{-4}	12.5×10^{-4}

*Calculated from Figure 28

TABLE 30

Typical Removals Obtained with Reverse Osmosis Systems with Actual Acid Mine Wastes

Component	% Removal	Permeate Concentration
Conductivity	0.980-0.992	10-100 µmho/cm
Acidity	0.870-0.950	20-40 mg/l as $CaCO_3$
Total Dissolved Solids	0.990-0.996	10-30 mg/l
Al	0.990-0.992	0.2-1.1 mg/l
Ca	0.996-0.998	0.5-1.8 mg/l
Fe	0.994-0.998	0.5-1.9 mg/l
Mg	0.994-0.998	0.6-1.1 mg/l
Mn	0.990-0.998	0.08-0.5 mg/l
SO_4^{2-}	0.980-0.997	4-14 mg/l

concentration except at very high concentrations where the water recovery is limited. The solute removals are all above 98% and the solute concentrations are all below 2 mg/l with the exception of sulfate. Although the effluent qualities obtained with a reverse osmosis system would always be better than the effluent from any other process, hydrolysis (due to pH effects) must be minimized in order to maintain long term high rejection.

Typical reverse osmosis treatment results for acid mine drainage appear in Figure 44. With this process the raw waste should be acidified to pH3 before treatment to prevent iron hydroxide precipitation, instead of raising the pH to 4.0 to 4.5 as was done in the ultrafiltration studies. After acidification the waste would require filtration (particularly for spiral-wound and hollow-fiber modules) to reduce suspended solids concentrations. The Ebensburg,Pennsylvania water (Table 9) is very similar to the 1X waste used in this investigation. Figure 44 shows the effluent concentrations from a reverse osmosis process operating at 84% recovery using the 1X waste as the feed water. All product water concentrations were less than those obtained with an ultrafiltration process.

The main limitations with the operation of a reverse

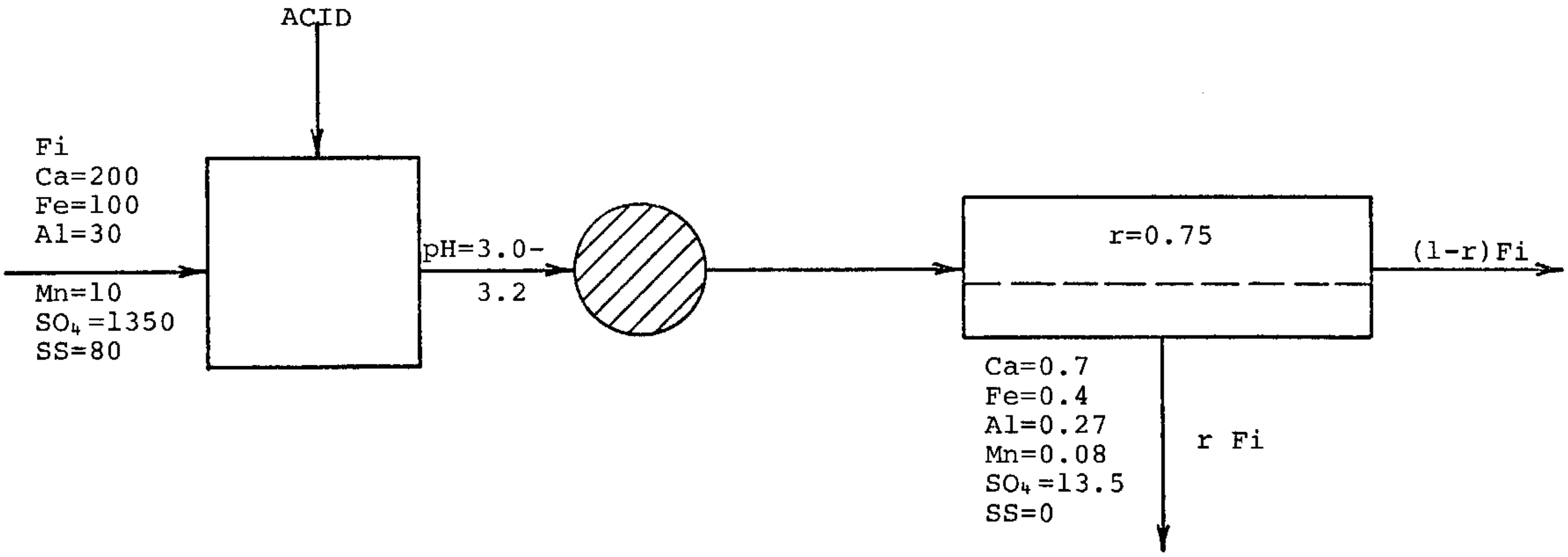


Figure 44. Product (Permeate) Water Quality Obtained With a Reverse Osmosis Unit

osmosis treatment process with acid mine drainage are membrane fouling and high pressure compaction problems which result in flux declines with time. Table 10 (previously presented) shows that the average flux obtained from a spiral-wound reverse osmosis unit ranges from 6.0×10^{-4}cm/sec to 9.0×10^{-4}cm/sec.

The drop in flux due to membrane compaction problems can be described by the following equation

$$J_w = J_{w_i} t^m \qquad (28)$$

where m is the compaction slope and J_{w_i} is the initial water flux of the new membrane. From the above equation the average water flux over a given period beginning at one day can be easily evaluated by integrating the expression with respect to time,

$$\text{average flux} = J_{w_D} \frac{\tau^m}{(1+m)} \qquad (29)$$

where J_{w_D} is the water flux at one day and τ is the time in days. Typical flux drops with time due to compaction as a function of m are given in Figure 45. Membranes with log-log slopes greater than 0.08 cannot be used for long term acid mine waste treatment due to the large flux drops present. The membranes used for actual acid mine

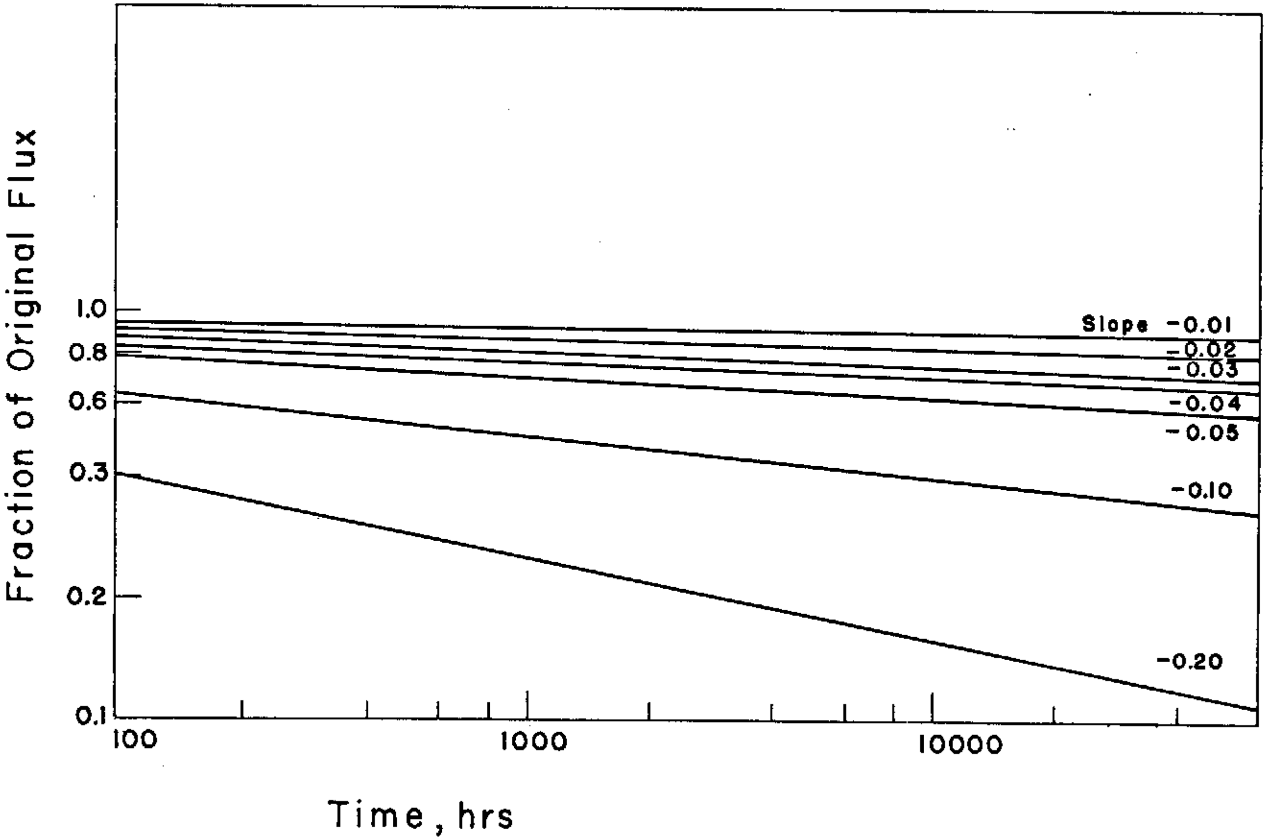


Figure 45. Flux Loss Due to Membrane Compaction of High Pressure Reverse Osmosis Membranes (10)

drainage treatment exhibit log-log slopes between -0.01 and -0.06 (10). Using Equation 29, the ratio of the flux at two years (typical membrane life) to the flux at one day would be reduced to 0.72 if the compaction slope was -0.05. Thus for a two year operation the average flux values shown in Table 10 would be 20% to 30% lower. With reverse osmosis, the long term flux loss due to compaction must be taken into account for proper design considerations.

With acid mine drainage, calcium sulfate fouling is also an important factor in water recovery limitations. Utilizing Equation 27, the maximum expected water recovery can be computed. For example, with the synthetic (1X) waste (Ca in the feed = 200 mg/l and SO_4^{2-} = 1350 mg/l) used in this study, the maximum water recovery that would be expected from a reverse osmosis unit is 71%, which is low compared to the 97% recovery obtained with the combination ultrafiltration - interstage settling process. With negatively charged ultrafiltration membranes, the fouling due to $CaSO_4$ precipitation was found to be minimal.

2. Lime Precipitation

The use of a lime precipitation - settling process to treat acid mine wastes is limited by several factors; poor effluent water quality, the need for post filtration, and product water of very high hardness. As previously discussed, the effluent water quality from a lime treatment process is strongly dependent upon the extent to which precipitation of metal hydroxides occurs. The results from the precipitation studies made in this investigation with a 1X waste show that hydroxide precipitates of Al, Fe and Mn are adequately removed with a 60 minute settling process (refer to Table 15). However, as expected, the calcium concentration in the effluent water was higher than that in the feed due to the addition of lime for pH adjustment. It should be noted that the results obtained in this investigation were very similar to those reported for actual mine wastes of approximately the same quality (see Tables 5 and 7).

A very important consideration in the treatment of acid mine wastes by a precipitation process is the type of iron (Fe^{2+} or Fe^{3+}) present in raw waste. Figure 46 shows a typical treatment scheme for ferric iron mine waste. The necessity of the final filtration step is dictated by the degree of suspended solids removal obtained during settling. If the treated water is to be reused, the suspended solids concentration would have to be reduced. The filtering process would reduce the suspended solids concentration below 20 mg/l depending upon

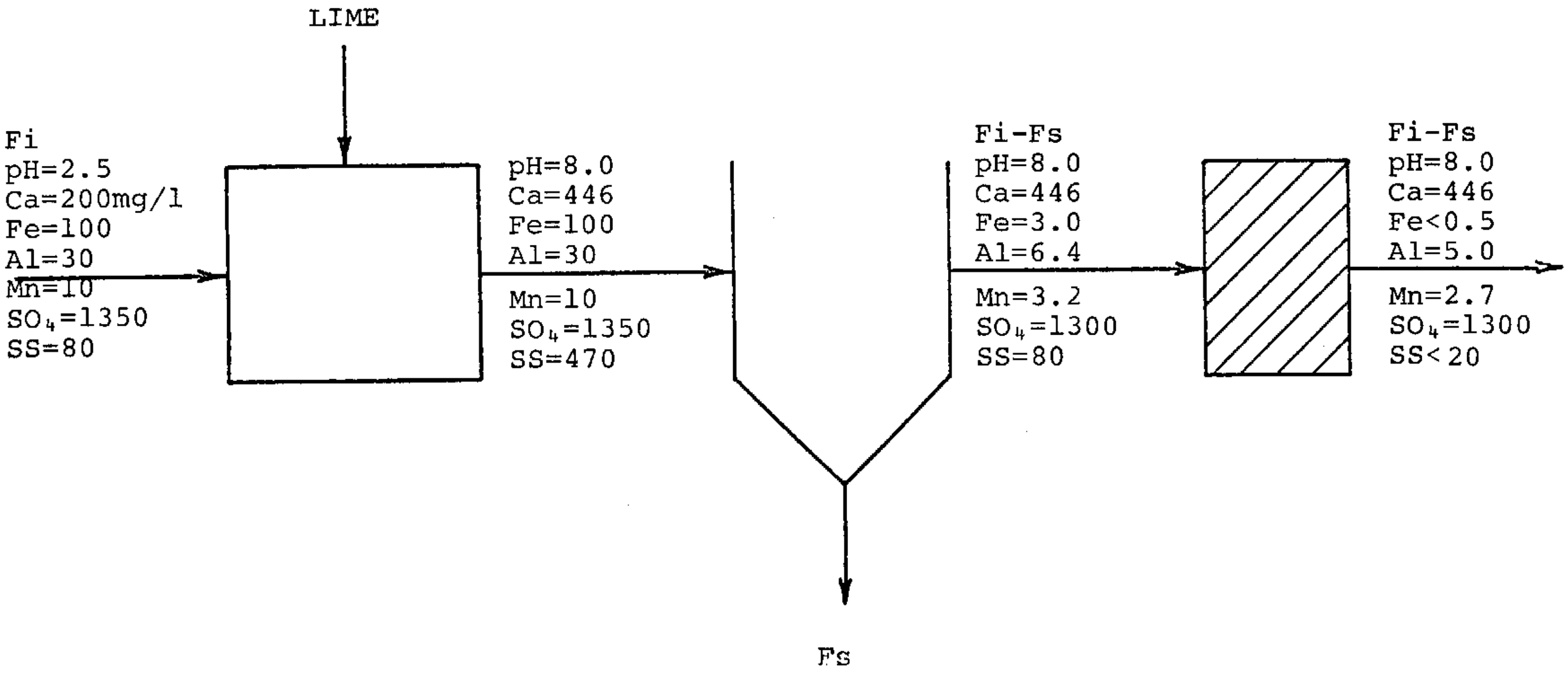


Figure 46. Lime Precipitation Process Behavior with Acid Mine Water Containing Ferric Iron

the type of filter used.

If the iron is present in the ferrous state, certain pretreatment steps must also be made to ensure precipitation of the iron hydroxide. Figure 47 shows two alternate treatment schemes that have proven to effectively remove the Fe (3, 31). The first process uses lime to adjust the pH $\geq$ 9.5 to precipitate Fe as $Fe(OH)_2$. At this pH the removal of Fe is 99.9% (Table 7). The second scheme utilizes pre-aeration of the waste (at $pH > 6$) to oxidize Fe^{2+} to Fe^{3+} to allow precipitation of Fe as $Fe(OH)_3$. After neutralization and oxidation, the iron can be removed with 99.9% effectiveness as shown in Figure 47. In both cases, the Al and Mn concentrations are reduced to 3 - 7 mg/l, but for a 1X feed waste no removal of Ca occurs, thus making the effluents near the saturation point for $CaSO_4$. Again, for both treatment schemes a post-treatment filtration step should be employed to reduce the suspended solids concentration.

Precipitate settling rates and the volume of sludge produced from a settling process are also important design parameters. Typically, the observed settling rates (from experimental results) for the lime neutralization process range between 0.9 and 3.0 cm/min (Table 18) depending upon the influent waste concentration. For a feed waste of

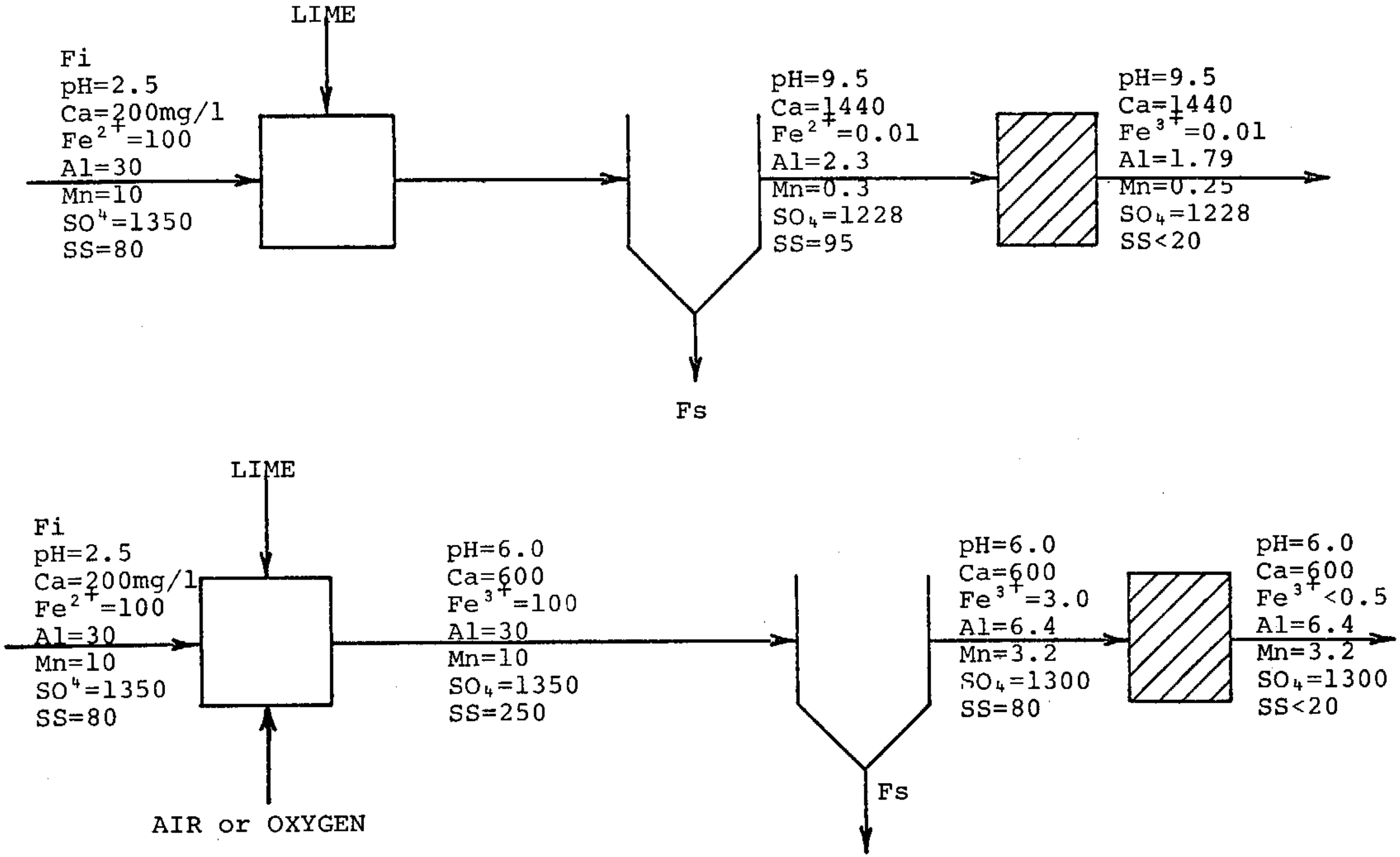


Figure 47. Comparison of Two Types of Lime Precipitation Schemes for Treatment of Acid Mine Water Containing Ferrous Iron

approximately 1X concentration, the settling rate at pH8 is 3.0 cm/min. Since clarification area requirements for (a fixed flow rate) is inversely proportional to subsidence settling velocity, selection of proper operating conditions is important to maximize settling rates. For the treatment of acid mine water of flow rate 4.0×10^6 l/day the clarification area would be 93 m^2, if the settling rate was 3.0 cm/min. The volume of sludge produced from a precipitation - settling process is an important factor in determining the feasibility of the process. The results from this investigation show that the sludge volume may vary from 12% to 69% (Table 19) of the total water volume depending upon the waste concentration and detention time; however, sludge volumes of 5% of the total volume have been reported in the literature (2,3). It should be noted that addition of coagulants could reduce the volume further.

D. Water Reuse Considerations

The construction of coal conversion facilities creates a demand for large quantities of water, part of which could be supplied by treated acid mine waste. The waste may be treated by any process that can produce a large quantity of treated water with no suspended solids and low calcium sulfate content ($[Ca^{2}]$ $[SO_4{}^{2-}]$ << Ksp of $CaSO_4$) which causes scale if the water is reused.

The treatment processes discussed previously are summarized in Table 31 in terms of parameters pertinent to water reuse. Although both lime precipitation - settling processes are capable of producing a large quantity of treated water (r=0.95), the high concentration of calcium sulfate in the water is sufficient criteria to reject the processes as possible treatment methods for a water reuse scheme. For example, if the treated water from a lime process is used in a recycle operation where 50% of the water volume is consumed, the concentration of calcium sulfate ($[Ca^{2+}]$ $[SO_4{}^{2-}]$ = 1.2×10^6) would exceed the saturation concentration during the first pass. Precipitation of $CaSO_4$ is intolerable due to the scaling problems; therefore, the lime treatment processes are rejected.

The reverse osmosis process produces a water quality highly suitable for reuse; however, the low levels of water recovery (< 85%) could warrant the process unsuitable for a water reuse scheme because of concentrate disposal problems. For example, a reverse osmosis unit operating at 80% water recovery with 4.0×10^6 l/day of feed acid mine waste would produce 0.8×10^6 l/day of concentrate stream

TABLE 31

Comparisons of Processes in Terms of Product Water $CaSO_4$ and Suspended Solids Concentrations and Recovery

Process	Product Water $[Ca^{2+}][SO_4{}^{2-}]$ $(mg/l)^2$*	Product Water Suspended Solids mg/l	% Recovery
Lime Precipitation-Settling	$5.8x10^5$	80	95
Lime Precipitation-Settling with Post-Filtration	$5.8x10^5$	<20	95
Reverse Osmosis	10	0	70-80
Ultrafiltration (Single-Stage)**	$7.4x10^3$	0	80
Ultrafiltration (Single-Stage)**	$2.9x10^4$	0	90
Ultrafiltration (with Inter-Stage Settling at r = 0.80)**	$1.5x10^4$	0	97

*Saturation Concentration Based on Ksp = $2.4x10^{-4}$, $[Ca^{2+}][SO_4{}^{2-}] = 9.2x10^5 (mg/l)^2$
**PSAL Membranes

and 3.2 x 10^6 l/day of permeate which could be reused.

The charged membrane ultrafiltration process studied in this investigation is capable of producing treated water low in calcium and sulfate at high water recoveries. Even at 90% recovery (in single-stage operation), the initial product of concentration is only 3% of the saturation value. Water recovery (up to 97%) and ultrafiltrate quality can be further improved by interstage settling as shown in Table 30. Thus, an ultrafiltration process would be feasible for a water reuse scheme.

A treatment plant concept utilizing charged membrane ultrafiltration to convert acid mine drainage (after the necessary pH adjustments) for reuse in mine-mouth coal conversion facilities is shown in Figure 48. The treated water from the ultrafiltration unit is recycled through a coal conversion process in which a certain fraction of the process water is consumed (such as by evaporation) during each pass. To prevent the concentration (of $CaSO_4$, suspended solids, etc.) in the recycle stream from rapidly increasing, a fraction of the water exiting the process is blown down and returned to the ultrafiltration feed stream.

The amount of blowdown required to maintain the concentration in the process at an acceptable level can be

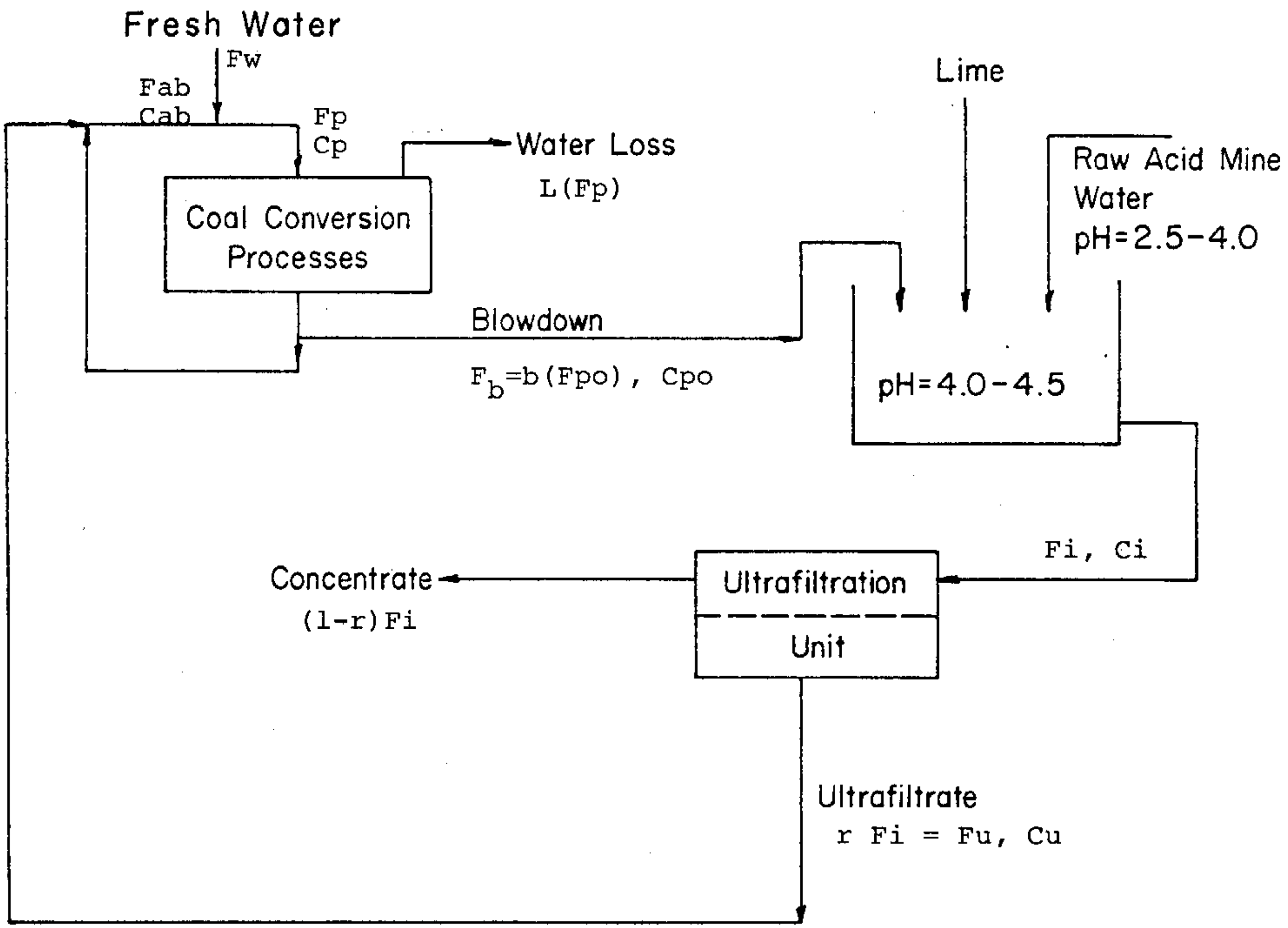


Figure 48. Schematic of Acid Mine Water Treatment Process for Ultrafiltrate Reuse

determined by the maximum concentration that can be tolerated in the recycle stream. The concentration build-up ratio (C_{po}/C_u) in the recycled water can be determined by recursive mass balances and is given by

$$\frac{C_{po}(N)}{C_u} = \frac{(1-b)^{N-1}}{(1-L)} + \frac{F_u}{(1-L)\ F_p} \sum_{i=1}^{N-1} (1-b)^{i-1} \qquad (30)$$

which gives the concentration during the N^{th} pass. A computer simulation was also developed to determine the value of the concentration build-up ratio during each pass by taking successive mass balances after each pass. Results of the simulation appear in Figures 49 and 50 for process water losses of 0.50 and 0.75, respectively. From these figures, the necessary fractional blowdown can be determined with knowledge of the maximun allowable concentration build-up in the recycle stream. Once the blowdown has been determined, the amount of fresh water needed to supplement the treated water can be determined by

$$F_w = L(F_p) + (b-1)F_u \qquad (31)$$

Any addition of fresh water also acts to dilute the water in the recycle process.

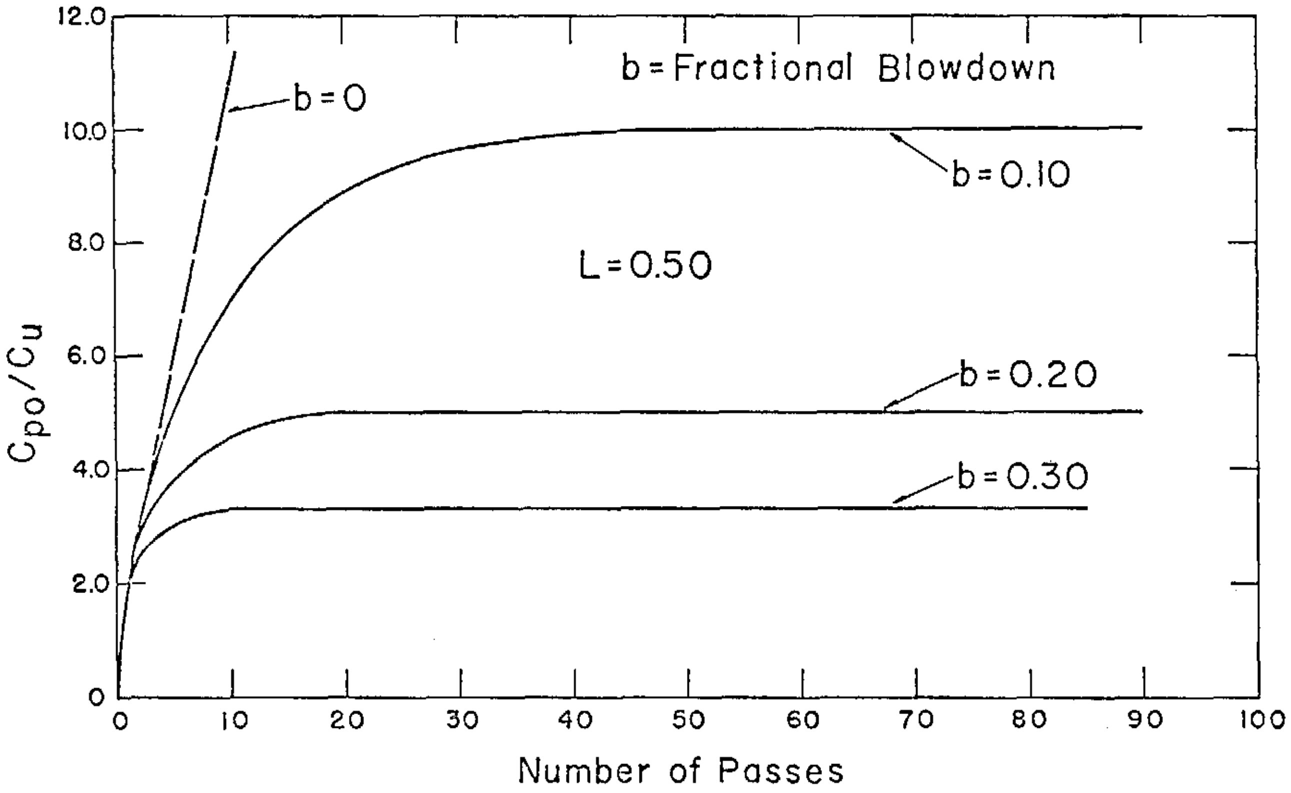


Figure 49. Effect of Multiple Recycle Passes on Reuse Water Quality for L = 0.50

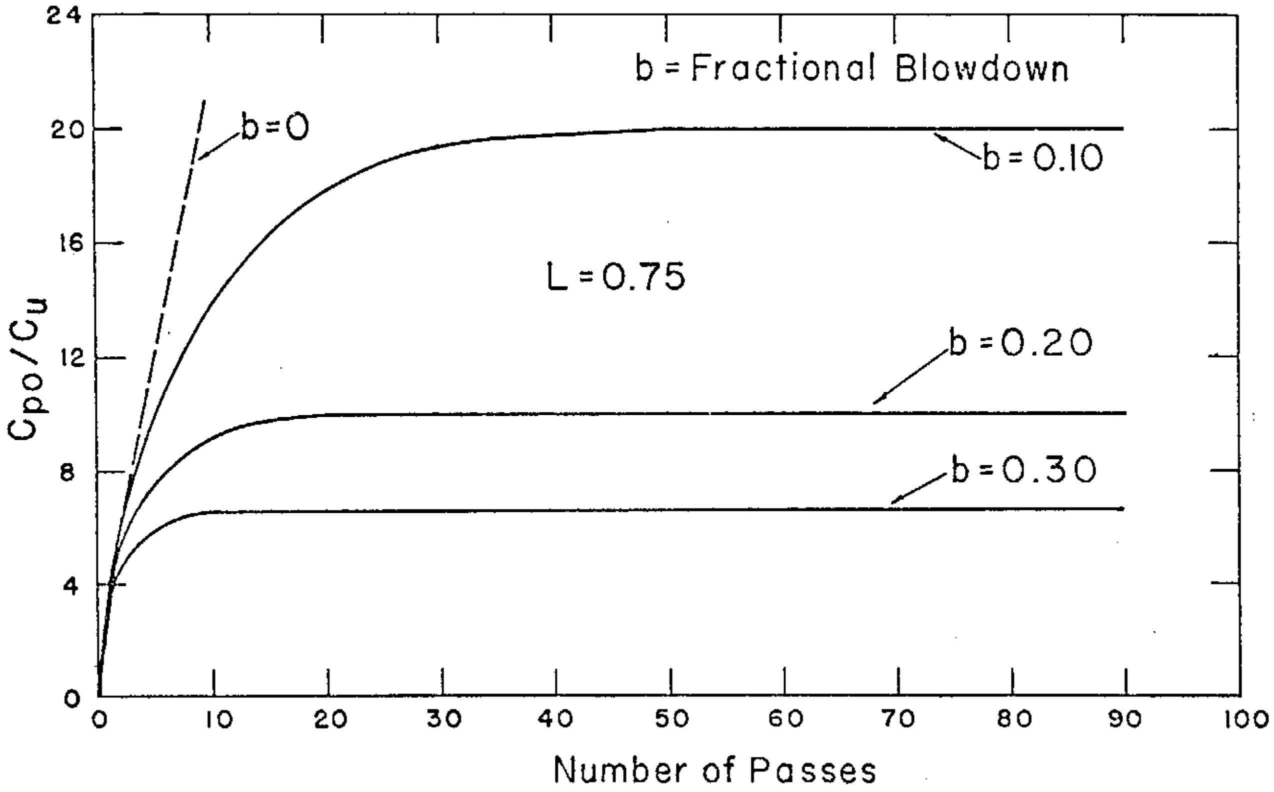


Figure 50. Effect of Multiple Recycle Passes on Reuse Water Quality for L = 0.75

A typical water reuse example utilizing an ultrafiltration unit (with inter-stage settling) to treat acid mine water (3.7×10^6 l/day) is shown in Figure 51 for the case of 97% water recovery using PSAL type membranes. The raw acid mine water is assumed to of the composition shown in Table 12. Only concentrations of suspended solids, calcium, and sulfate are shown, but concentrations of other components could easily be computed utilizing Table 31. The flowrates and the steady state concentrations ($N=\infty$) in Figure 51 (with PSAL membranes) were computed from Table 31 and 50 (for $b=0.10$). For a maximum $[Ca^{2+}]$ $[SO_4{}^{2-}]$ of 2xKsp in the recycle water, a blowdown rate of 0.4×10^6 l/day would be sufficient. This condition corresponds to at Cpo/Cu of 10.0 in Figure 49. By increasing the blowdown rate to 0.8×10^6 l/day, both PSAL (average flux at $r=0.97$ of 5.8×10^{-4} cm/sec) and PTAL (average flux at $r=0.97$ of 12.5×10^{-4} cm/sec) membranes would provide recycle water quality considerably below the $CaSO_4$ saturation concentration. The membrane area requirements to produce 4.0×10^6 l/day of ultrafiltration would be 4000 m^2. The major operating costs for the ultrafiltration unit would be the sum of membrane replacement costs (2 yr. life) plus pumping costs to overcome pressure losses plus operating (and maintenance labor) cost plus chemical costs.

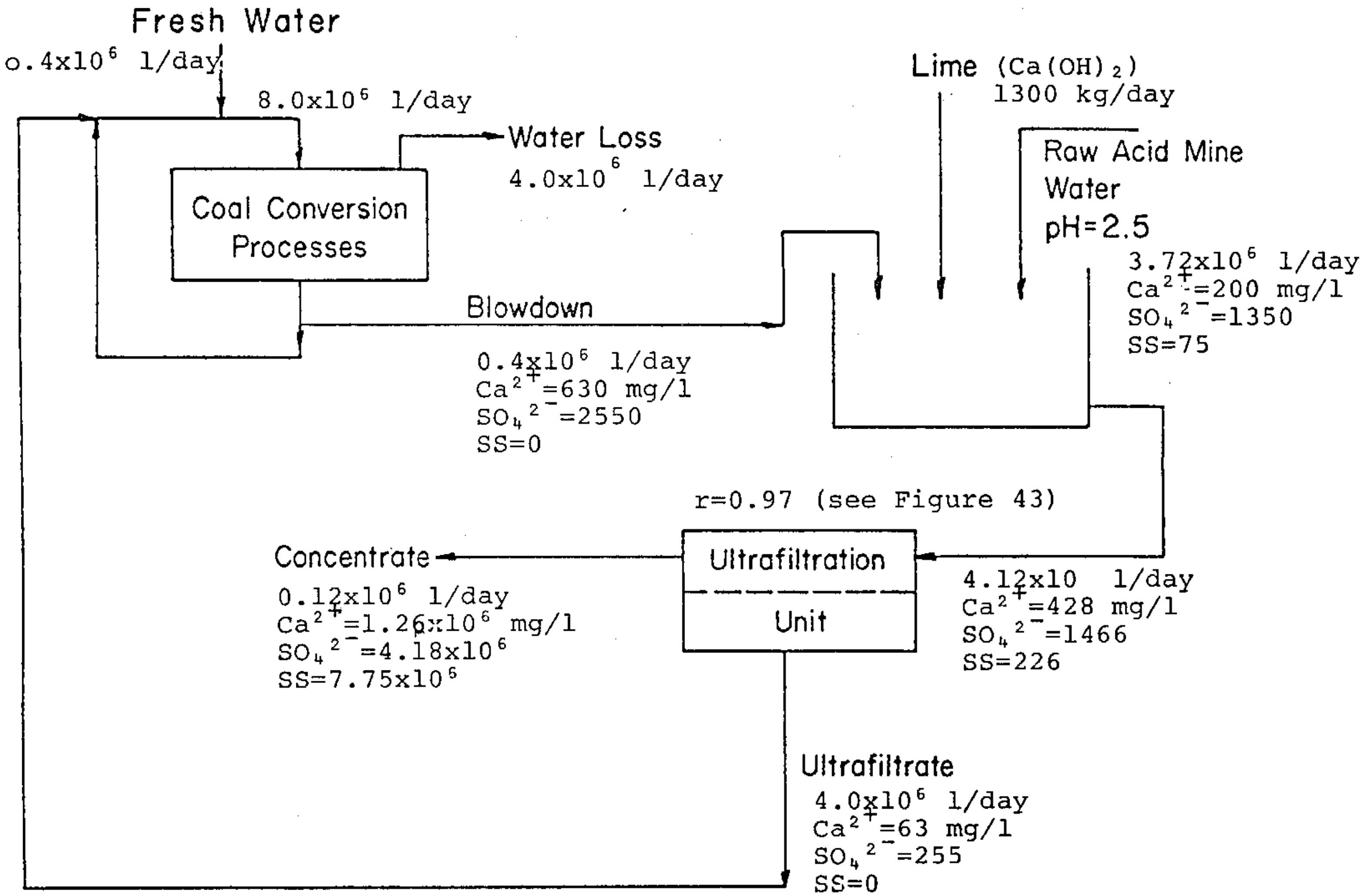


Figure 51. Example of Water Reuse Scheme with Ultrafiltration-Inter-stage Settling Process

For the unit shown in Figure 51 (with PSAL membranes), the membrane replacement cost of (100 $\$/m^2$ membrane area, 2 yr. life) \$1100/day and pumping cost of (0.025 \$/Kwh) \$250/day and pH adjustment cost of (0.04 \$/kg lime) \$52/day, hence to produce 4 x 10^6 l/day of treated water, the membrane replacement costs plus pumping cost plus lime costs per 1000 gal. of water is \$1.33. Depending on the labor requirements, maintenance requirements, and concentrate disposal requirements, the actual operating costs may be 30 to 40% higher.

IX. CONCLUSIONS

Low-pressure ultrafiltration with negatively-charged non-cellulosic membranes is shown to be a feasible process in terms of achieving the simultaneous separation of dissolved metals (and sulfate) and of suspended solids from acid mine water. The process is evaluated in terms of the simultaneous achievement of good water flux without membrane fouling, and of adequate ultrafiltrate quality at high water recovery for water reuse operation. A combination ultrafiltration process with inter-stage settling is found to be optimum in terms of good water quality and high (up to 97%) water recovery.

Among the various commercially-available, charged ultrafiltration membranes that were evaluated in a continuous-flow unit, membranes of initial water flux (at a pressure of 5.6×10^5 N/m^2) 8.2×10^{-4} cm/sec to 17.3×10^{-4} cm/sec were found to be the best suited for the treatment of acid mine waters. At the optimum operating pH of 4.0 to 4.5, a channel velocity of 200 cm/sec to 250 cm/sec (Re = 6,000 to 7,500) was sufficient to minimize fouling. Even with a concentrated acid mine water (10X waste) containing 16,000 mg/l total solids (including a high $CaSO_4$

concentration), the flux drop was less than 30%. With a single-stage operation, the water recovery would be limited to 80% to 90% due to a sharp decline in ultrafiltrate quality (particularly Mn and Al) above this range of water recoveries. However, a significant increase in water recovery and overall removal was obtained with an ultrafiltration-interstage settling process operating at an overall water recovery of 97%. At this recovery, the percent removal of 95% for Al, 85% for Ca, 98% for Fe, 65% for Mn, 81% for SO_4^{2-}, and 100% for suspended solids were obtained with a membrane of average flux equal to 5.8×10^{-4} cm/sec, metal separations were somewhat lower. Thus, proper membrane selection would depend on the design water quality and water flux desired. The membrane area requirements to produce 4.0×10^{6} l/day of treated water would be between 4000 m^2 and 8000 m^2.

With high pressure reverse osmosis processes, field test results indicate that although excellent metal rejections can be obtained, the flux drop due to membrane compaction and $CaSO_4$ fouling limit water recovery to 70 - 80%. The product water (permeate) was approximately independent of water recovery and feed waste composition. The removal of all metals including calcium, total dissolved solids, and sulfate were greater than 99%. With cellulosic type reverse osmosis membranes, an average water flux of 5.5×10^{-4} cm/sec could be obtained for long term operation. At water recoveries less than 85%, concentrate stream disposal would be a problem and thus further processing may be required.

With regard to treated water reuse possibilities, the charged membrane ultrafiltration process consistently produces water with calcium sulfate concentrations ($[Ca^{2+}][SO_4^{2-}] = 7.4 \times 10^3$ to 2.9×10^4 $(mg/l)^2$) considerably below the saturation concentration ($[Ca^{2+}][SO_4^{2-}] = 9.2 \times 10^6$ $(mg/l)^2$); whereas, with the lime-precipitation-settling-filtering process, the treated water will be very high in calcium sulfate concentration ($[Ca^{2+}][SO_4^{2-}] = 5.8 \times 10^5$ $(mg/l)^2$). Although the reverse osmosis process produces water highly suitable for reuse as far as water quality is concerned, membrane compaction and water recovery problems must be minimized.

NOMENCLATURE

A = Membrane area, cm^2

A' = Membrane constant (Equation 22)

B = Solute permeation constant, cm/sec

b = Fractional blowdown from recycle stream in coal conversion process (Figure 48)

C = Concentration of solute in inlet stream, mM

(Ca) = Calcium concentration in acid mine waste (Equation 27), mg/l

Cab = Concentration of combination ultrafiltrate - recycle stream in water reuse scheme (Figure 48), mg/l

C_f = Concentration of a solute in ultrafiltrate stream, mM or mg/l

C_i = Concentration of a solute in inlet stream, mM or mg/l

$C_{j(m)}$ = Concentration of jth ion in membrane, mM

Cp = Concentration of any component in coal conversion process water (Figure 48), mg/l

Cpo = Concentration of any component in recycle stream in coal conversion process (Figure 48), mg/l

Cu = Ultrafiltrate concentration (=C_f) (Figure 48), mg/l

D_j = Diffusion coefficient of jth ion in membrane, cm^2/sec

D_s = Membrane phase diffusivity of the solute, cm^2/sec

D_w = Membrane phase diffusivity of water, cm^2/sec

F = Faraday constant

F_s = Flowrate of sludge from settling process, 1/day

Fi = Flowrate of inlet stream to membrane unit, cm^3/sec

Fp = Flowrate of water into coal conversion process (Figure 48), 1/day

Fpo = Flowrate of water out of coal conversion process (Figure 48), 1/day

Fu = Ultrafiltrate flowrate, cm^3/sec or 1/day

Fw = Fresh water flowrate to coal conversion process (Figure 48), 1/day

i = Ionization factor (Equation 15)

Js = Solute flux, mmol/(sec cm^2 of membrane area)

$(Js)_j$ = Flux of jth ion, mmol/(sec of cm^2 of membrane area)

J_w = Membrane water flux, cm^3/(sec cm^2 of membrane area)

J_{wD} = Membrane water flux at one day, cm^3/(sec cm^2 membrane area)

J_{wi} = Membrane water flux of new membrane, cm^3/(sec cm^2 membrane area)

K = Constant (Equations 25 and 26)

K_1 = Distribution coefficient of the solute between the membrane and solution phases, dimensionless

Ksp = Solubility product, $(moles/l)^2$

Ksp_c = Solubility product corrected for ionic strength, $(moles/l)^2$

L = Fractional water loss from coal conversion process

m = Membrane compaction slope (Equation 28)

N = Number of passes made by recycle water in coal conversion process

n' = Constant (Equations 25 and 26)

P_i = Membrane feed stream pressure, N/m^2

P_o = Membrane concentrate stream pressure, N/m^2

ΔP = Transmembrane pressure (Equation 14) N/m^2

Pmc = Product of concentrations of calcium and sulfate, $(moles/l)^2$ or $(mg/l)^2$

R = Solute rejection, (Equation 17)

R' = Gas constant

R_f = Resistance of suspended solids layer on membrane surface, $N/m^2/cm/sec$

R_m = Resistance of ultrafiltration membrane to water flux $N/m^2/cm/sec$

r = Ultrafiltrate (permeate) water recovery (Equation 17)

(SO_4) = Sulfate concentration in acid mine waste (Equation 27), mg/l

T = Absolute temperature of solution, °K

t = Time, days

U = Average channel velocity, cm/sec

Z_j = Valence of jth ion

λ = Membrane thickness, cm

Πi = Osmotic pressure of membrane inlet stream, N/m^2

Π_f = Osmotic pressure of ultrafiltrate (permeate) stream, N/m^2

$\Delta\Pi$ = Osmotic pressure difference, N/m^2

τ = Time, days

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