

付属資料 7.1.2-5

膜汚染物の分析結果

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1. 目的

RO海水淡水化プラントは原料海水の性質に影響を受ける。前期において、紅海側のウムルジにあるRO海水淡水化プラントの汚染膜を入手し分析を行った。紅海に比べてガルフ湾側の海水は濁度が高いことが予想されるので、ガルフ湾で汚染された膜の分析を行い、汚染原因究明と防止法を確立する必要がある。SWCCはガルフ湾側の汚染膜の入手を約束しているので、今期はSWCCの入手した汚染膜について、JICA側の援助のもとにSWCC R&D研究センターで行う。

今回はSWCCの入手した汚染膜について、JICA側の援助のもとにSWCC R&D研究センター(RDTC)で汚染膜のサンプリング法、汚染膜の観察方法、汚染物の分析方法の指導を行った。また、膜汚染機構の解説指導を行った。

2. 実験方法

現地の汚染膜として2種の膜を入手し、JICA側で分析を行い、SWCC側に報告する資料としてとりまとめた。

すなわち、今回はSWCCの入手した汚染膜について、JICA側の援助のもとにSWCC R&D研究センター(RDTC)で汚染膜のサンプリング法、汚染膜の観察方法、汚染物の分析方法の指導を行った。また、膜汚染機構の解説指導を行った。

汚染膜の分析方法には、次の手順が必要である。

- A. SAMPLING AND SAMPLE SELECTION
- B. PERFORMANCE EVALUATION OF FOULED MEMBRANES
- C. GENERAL APPEARANCE OF DISASSEMBLED RO ELEMENTS(AUTOPSY TEST)
- D. DETERMINATION OF STRUCTURE AND COMPOSITION OF DEPOSITS
- E. MEMBRANE SURFACE ANALYSIS
 - 1. SCANNING ELECTRON MICROSCOPE(SEM)
 - 2. ENERGY DISPERSIVE X-RAY SPECTROSCOPY(EDS)
 - 3. STRUCTURE IDENTIFICATION OF ORGANIC MATTER BY FOURIER TRANSFORM INFRARED(FT-IR)
- F. DETERMINATION OF PHYSICAL AND CHEMICAL PROPERTIES OF THE MEMBRANE
 - 1. STRENGTH AND ELONGATION
 - 2. MOLECULAR WEIGHT DETERMINATION
 - 3. VISCOSITY MEASUREMENT
 - 4. DEGREE OF POLYMER ACETYLATION

これらの分析手順、及び分析機器はSWCCのRDT Cで実施可能である。
(付属資料-7.1.2-1)今回は上記のA, B, C, D, Eについて習熟するための指導を行った。

SEM、EDX分析操作マニュアルを付属資料-7.1.2-2に、FT-IR分析操作マニュアルを付属資料-7.1.2-3に示す。

実験方法の詳細を下記に示す。

2-1 MF膜捕捉汚染物サンプル

- ・場所：サウディ・アラビアの Al Jubail に所在するSWCC、
Research & Development Training Center内の
海水淡水化実験のために設置されている前処理装置
――原海水中の濁質成分を除去するため
- ・方法：精密ろ過膜を用いて下記のサンプル・ポイントで、SDI測定
に準じた通水条件にて膜面上に汚染物質サンプルを収集
ミリポア製のHAタイプ0.45 μ mを使用

・海水の一般的性状：

場所： アラビア湾 Al Jubail

年月： 1993年10月

温度： 33 $^{\circ}$ C

pH： 8.1

電気伝導度： 63000 μ S/cm

・サンプル採取位置：

サンプル(1)：インテイク配管の前処理装置の入口部原海水

SDI値： 5.3

通液量：10 liter

サンプル(2)：原海水サンプル(1)と別の日のサンプル

SDI値： 5.6

サンプル(3)：凝集ろ過層(DMF)で処理された海水

SDI値： 3.6

サンプル(4) : 砂ろ過ポリッシャの出口海水

SDI値 : 3.1

サンプル(5) : 10 μ mカートリッジフィルター出口海水

SDI値 : 3.4

サンプル(6) : 日本近海での海水淡水化装置の前処理部分の
汚染物-ファウリングの比較サンプル

2-2 RO膜汚染物サンプル-A

- ・場所 : 上記と同じSWCC、Research & Development Training Center内の
海水淡水化実験用前処理装置の海水を用いて実験されたポリアミ
ド系Composite RO膜のサンプルについて膜面観察を実施した。

サンプル(7) : Nitto Denko 製の Polyamide Composite

NTR-759SW の Part-A 1部分

(Hydranautics にて 2" x 40" サイズ)

ミニROエレメントとして組立られた製品)

サンプル(8) : 同上 の Polyamide Composite RO膜

NTR-759SW の Part-A 2部分

2-3 RO膜汚染物サンプル-B

- ・場所 : 上記と異なるがサウディアラビアの脱塩プラントにて使用され
ていたポリアミド系Composite RO膜のサンプルについて膜面観
察を実施した。

サンプル(9) : Desalination 製の Polyamide Composite

Part B-1部分, ただし製品番号不詳

サンプル(10) : 同上 の Polyamide Composite RO膜

Part B-2部分

サンプル(11) : 同上 の Polyamide Composite RO膜

Part B-3部分

サンプル(12) : 同上 の Polyamide Composite RO膜

Part B-4部分

2-4 分析機器

既報の膜面観察に通常使用している下記の装置

* 汚染物質の観察

SEM: 走査型電子顕微鏡

* 無機性汚染物質の同定

EDX: エネルギー分散型エックス線マイクロアナライザー

* 有機性汚染物質の同定

FT-IR: フリエ変換赤外分光光度計

3. 分析結果

3-1 MF膜捕捉汚染物サンプル

* SEM, EDXおよびFT-IRによる膜面汚染物質の観察結果

・サンプル(1): 原海水のサンプルをPhoto. 1-1~1-5に示す。

NaCl, MgCl₂, Ca塩の結晶と海洋生物の存在をしめす。

FT-IRのチャートFigure 1よりCa塩の吸収ピーク: 1450cm⁻¹、
海洋生物に由来の各吸収ピーク1650cm⁻¹(-NHCO-), 1050cm⁻¹, 3300cm⁻¹
(-OH)が認められた。

Feさびによると考えられるピーク、450cm⁻¹も認められた。

・サンプル(2): 上記と同じ原海水のサンプルをPhoto. 2-1~2-5に示す。

NaCl, MgCl₂などの結晶と海洋生物の存在をしめす。

FT-IRのチャートFigure 2よりCa塩の吸収ピーク1450cm⁻¹、
海洋生物に由来の各吸収ピーク1650cm⁻¹(-NHCO-), 1050cm⁻¹, 3300cm⁻¹
(-OH)が認められた。

Feさびによると考えられるピーク(450cm⁻¹)も認められた。

・サンプル(3): DMF出口のサンプルをPhoto. 4-1~4-5に示す。

SEMとEDXより立方体の結晶はNaClと推定、他にCa, K, Mg, およびSO₄
イオンのSがEDXスペクトルのピークとして認められた。

NaCl, MgCl₂の結晶と海洋生物の存在をしめす。

FT-IRのチャートFigure 4 より前記のような特異な吸収ピークは認められなかった。

Feさびによると考えられるピーク、450cm⁻¹が少し認められた。

- ・サンプル(4) : 砂ろ過ポリッシャー出口のサンプルをPhoto. 5-1~5-5に示す。SEMとEDXより立方体の結晶はNaClと推定、他にCa, K, Mg, およびSO₄イオンのSがEDXスペクトルのピークとして認められた。

NaCl, MgCl₂の結晶と海洋生物の存在をしめす。

FT-IRのチャートFigure 5 より前記と同様に特異な吸収ピークは認められなかった。

Feさびによると考えられるピーク、450cm⁻¹が少し認められた。

Photo. 5-3に、大きさ約0.8μmに球状の連続体が認められ、カビの一種の真菌類が認められた。

- ・サンプル(5) : カートリッジ・フィルター出口サンプルをPhoto. 3-1~3-6に示す。SEMとEDXよりFeCl₃, MgCl₂と推定、他にCa, K, およびSO₄イオンのSがEDXスペクトルのピークとして認められた。

FT-IRのチャートFigure 3より、Fe及び水酸化物と推定される800~400cm⁻¹, ならびに(-OH)の吸収ピーク3300, 1600cm⁻¹が認められた。

- ・サンプル(6) : 日本近海の海水淡水化RO運転におけるプレフィルター・カートリッジ付着汚染物のMF回収サンプルをPhoto. 6-1~6-4に示す。EDXで強いFe, Clのピークが認められ、またSEM観察より前処理で使用する凝集剤FeCl₃がコロイド状で存在することが推定された。

FTIRのチャートFigure 6より、Fe及び水酸化物と推定される800~400cm⁻¹, (-OH)の1000cm⁻¹の各吸収ピークが認められた。

有機物の吸収は少ない。

3-2 RO膜汚染物サンプル-A

- ・サンプル(7) : Nitto Denko製の Polyamide Composite RO膜 Part-A 1

Photo. 7-1と7-2に示す。SEMとEDXより Fe, Cl, Si無機塩と推定、汚染物の存在がEDXスペクトルのピークとして認められた。

FTIRのチャートFigure 7より、Fe及び水酸化物と推定される $800 \sim 400 \text{ cm}^{-1}$, ならびに(-OH)の吸収ピーク 1000 cm^{-1} が認められた。

- ・サンプル(8) : 同上のRO膜 Part-A 2

Part-A 2部分においてもPhoto-8-1と8-2, Figure 8に示すように、上記と同じ結果のSEMならびにEDXのスペクトルが認められた。

特に、Photo-8におけるSEM4000倍の観察で解るように、画像がぼやけて見えるのは菌由来のスライムが膜面上に存在することを示している。

3-3 RO膜汚染物サンプル-B

- ・サンプル(9) : Desalination製のRO膜 Part B-1

Part B-1部分のSEM観察およびEDXのスペクトル分析結果をPhoto-9に示した。このEDXスペクトルから Ca, Si塩の存在を確認できる。但し、EDXのスペクトルとして観測されたSの存在が、 SO_4 塩で無い事はFTIRのチャートFigure 9において、 SO_4 の特異的吸収ピークである $1150, 600 \sim 700, 3400 \sim 3600 \text{ cm}^{-1}$ が存在しないことよりRO膜の支持体層を構成しているPolysulfonの高分子鎖にある(- SO_2 -)スルホン基由来のSと判定された。

- ・サンプル(10) ~ (12) : 同上のRO膜 Part B-2 ~ 4

B-2、3およびB-4のSEM観察およびEDXのスペクトル分析結果をPhoto-10, 11および12に示した。

Photo-10, 11および12のEDXスペクトルからCa塩の他にFeの存在を確認できる。

FT-IR 差スペクトルに関して Part B-1 ~ 3 および B-4 の 4 つの部分の結果において、部分による著しい相違は認められなかった。

、特異的な吸収ピークとしてバクテリア由来の -NHCO- (1600cm^{-1})、Ca塩による (1450cm^{-1})、また、CaOHあるいはバクテリア由来の -OH ($3400, 1000 \text{ \& } 400\text{-}500\text{cm}^{-1}$) が観察された。

4. 考察

今回、海水淡水化プラントの前処理行程における原海水中的膜汚染成分の分析として、精密ろ過 (MF) 膜によって捕捉される原海水中的濁質成分である微粒子状の固形物を分析することを主目的とした。しかしながら、これらサンプルは海水の溶存イオン Na, Ca, Mg, Cl などを含む湿潤状態またはその後の風乾状態で保管されたものであるため、分析サンプルとしてこれら溶存イオンが固形物として膜面上に析出したものであったので、溶解性イオンの結晶成分の影響が大きいことが判った。

従って、海水のような高濃度 TDS の原水に使用した膜汚染物の分析においては、溶解性イオンの析出によるコンタミネーションを考慮し、汚染調整段階に超純水での予備洗浄による溶存イオン成分の塩抜きが、今後の海水中的膜面汚染物分析において開発すべき課題として残った。

分析法についてマニュアルを作成して SWCC 担当者に指導した。また、汚染膜エレメントを分解し点検方法、劣化状況の観察方法について実施指導を行った。

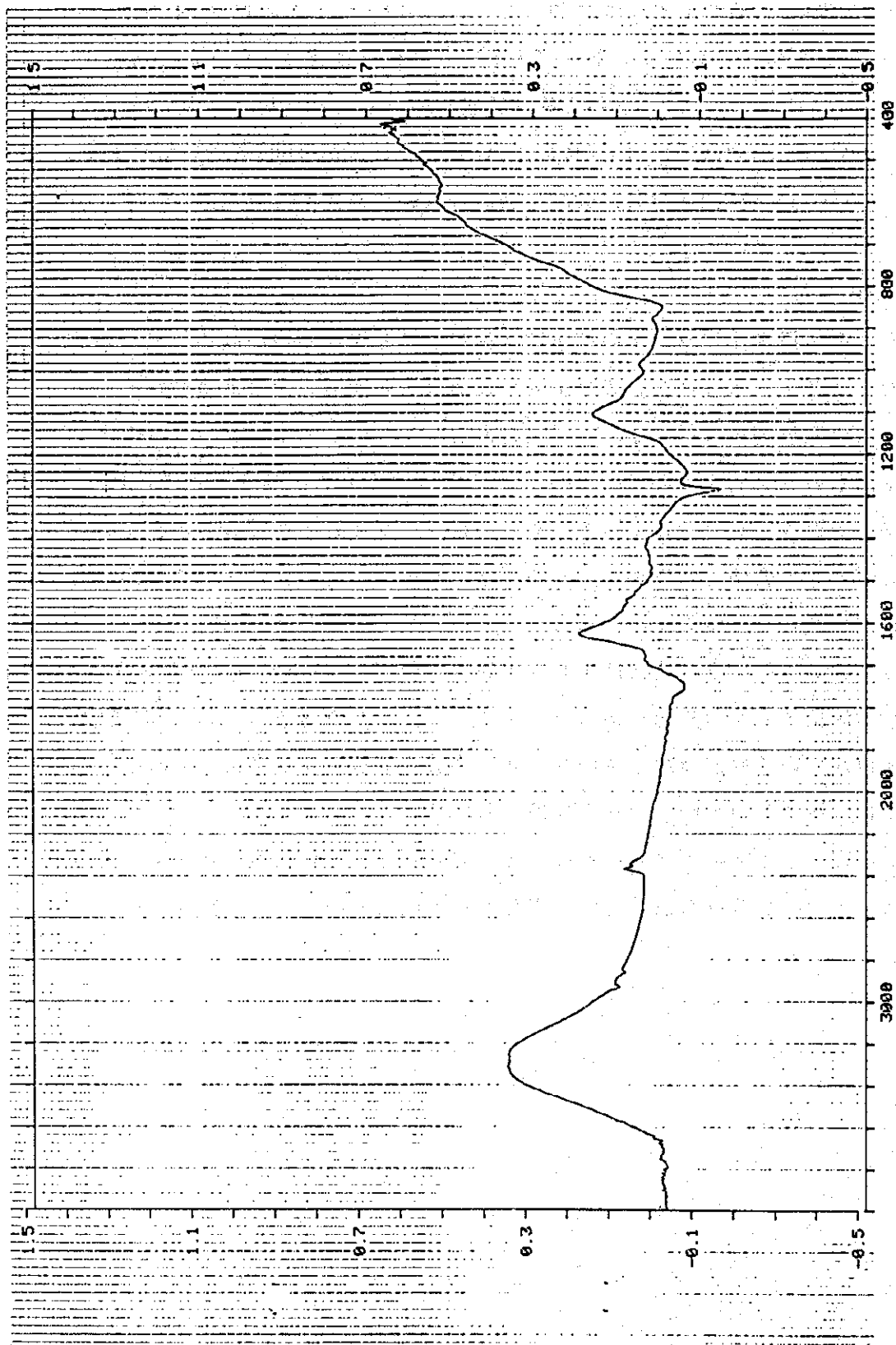


Figure 3. IR Chart of Fouling Material on MF Membrane Surface (sample 5)

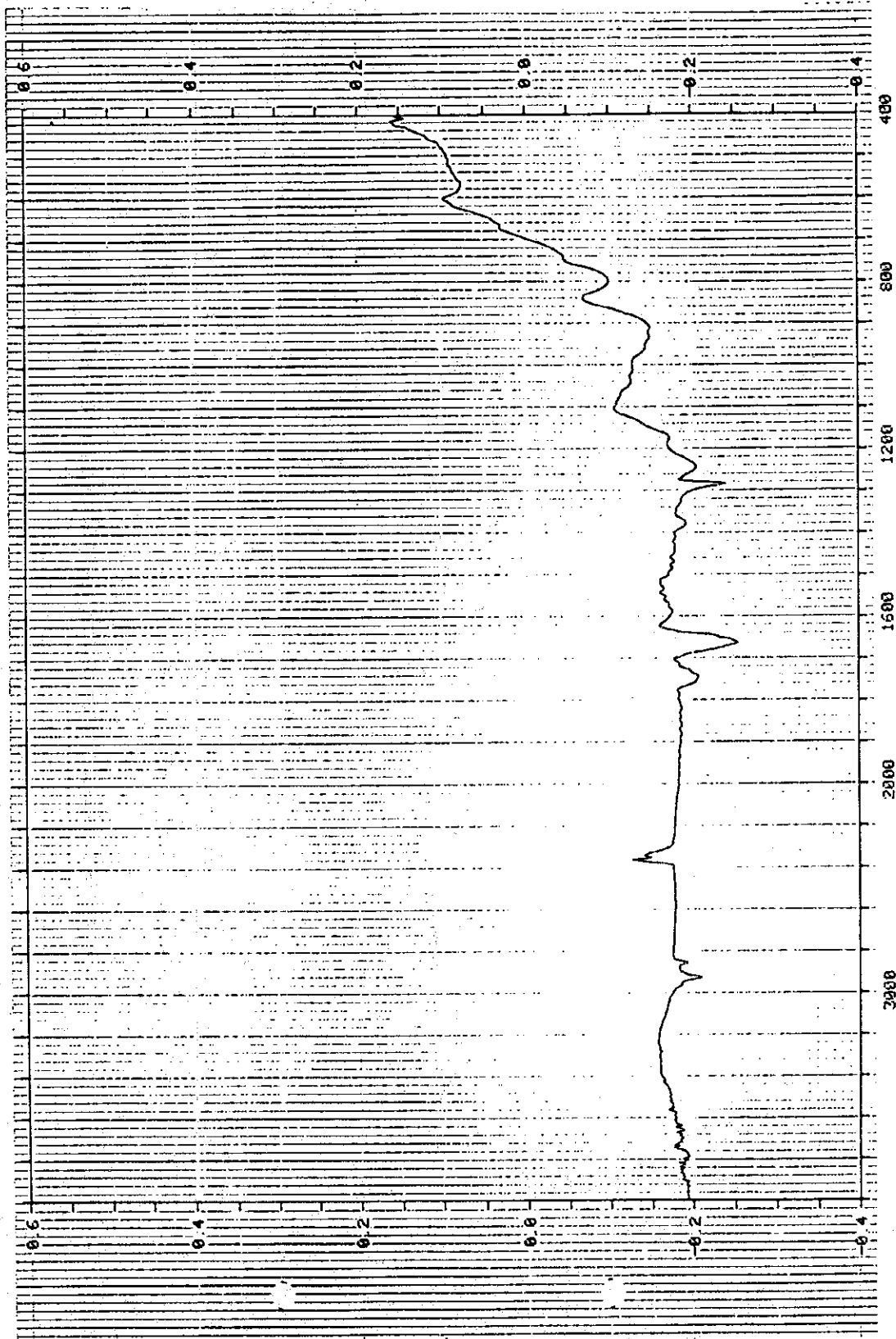


Figure 4. IR Chart of Fouling Material on MF Membrane Surface (sample 3)

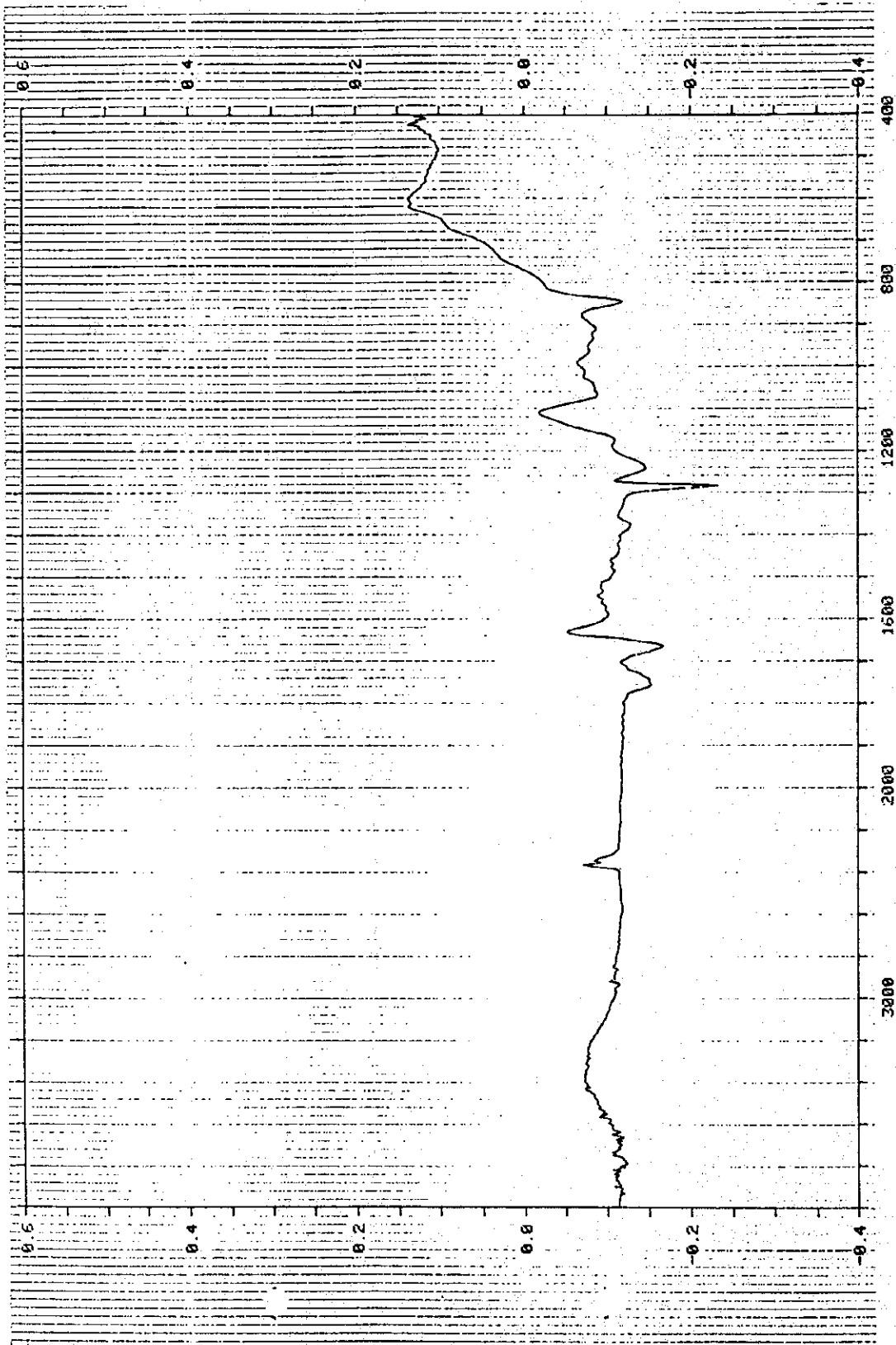


Figure 5. IR Chart of Fouling Material on MF Membrane Surface (sample 4)

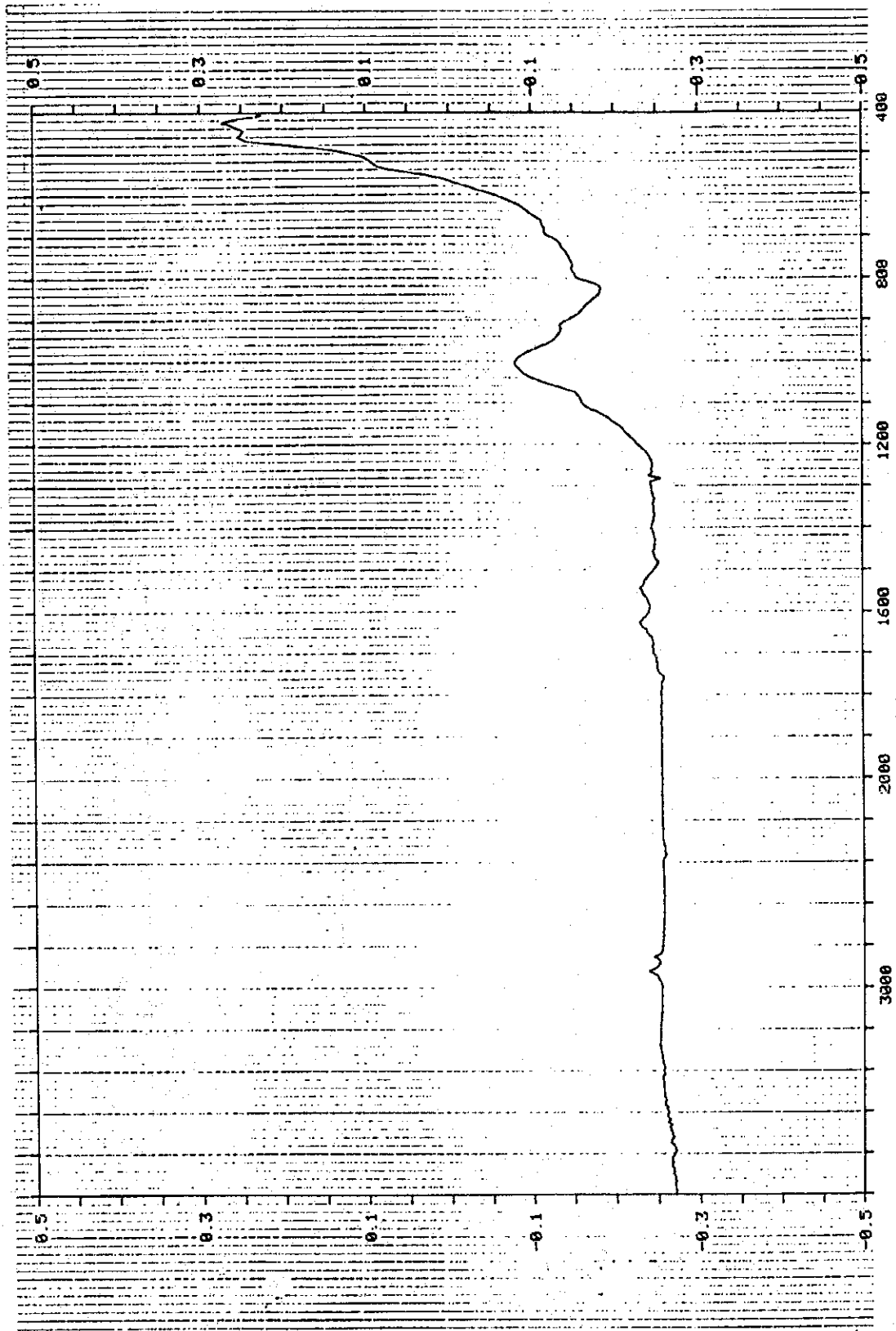


Figure 6. IR Chart of Fouling Material on MF Membrane Surface (sample 6)

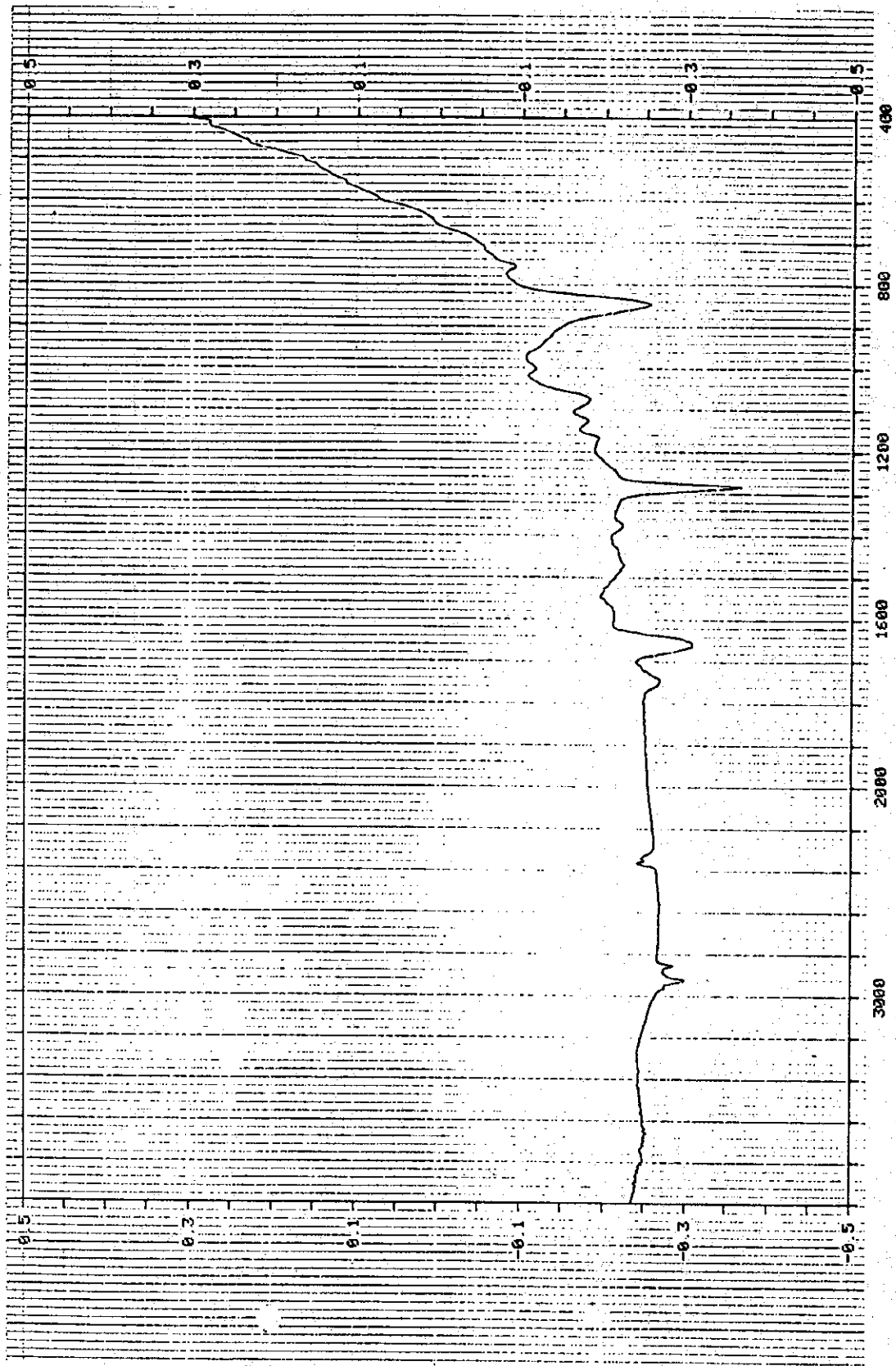


Figure 7. IR Chart of Fouling Material on RO Membrane Surface (sample 7)

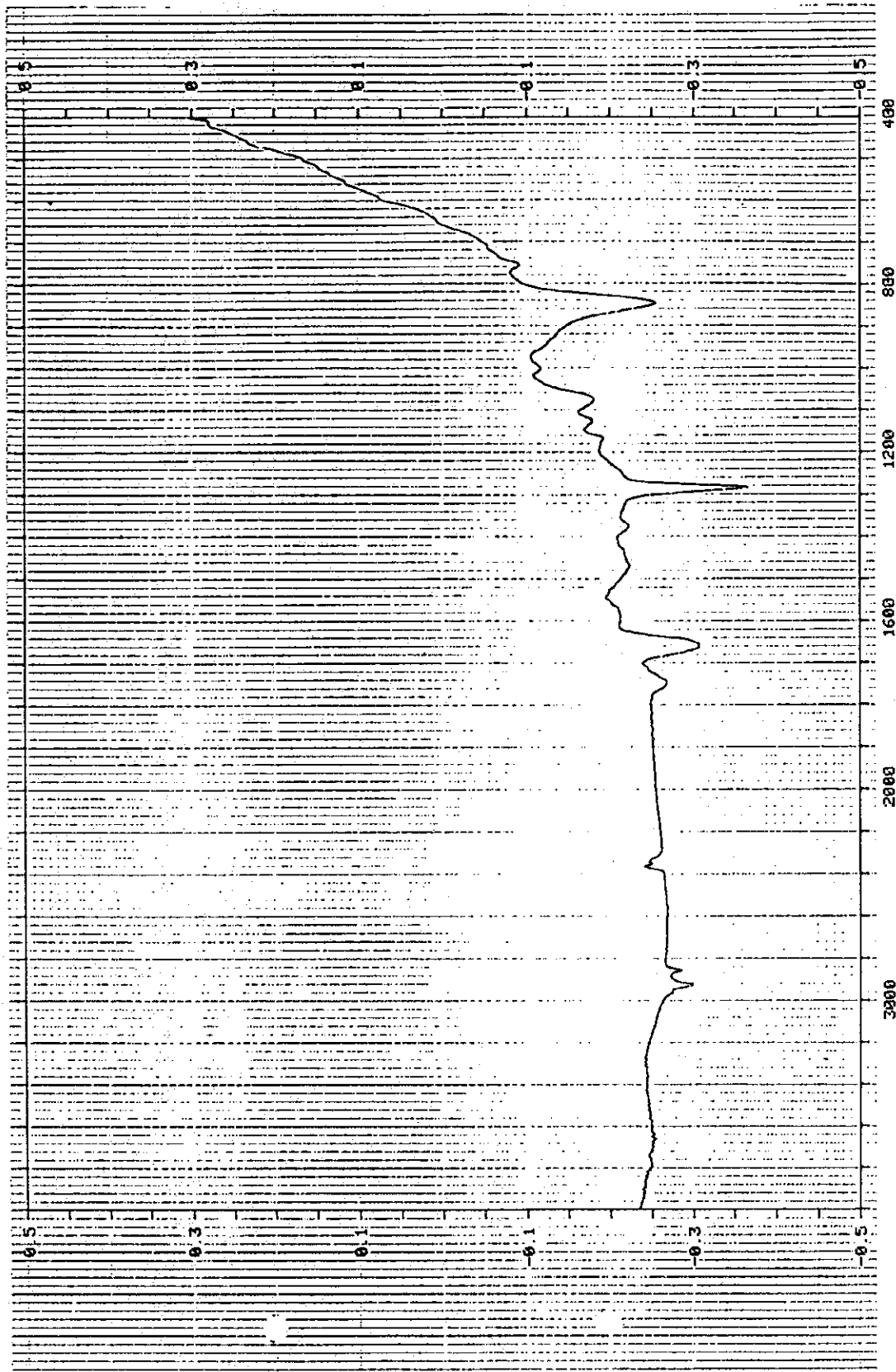


Figure 8. IR Chart of Fouling Material on RO Membrane Surface (sample 8)

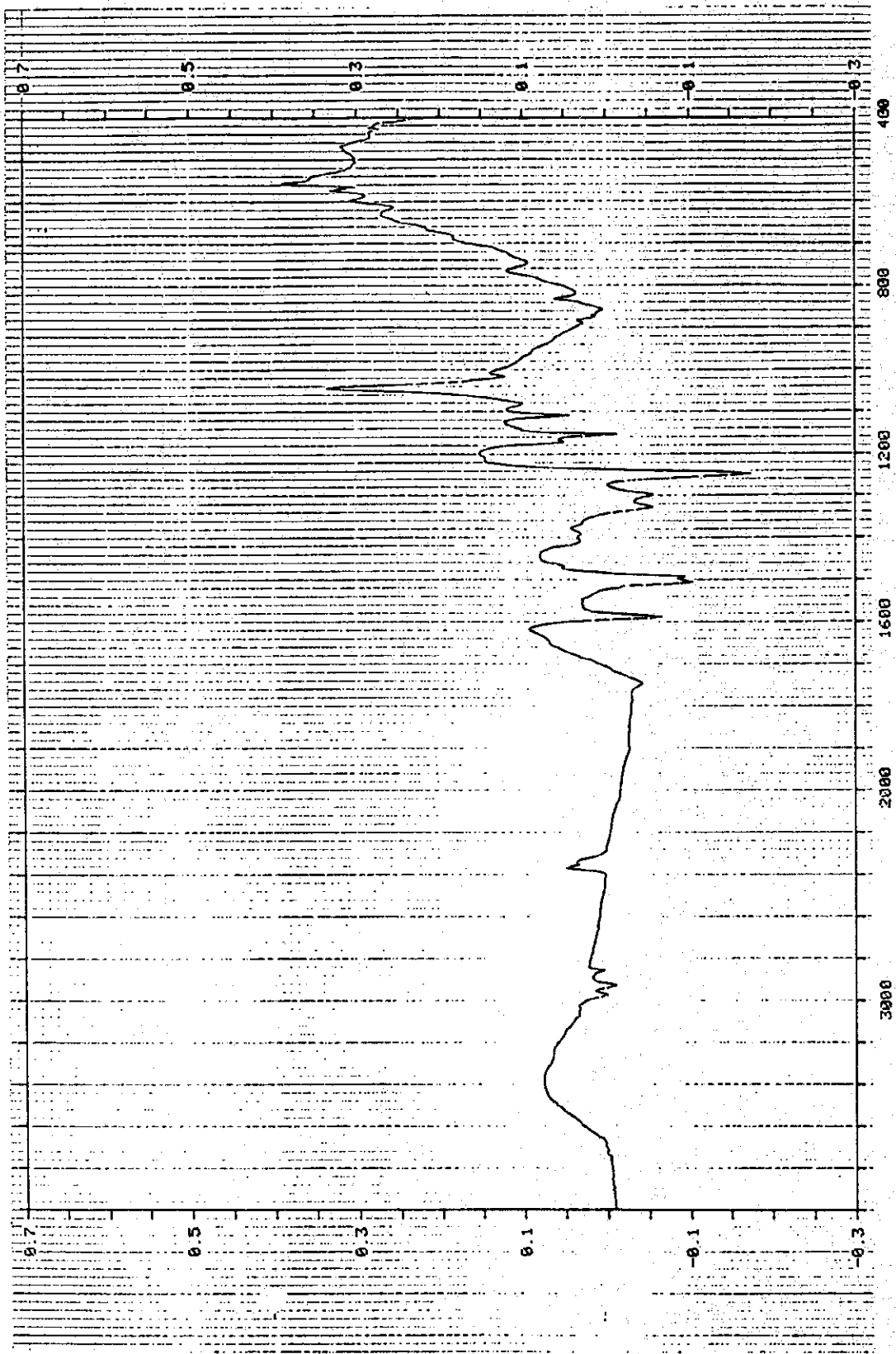
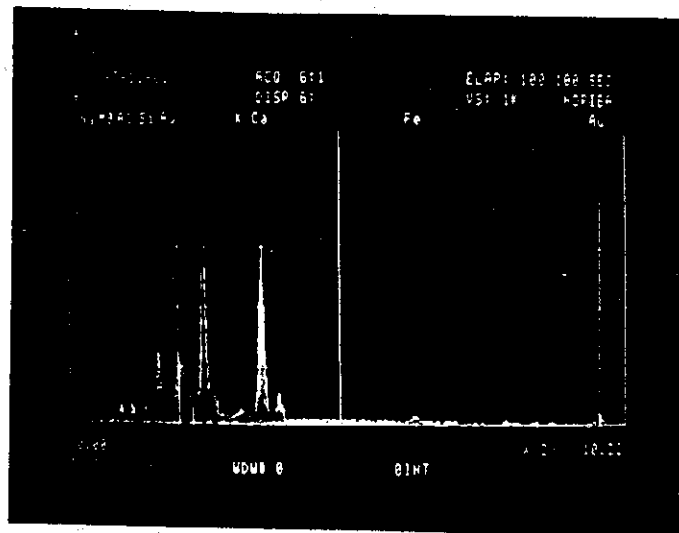


Figure 9. IR Chart of Fouling Material on RO Membrane Surface (sample 9)



SEM (X 800)



EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 1-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (1)

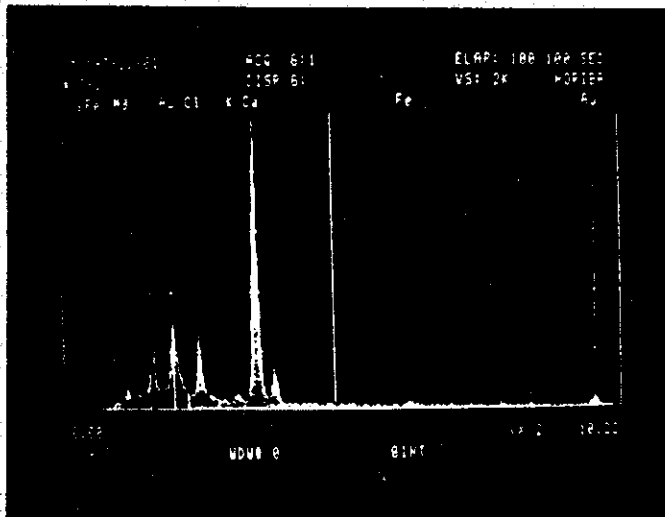


SEM (X 800)

PHOTO 1-2 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (1)



SEM (X 4000)

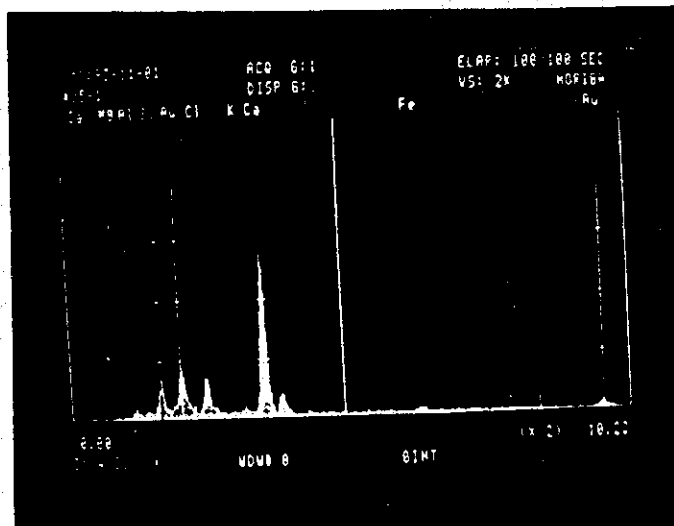


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 1-3 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (1)



SEM (X 4000)

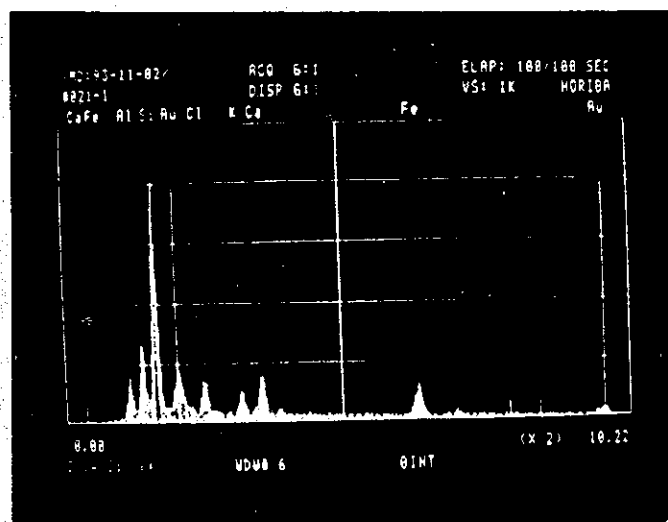


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 1-4 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (1)

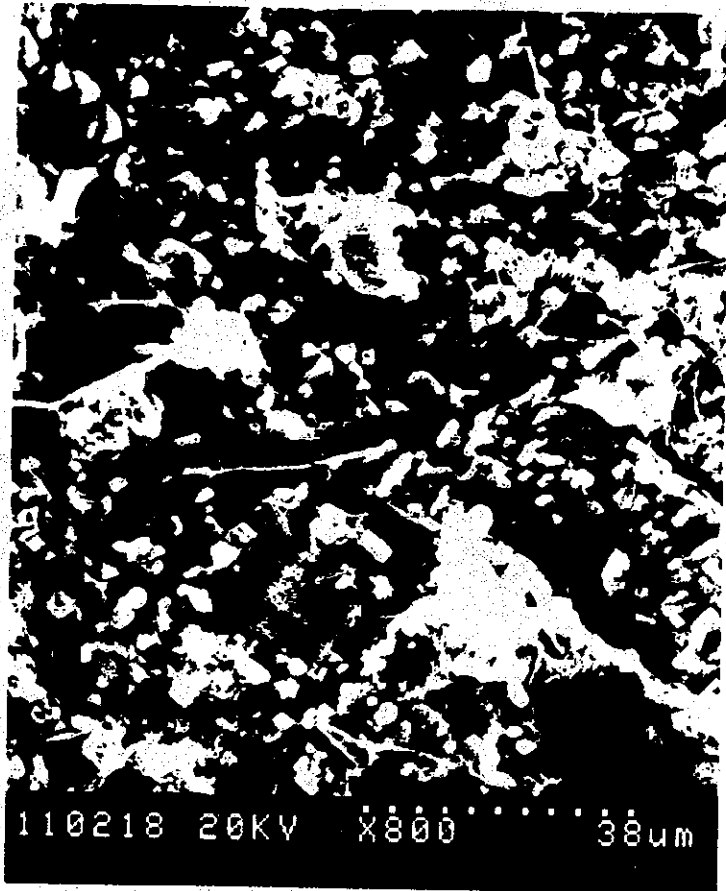


SEM (X 4000)

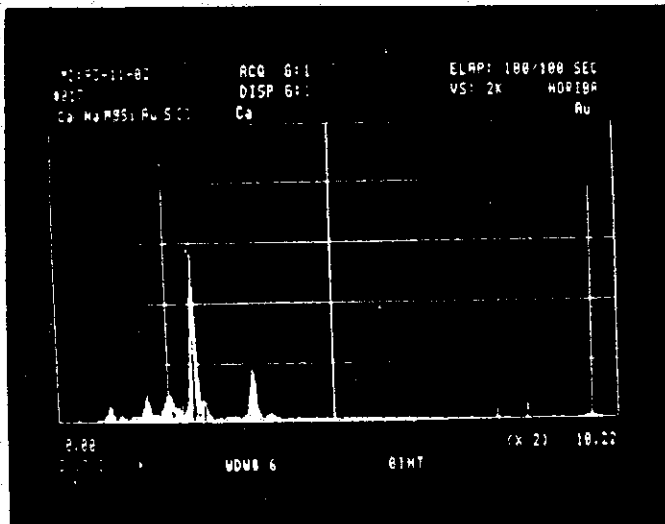


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 2-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (2)

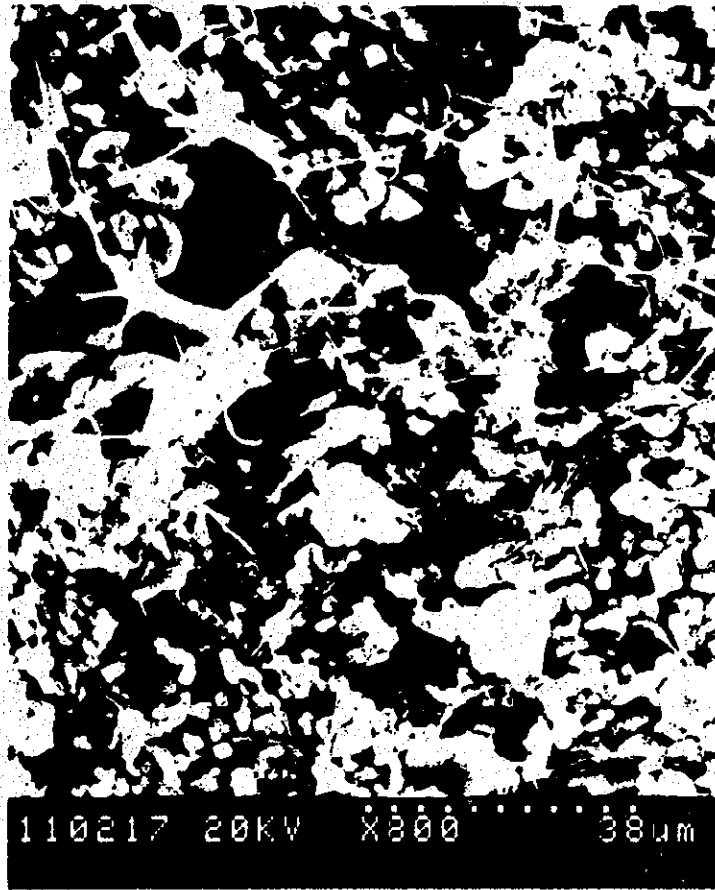


SEM (X 800)



EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 2-2 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (2)

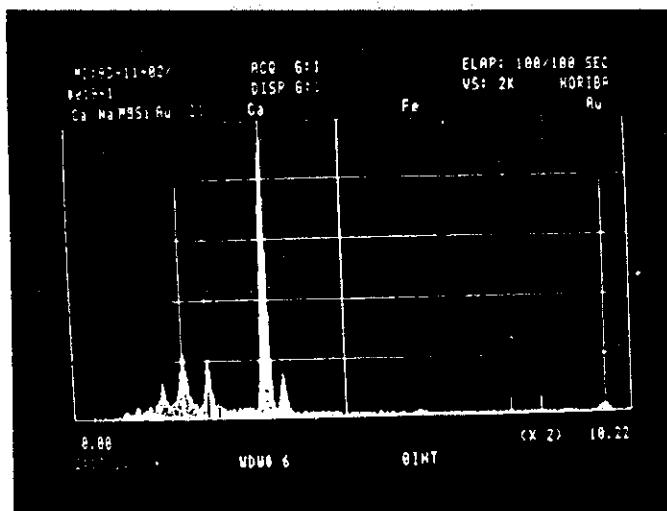


SEM (X 800)

PHOTO 2-3 SEM OF THE FOULED MEMBRANE SAMPLE (2)



SEM (X 4000)

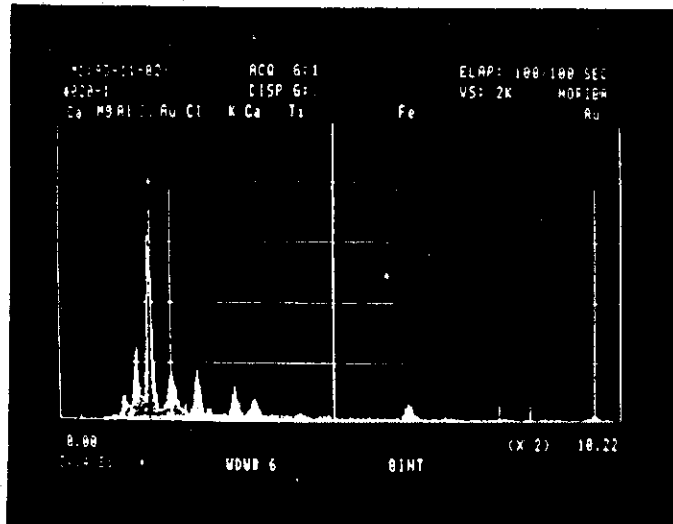


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 2-4 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (2)



SEM (X 4000)



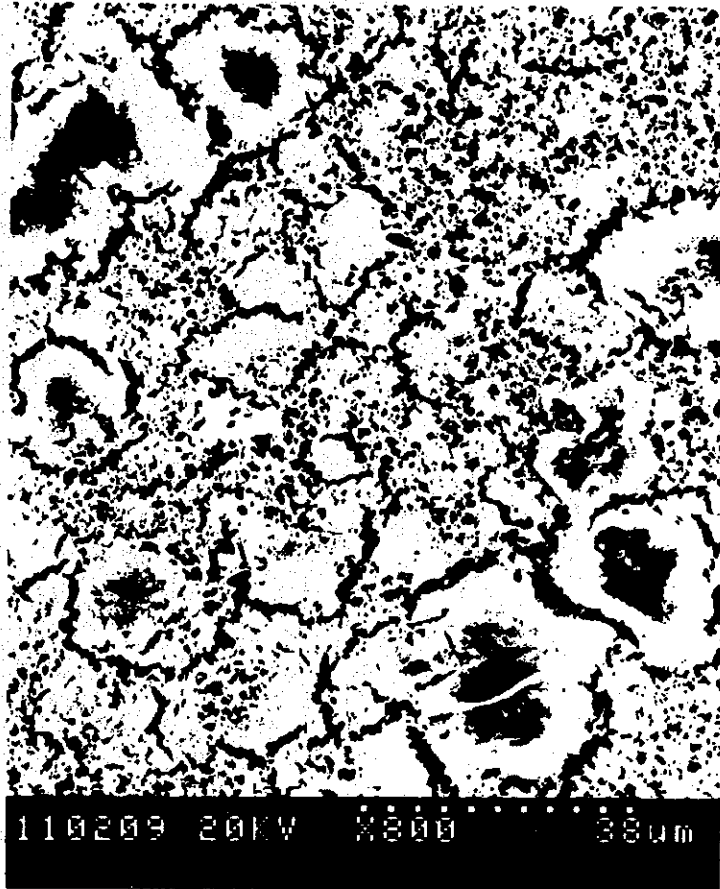
EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 2-5 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (2)

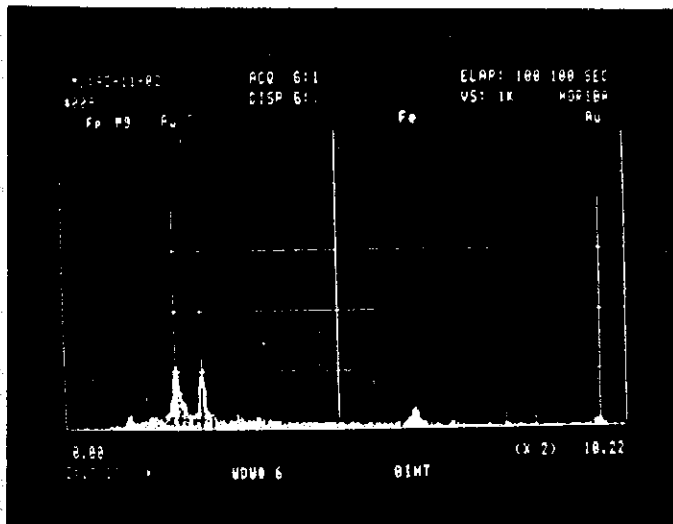


SEM (X 800)

PHOTO 3-1 SEM OF THE FOULED MEMBRANE SAMPLE (5)



SEM (X 800)

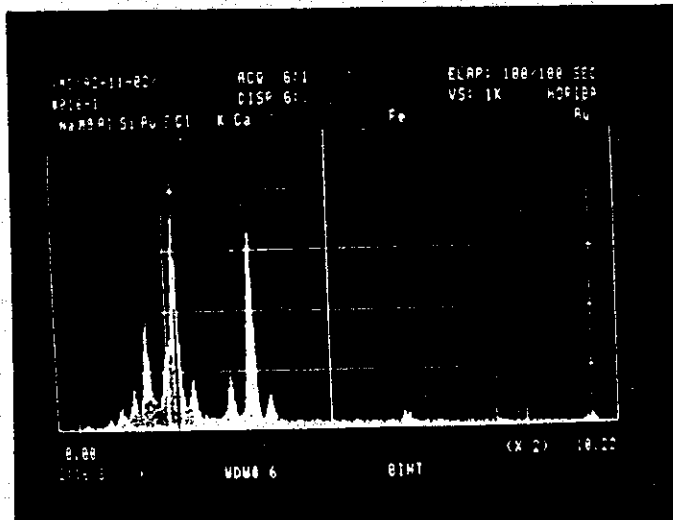


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 3-2 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (5)



SEM (X 4000)

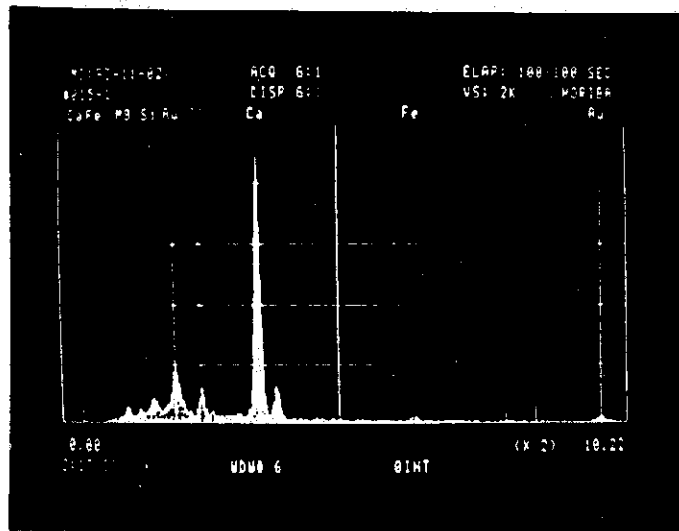


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 3-3 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (5)

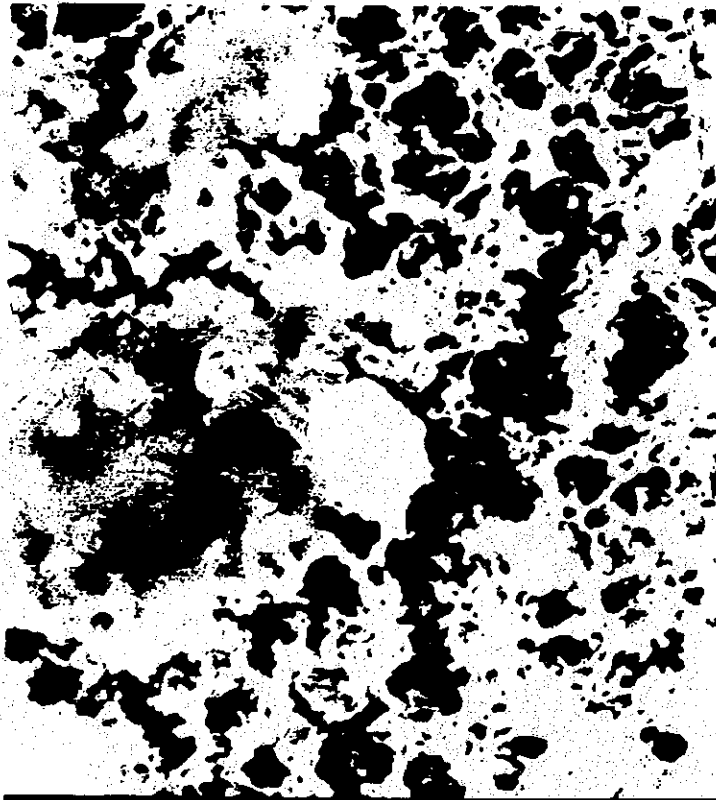


SEM (X 4000)



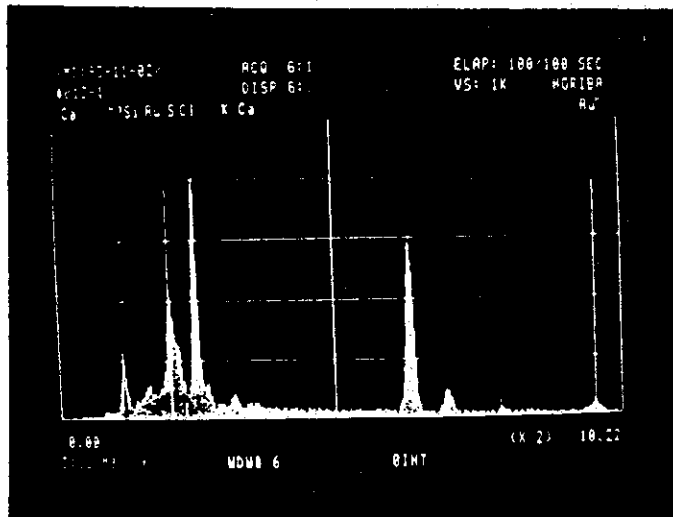
EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 3-4 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (5)



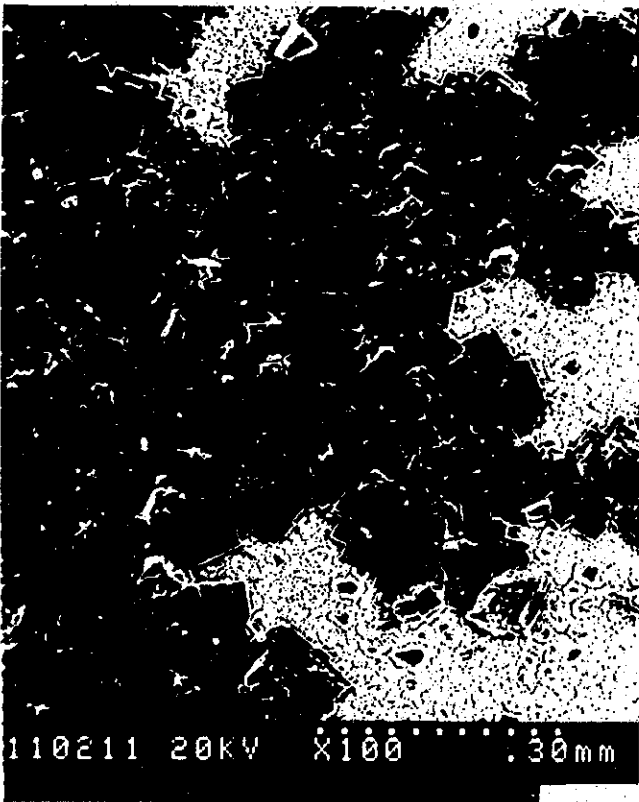
110213 20KV X4.00K 7.5um

SEM (X 4000)



EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 3-5 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (5)

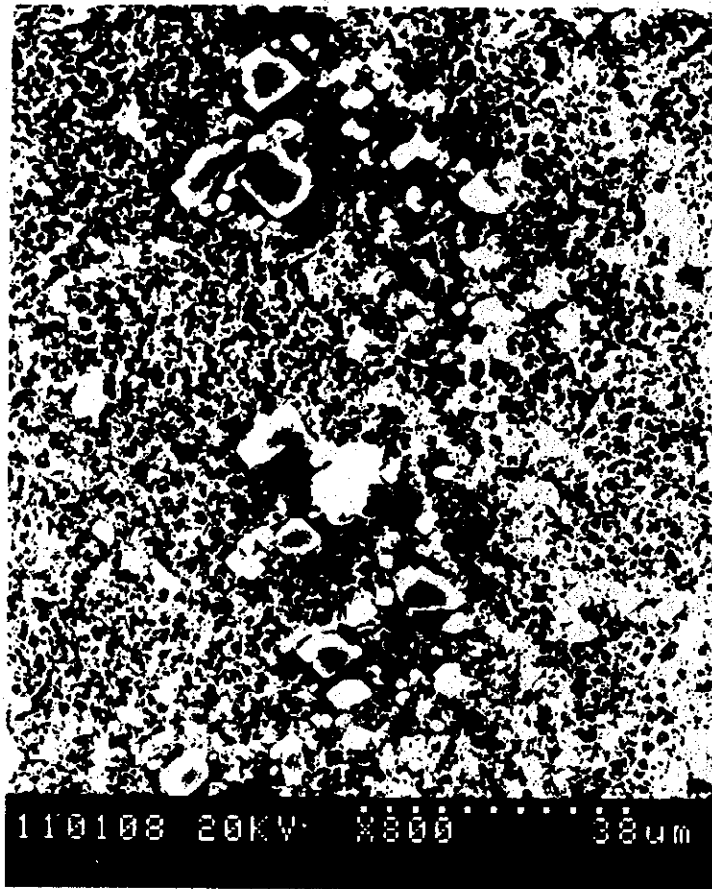


SEM (X 800)

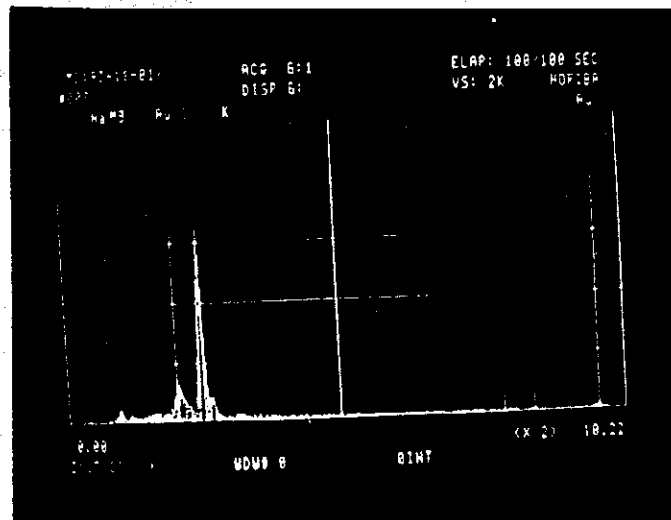


PHOTO 3-6 SEM OF THE FOULED MEMBRANE SAMPLE (5)

SEM (X 800)

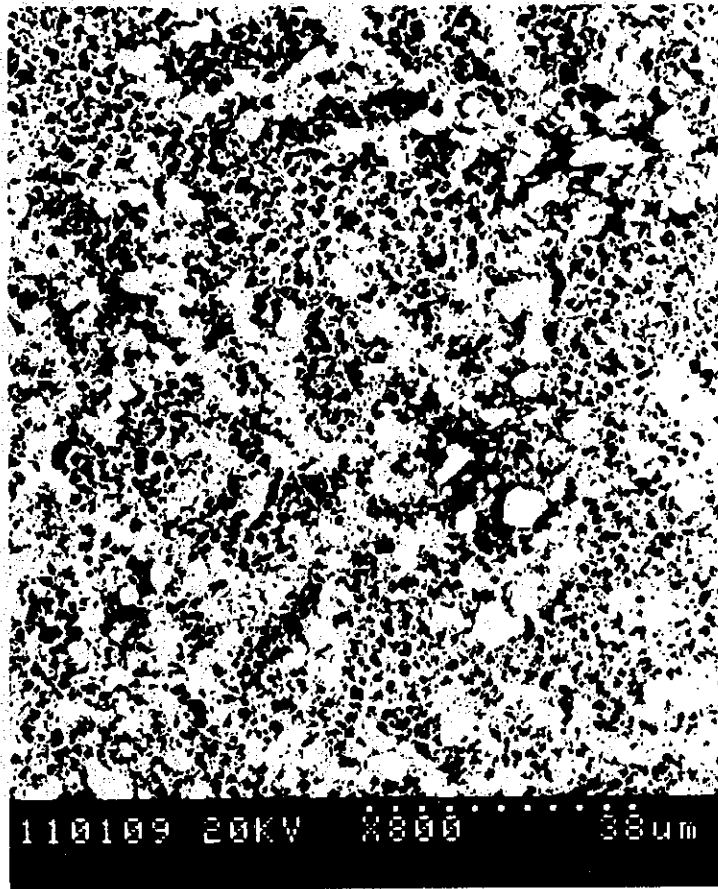


SEM (X 800)



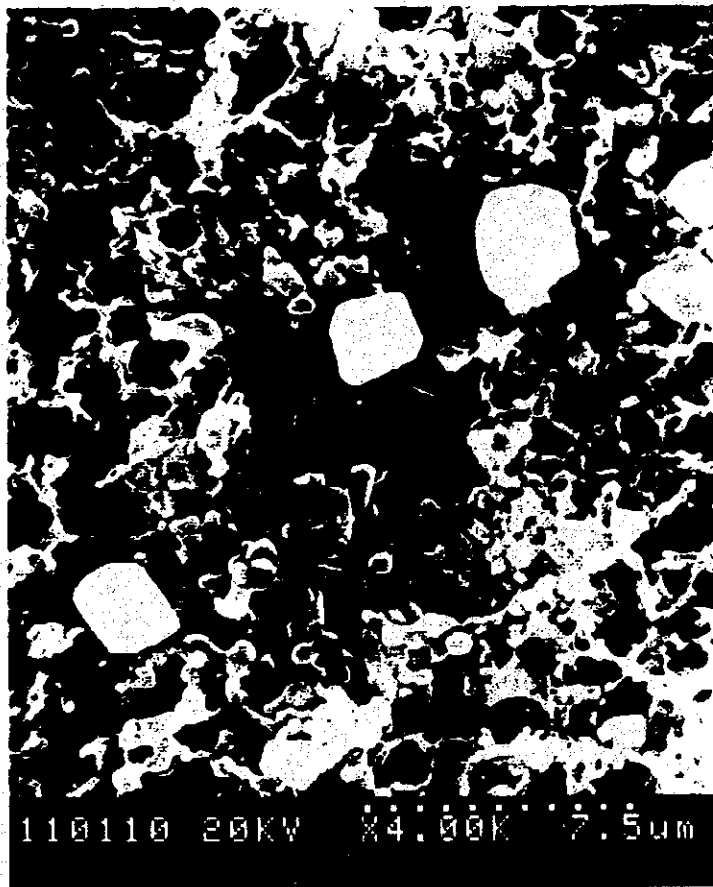
EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 4-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (3)

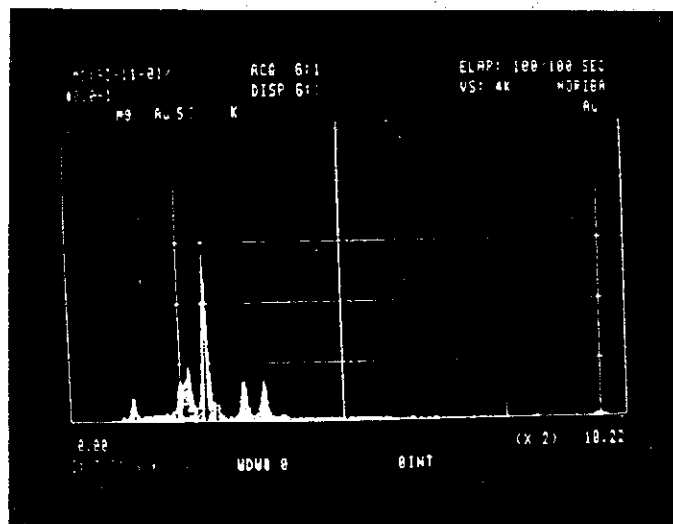


SEM (X 800)

PHOTO 4-2 SEM OF THE FOULED MEMBRANE SAMPLE (3)

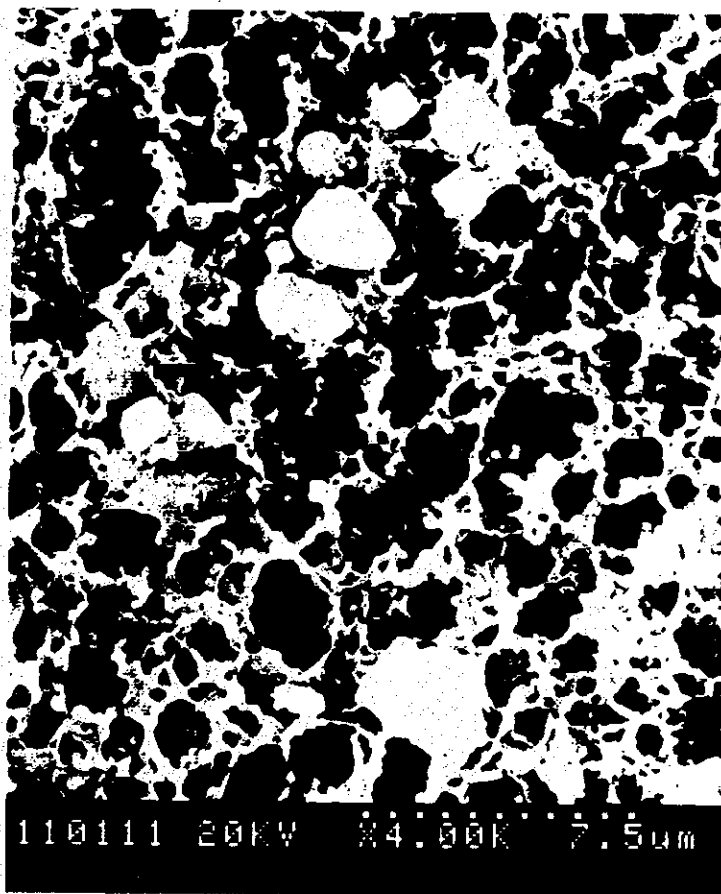


SEM (X 4000)

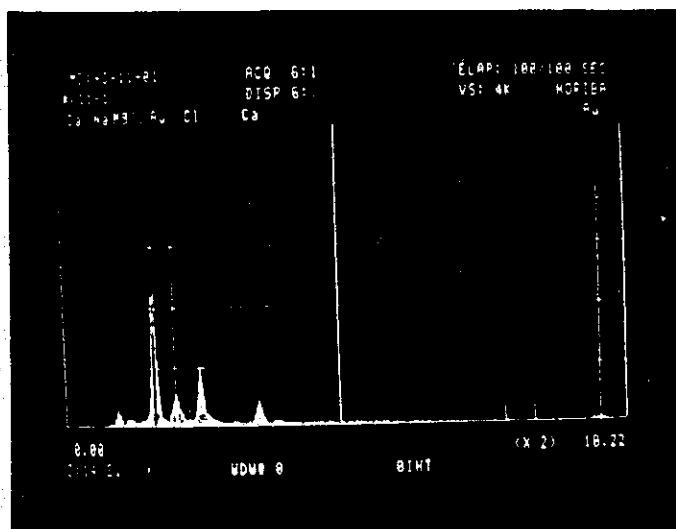


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 4-3 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (3)

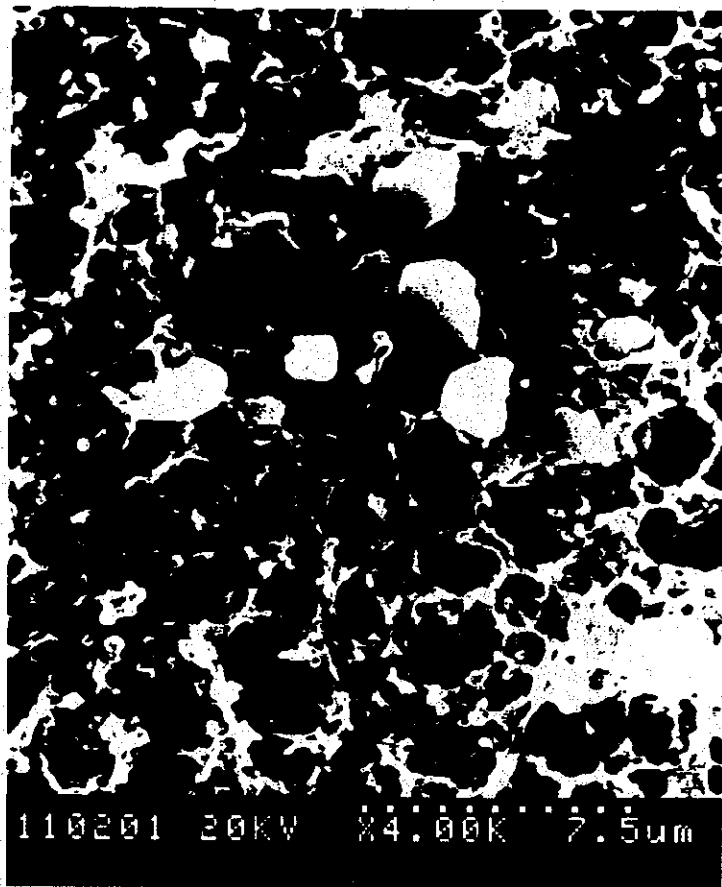


SEM (X 4000)

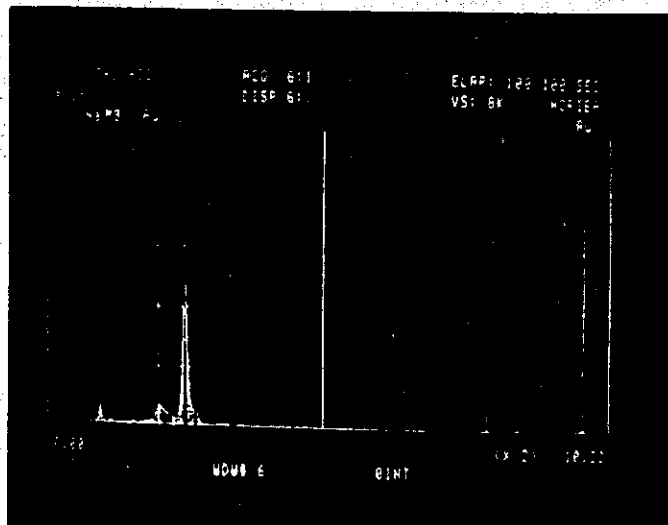


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 4-4 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (3)

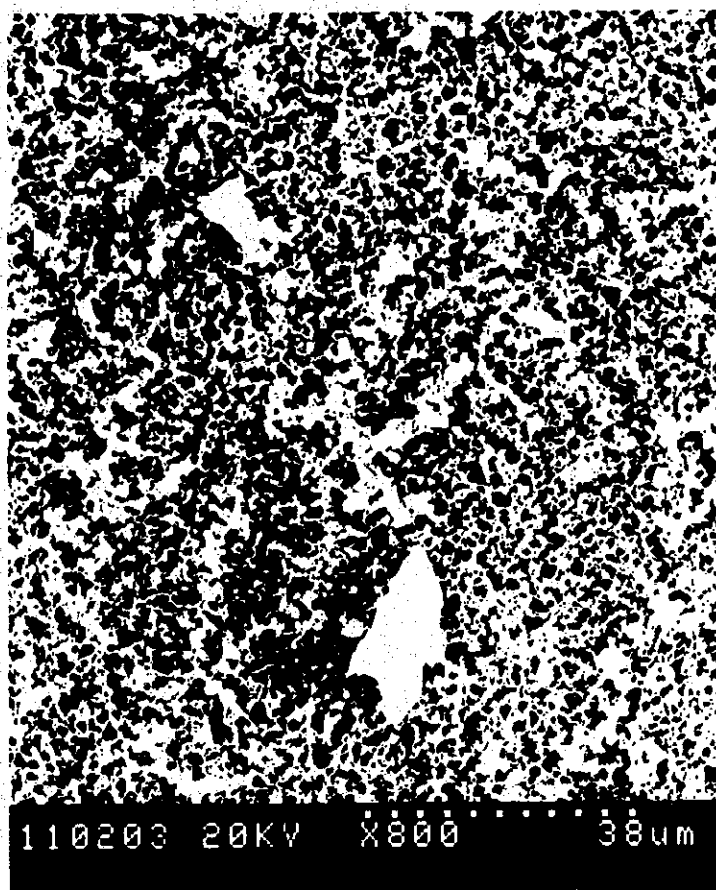


SEM (X 4000)

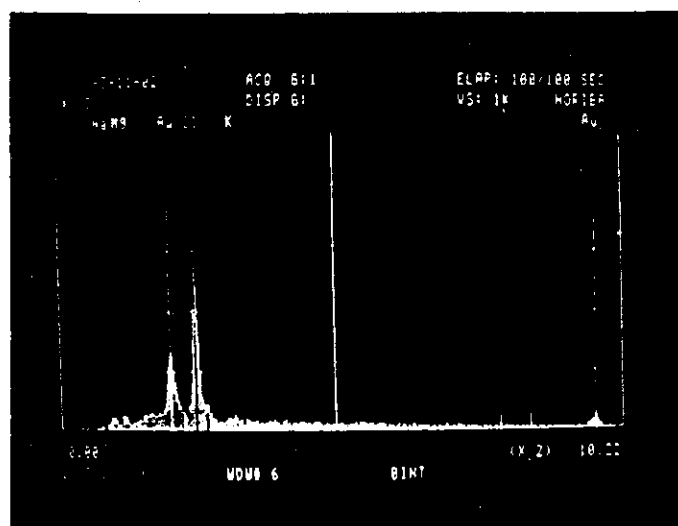


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 4-5 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (3)

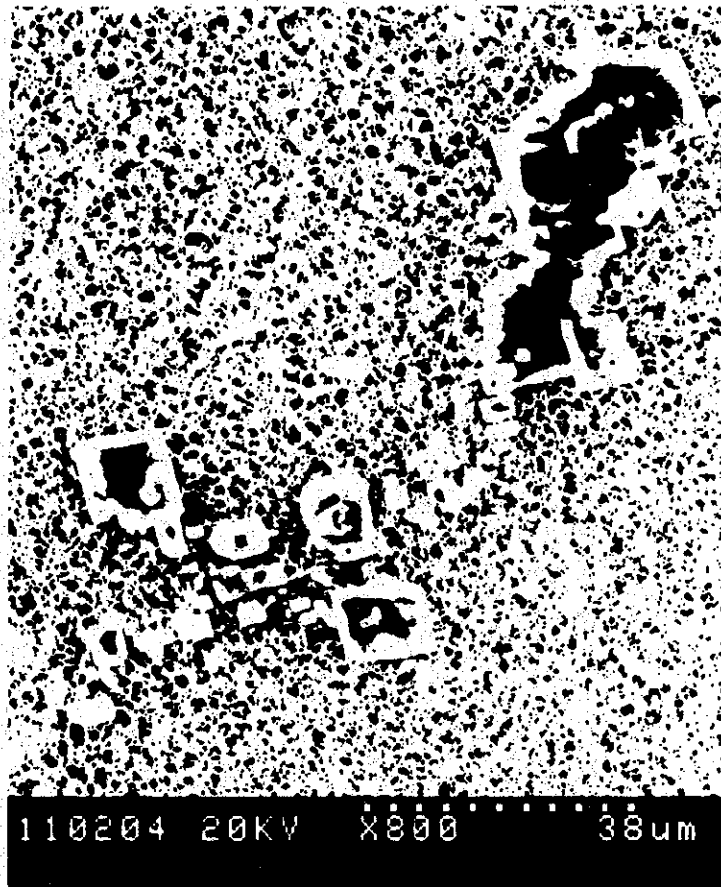


SEM (X 800)



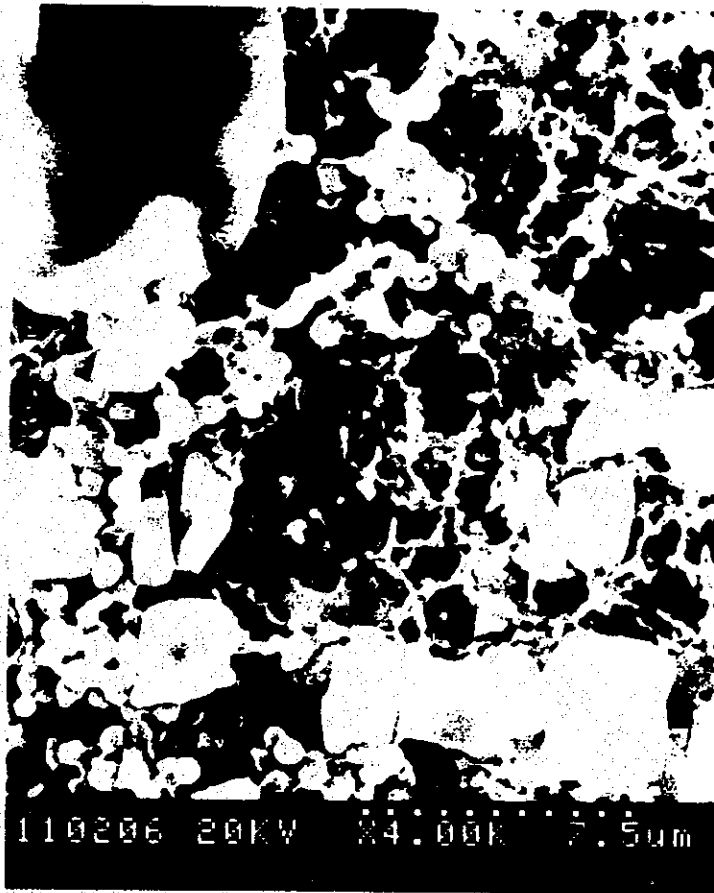
EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 5-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (4)

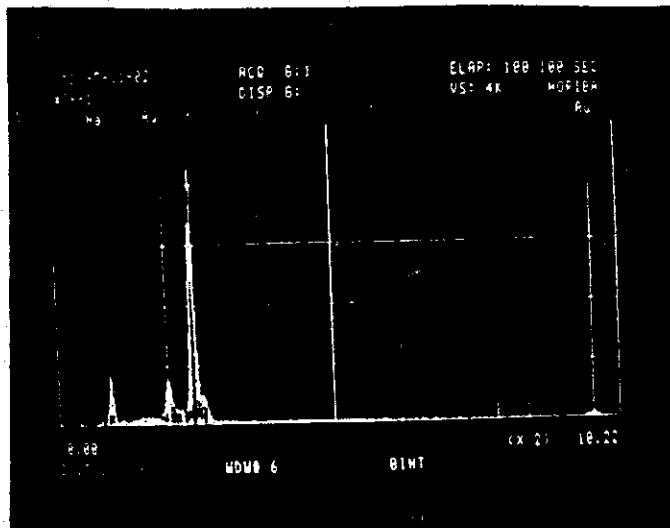


SEM (X 800)

PHOTO 5-2 SEM OF THE FOULED MEMBRANE SAMPLE (4)

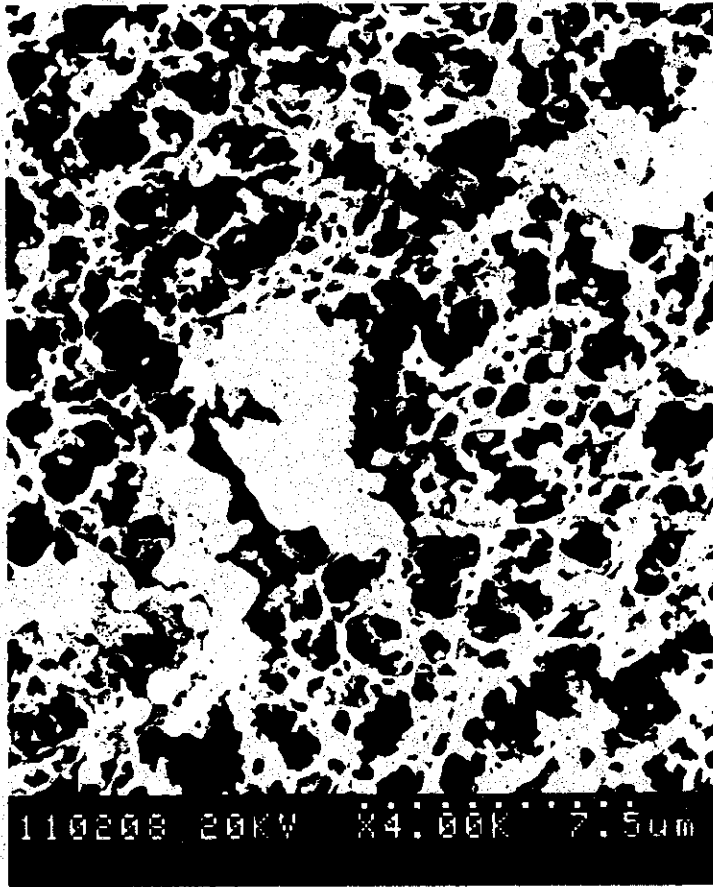


SEM (X 4000)

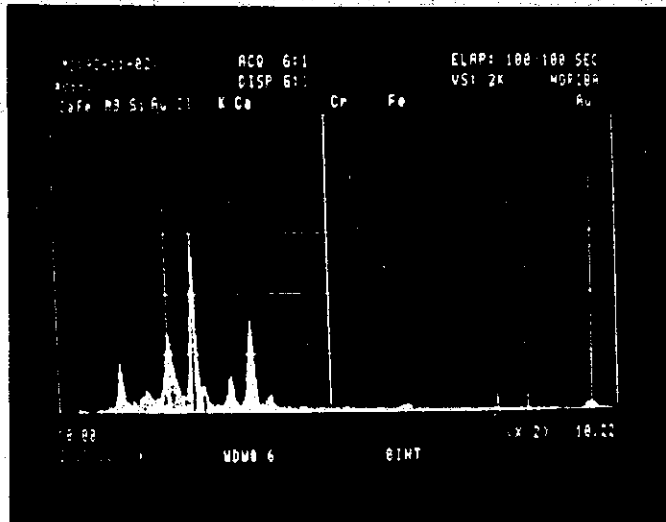


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 5-3 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (4)

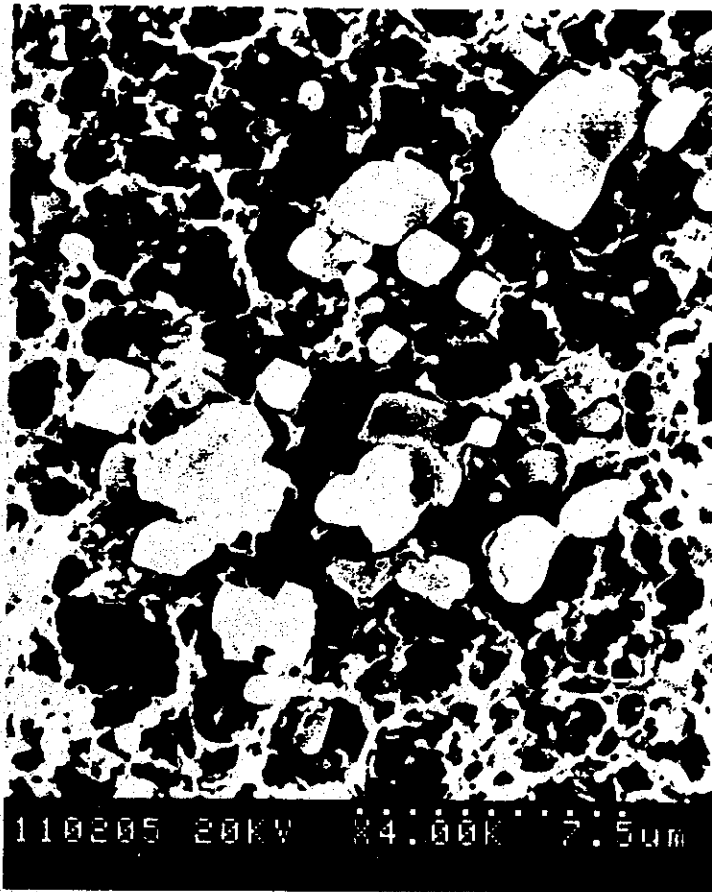


SEM (X 4000)

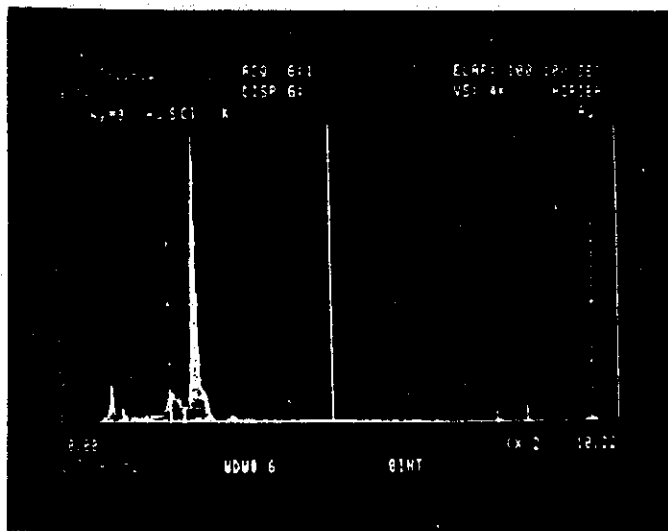


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 5-4 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (4)



SEM (X 4000)

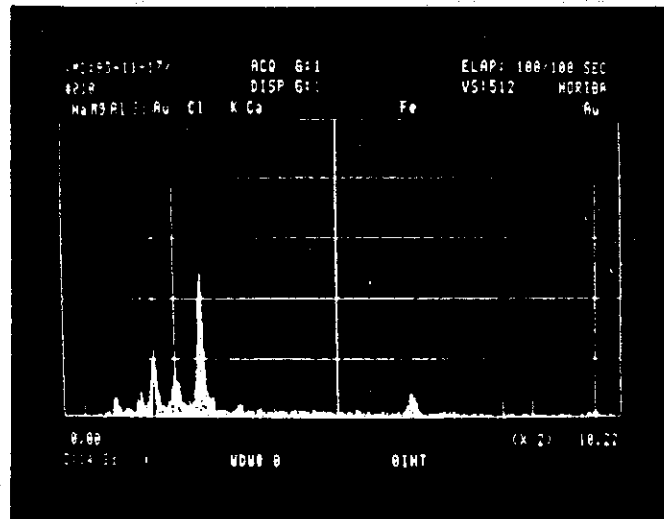


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 5-5 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (4)



SEM (X 800)



EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 6-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (6)



SEM (X 800)

PHOTO 6-2 SEM OF THE FOULED MEMBRANE SAMPLE (6)



SEM (X 4000)

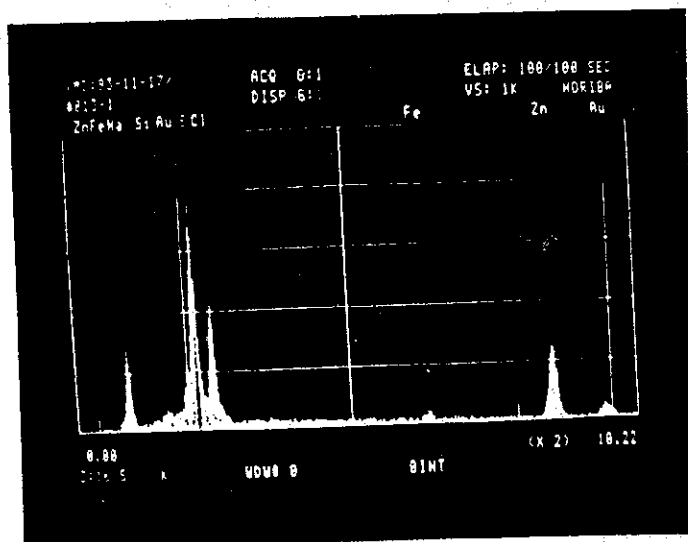
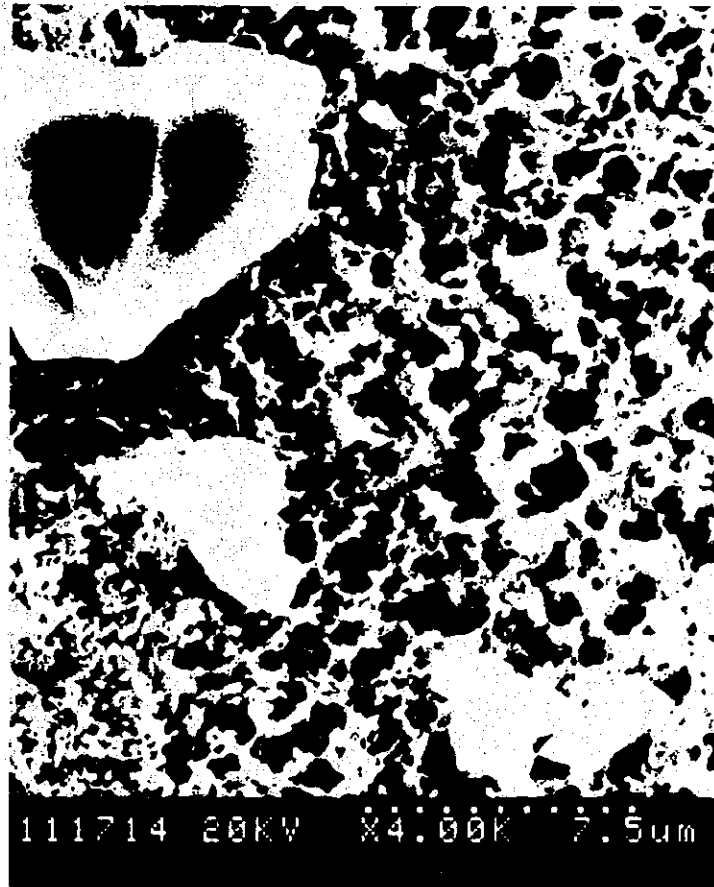
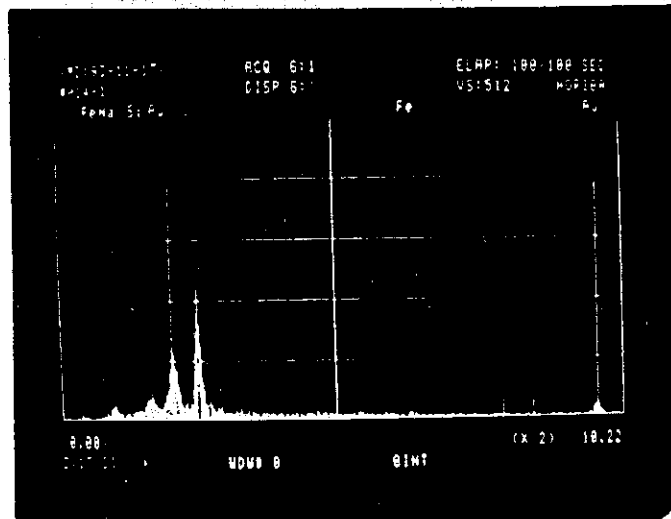


PHOTO 6-3 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (6)



SEM (X 4000)

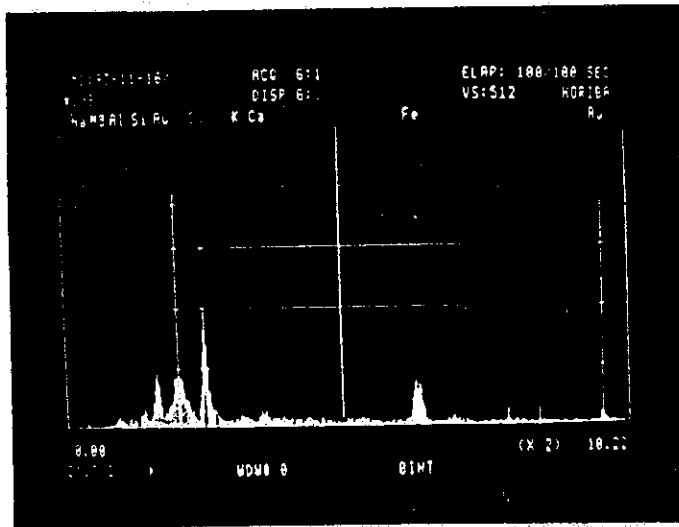


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 6-4 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (6)

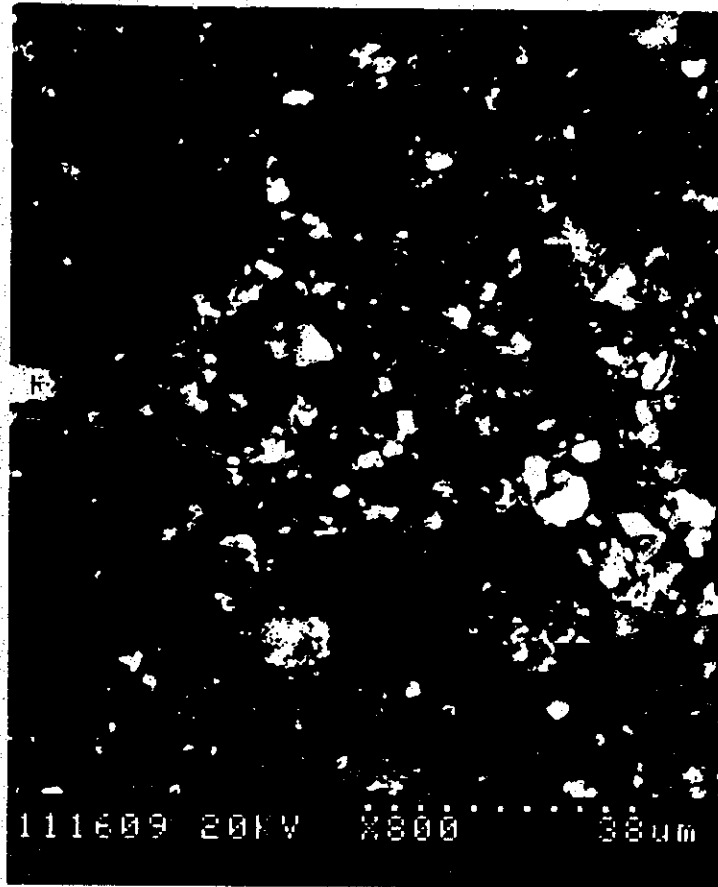


SEM (X 800)



EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 7-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (7)

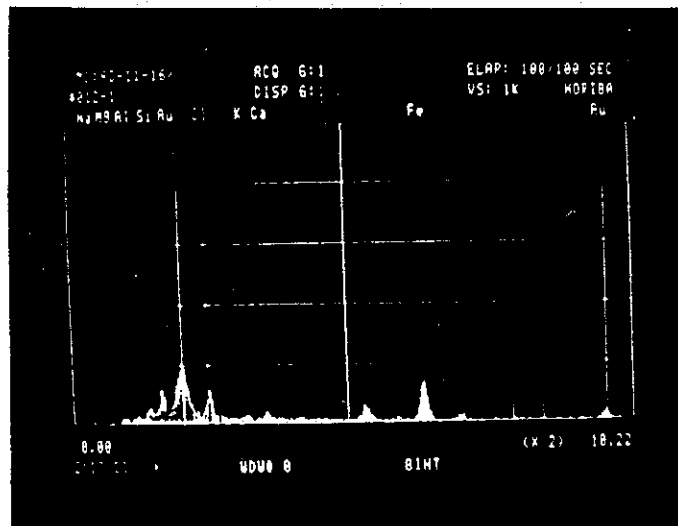


SEM (X 800)

PHOTO 7-2 SEM OF THE FOULED MEMBRANE SAMPLE (7)



SEM (X 4000)

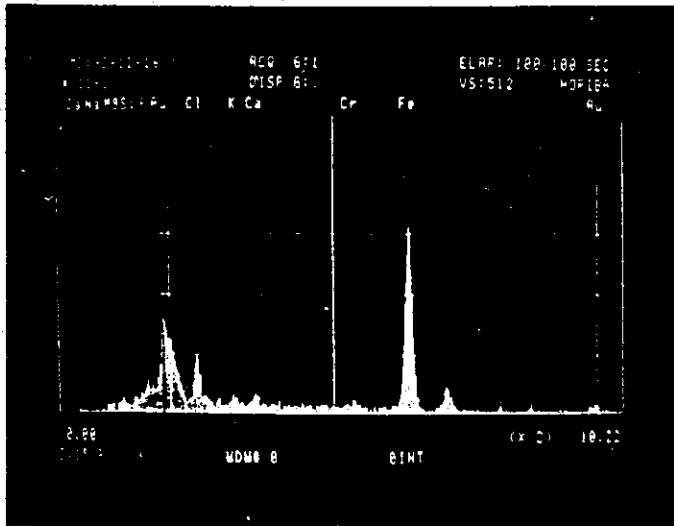


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 8-1 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (8)

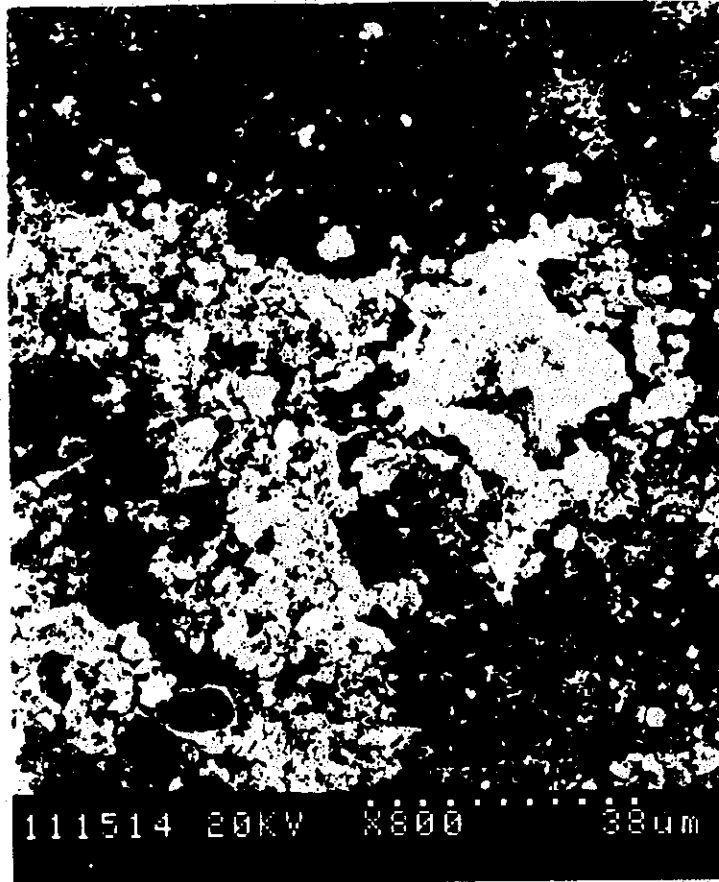


SEM (X 4000)

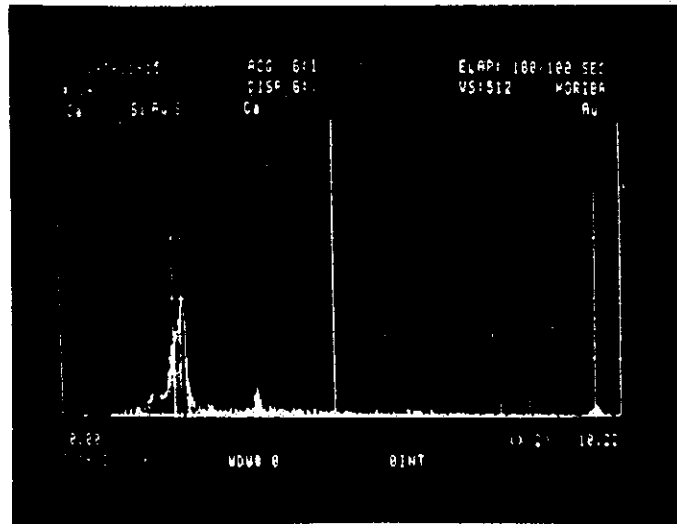


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 8-2 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (8)



SEM (X 800)

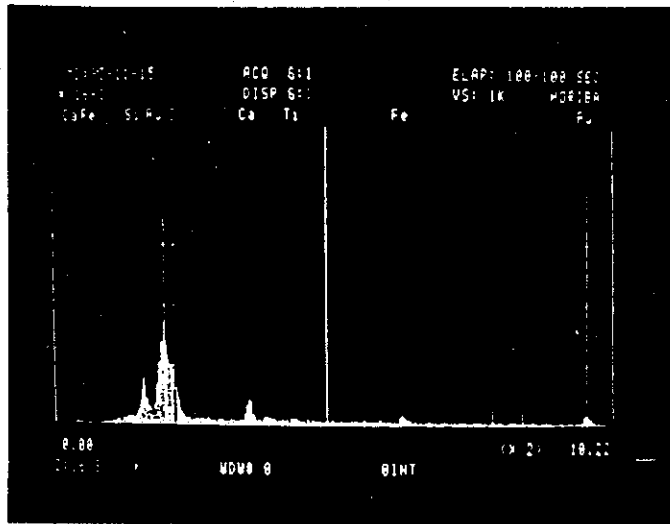


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 9 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (9)

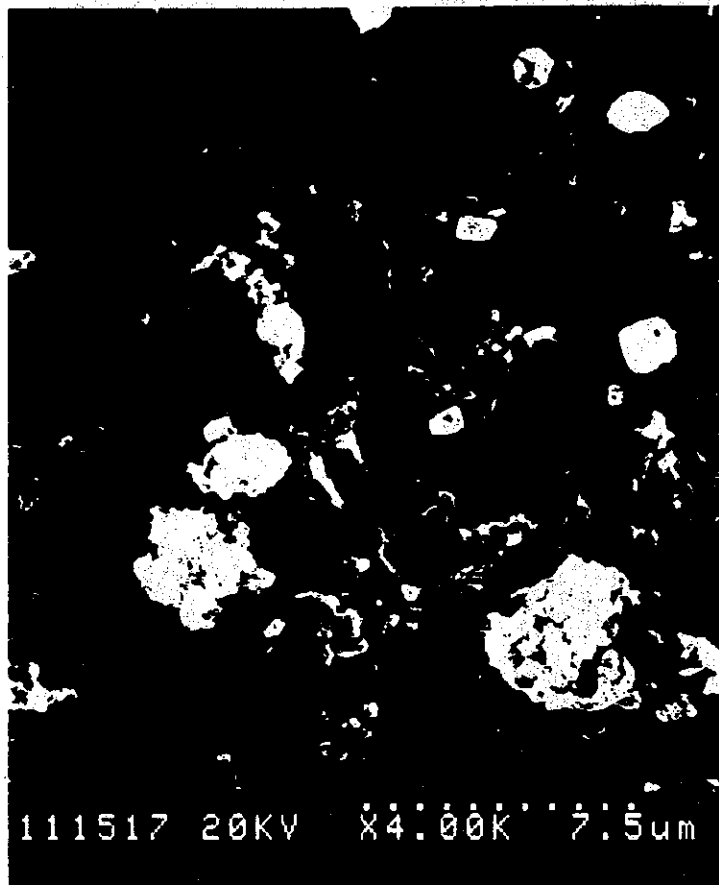


SEM (X 4000)

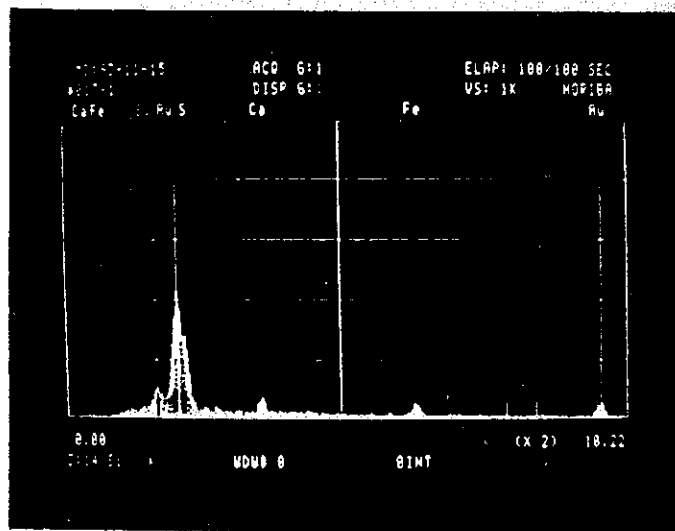


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 10 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (10)

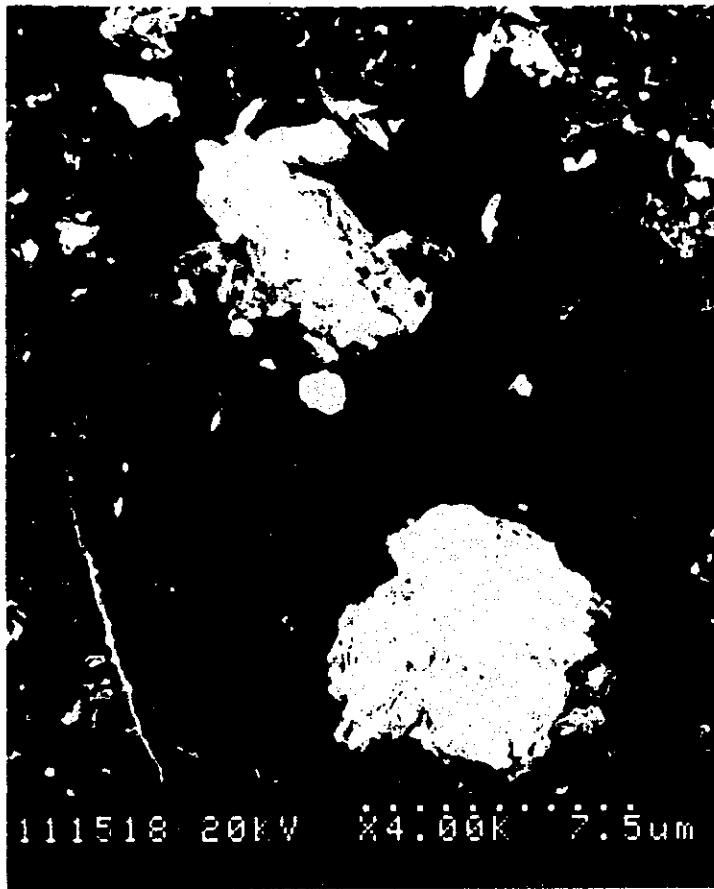


SEM (X 4000)

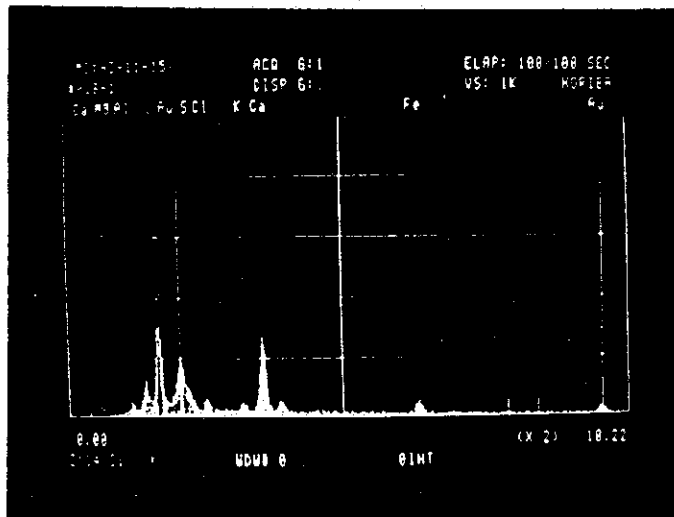


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 11 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (11)

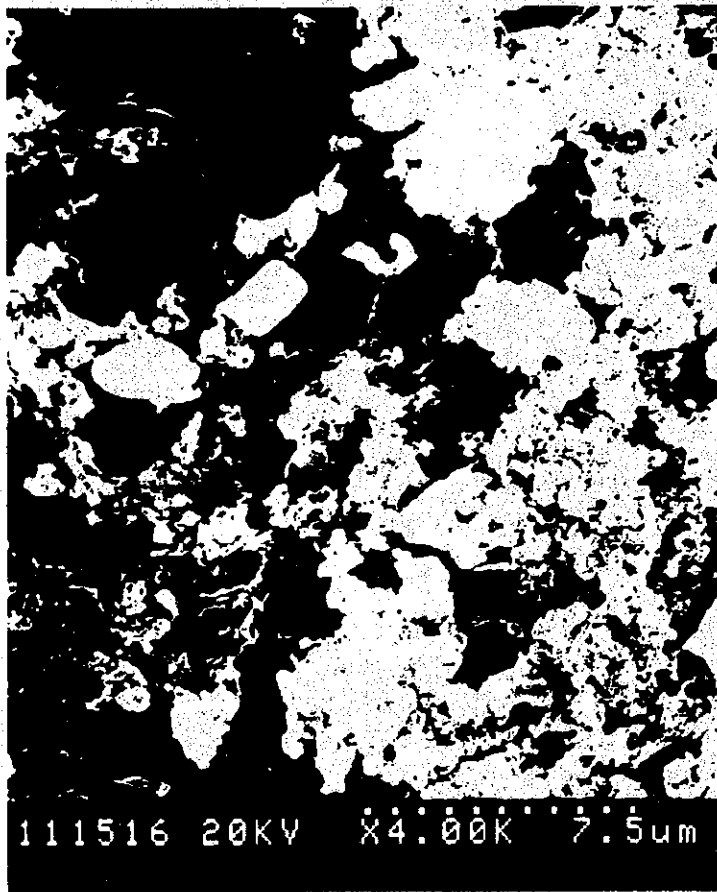


SEM (X. 4000)

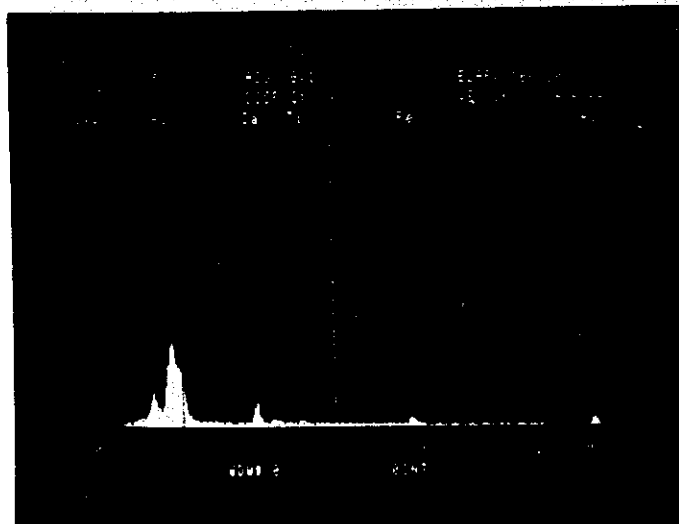


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 12 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (12)

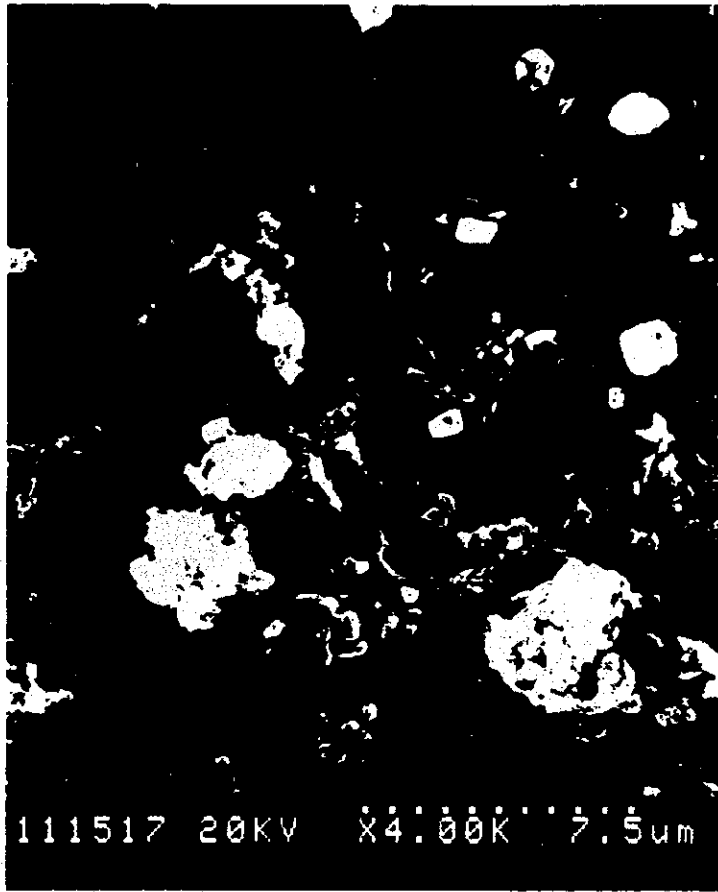


SEM (X 4000)

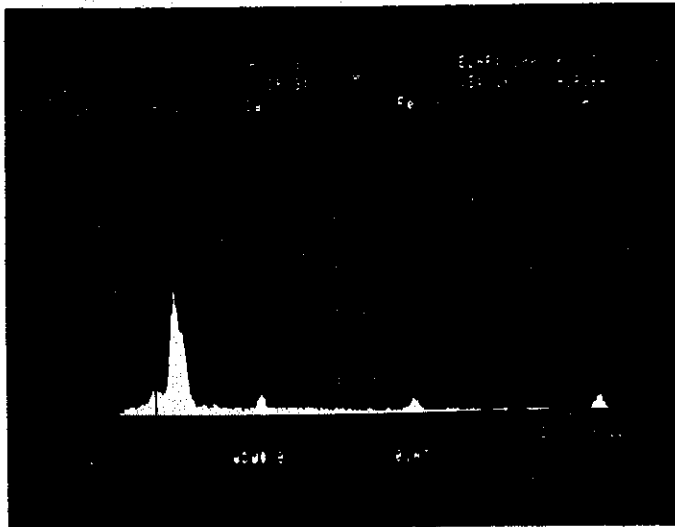


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 10 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (10)

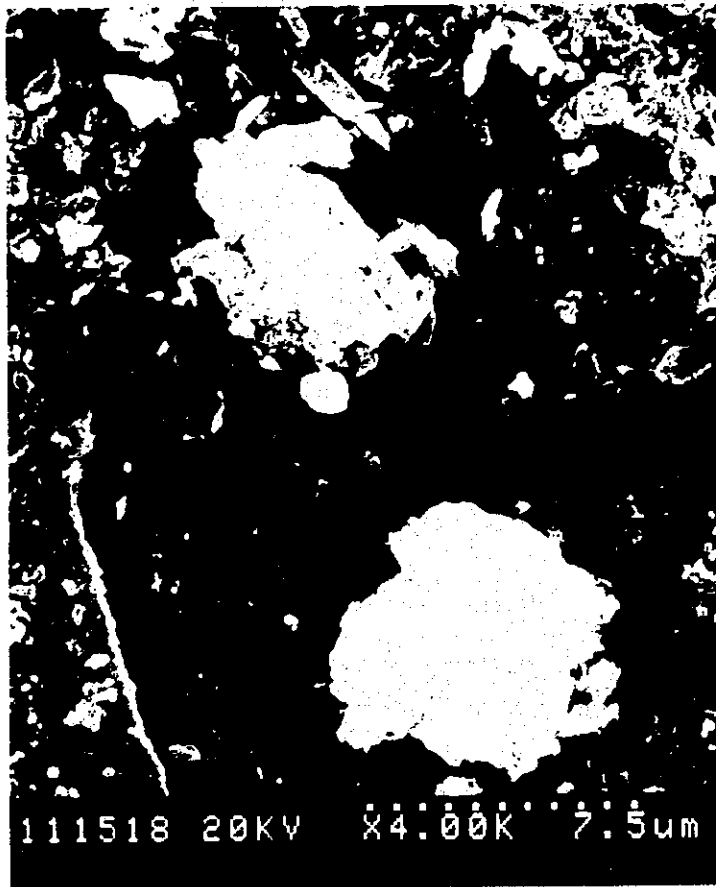


SEM (X 4000)

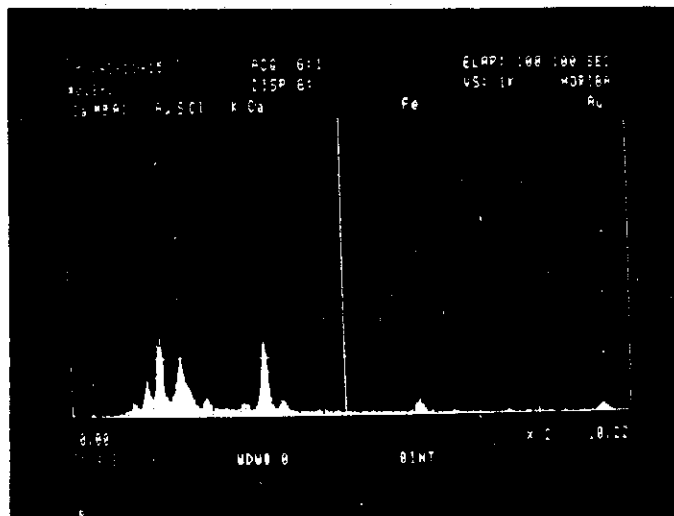


EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 11 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (11)



SEM (X 4000)



EDX SPECTRUM OVER THE ABOVE SCOPE

PHOTO 12 SEM AND EDX OF THE FOULED MEMBRANE SAMPLE (12)

付属資料 7.1.5-1

海水淡水化用前処理ろ過装置の逆洗排水処理実験例

1. はじめに

平成4年11月より1年余りの間、N市において逆浸透法による海水淡水化実験を行い、実施設計の際に必要なと思われる種々のデータを収集した。ここではその一連の実験の内、砂ろ過の逆洗排水の処理に関する実験結果について報告する。

2. 実験装置

全取水量100m³/dの内、2m³/dが逆洗排水として排出される。それを図1に示した逆洗排水処理装置を用いて処理し、運転データを採取した。また、回分試験も並行して実施し、連続試験の結果と合わせて検討した。

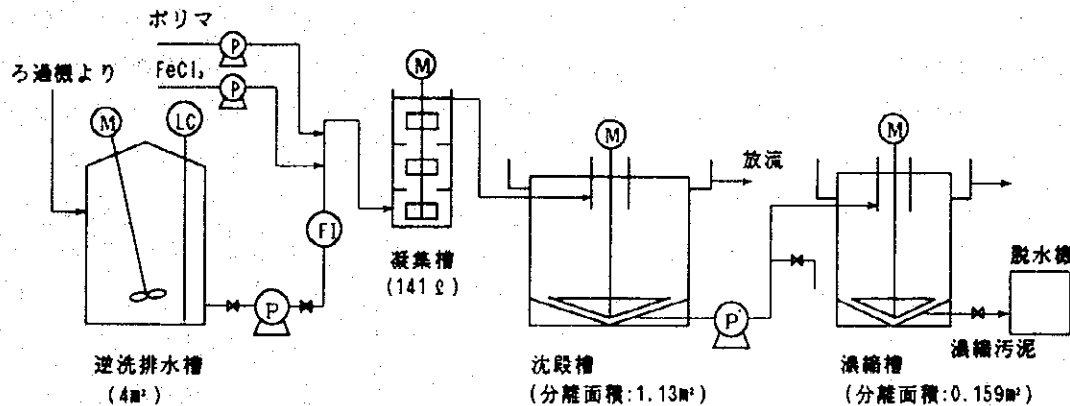


図1 逆洗排水処理装置

3. 実験結果

逆洗排水処理の実験は、春(3月)と夏(7月)の都合2回行った。季節による影響はあまり大きくなかったため、それぞれの代表的結果を以下に示す。

表1 逆洗排水の分析結果

3-1 逆洗排水の性状

逆洗排水は1日に1回排出され、全量逆洗排水槽に貯留される。その性状分析結果を表1に示す。SS濃度、濁度、Fe含有率については、夏の方がやや低い値となっている。

分析項目	測定値 (春)	測定値 (夏)
pH[-]	8.1~8.2	8.1~8.3
TS[g/ℓ]	37.2~37.5	37.8~38.8
SS[mg/ℓ]	290~340	120~340
濁度[度]	140~160	70~150
色度[度]	-	150~400
Fe[mg/ℓ]	78~99	22~64

3-2 逆洗排水処理装置の運転結果

1) 凝集槽、沈殿槽について

ジャーテストにより、あらかじめ最適な凝集剤の種類、組合わせについて検討した。それによると最適な凝集剤はアニオン系の有機高分子凝集剤(ポリマ)であり、それを単独に使用するか、もしくは塩化第2鉄を併用する場合が効果的であったので、それらの薬注条件にて実験を行った。凝集槽での滞留時間を25分、ポリマの注入率を1mg/ℓとしたとき、攪拌速度は15rpm(周速:0.26m/s)のとき最も良い凝集状態が

引用文献

- 1) 小林、日下部、畠山; 逆浸透法による海水淡水化実験(II)

逆洗排水の処理

第45回 全国水道研究発表会(平成6年5月)要旨集

得られたので、以後攪拌速度は15rpmとした。凝集槽の滞留時間を25分とし、薬注条件を種々変化させ回分沈降試験機(104φ×1100H)を用いて沈降試験を行った。その結果より沈殿槽でのSS除去性能について検討した。沈降速度を沈殿槽での上昇流速とし、SS除去率との関係を示したのが図2である。ポリマのみで1mg/ℓ注入したとき最も除去率が高く、塩化第2鉄を併用(10~30mg/ℓ)すると除去率はむしろ低下する傾向となった。上昇流速25mm/minのときと比較すると、ポリマ単独の場合の除去率は95%以上

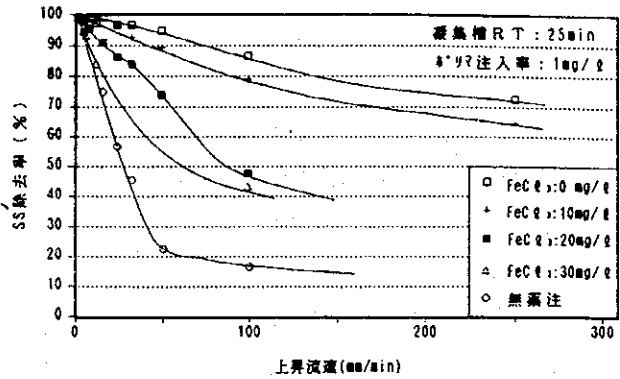


図2 上昇流速と除去率の関係(夏期)

上、塩化第2鉄を併用した場合は71~94%、無薬注の場合が55%であった。表2は実験施設での凝集槽、沈殿槽を使って連続処理したときの結果である。凝集槽での滞留時間を20~33分、沈殿槽での上昇流速を3.8~6.3mm/minまで変化させ薬注処理したときの結果は、沈殿槽溢流水の濁度が3.9~7.4°、SSが6~16mg/ℓであった。これらの値は回分沈降の結果と一致している。

表2 凝集槽、沈殿槽の運転結果(夏期)

2) 濃縮槽について

濃縮槽の実験は、予備タンクでSS濃度をあらかじめ5g/ℓに調整し、それを濃縮槽に連続供給することによって行った。濃縮槽での上昇流速が2.5~7.6mm/minの範囲では、溢流水濁度が4.3~8.1°、SSが4~14mg/ℓであった。回分濃縮試験での24時間濃縮濃度は87~104g/ℓとなり、かなり濃縮性の良い汚泥である

No	凝集槽					沈殿槽					
	濃度 mg/ℓ	流量 ℓ/min	滞留 時間 min	ポリマ 注入率 mg/ℓ	FeCl ₂ 注入率 mg/ℓ	上昇 流速 mm/min	逆流水				
							pH	濁度	SS mg/ℓ	Fe mg/ℓ	
1	336	5.6	25	1.0	0	5.0	7.9	5.6	7	1.3	
2	248	5.8	25	0.5	0	5.0	7.8	6.4	8	1.2	
3	248	5.6	25	1.5	0	5.0	7.9	5.4	6	0.9	29.2
4	194	7.1	20	1.0	0	6.3	7.8	7.4	6	0.9	46.9
5	126	4.3	33	1.0	0	3.8	7.7	3.9	8	2.1	
6	248	5.6	25	1.0	10	5.0	7.8	4.9	8	-	
7	130	5.6	25	1.0	20	5.0	7.6	7.4	16	2.7	
8	130	5.6	25	1.0	30	5.0	7.6	6.0	10	2.3	
9	164	5.6	25	0	0	5.0	8.1	23.2	26	6.4	

ことが判明した。

表3 フィルタープレスによる脱水試験結果(夏期)

3-3 逆洗排水汚泥の脱水試験結果

濃縮槽から排出される汚泥を用いて圧搾付きフィルタープレスの脱水実験を行った。その結果を表3に示す。ろ過時間、圧搾時間をそれぞれ変化させて

No	ろ過圧力 (kgf/cm ²)	ろ過時間 (min)	圧搾圧力 (kgf/cm ²)	圧搾時間 (min)	ケーキ含水率 (%)	ろ過速度 (kg/m ² ・h)
1	4	10	15	20	37.3	6.71
2	4	20	15	20	40.7	7.12
3	4	30	15	20	42.2	5.99
4	4	20	15	10	49.6	7.92
5	4	20	15	30	34.5	4.82

最適脱水条件を追求した。脱水ケーキの含水率を40%とすると、ろ過時間20分、圧搾時間20分にしたときろ過速度が7.1kg/m²・hとなり最大となった。この値は通常の上水汚泥を脱水したときと比べるとかなり大きい。濃縮性の良いことが起因していると考えられる。また、圧搾無しの高時間ろ過の実験も同時に行った。そのときろ過圧力は段階的に上昇させ、3時間後に15kgf/cm²とした後は一定とした。ろ過時間8時間での脱水性能は、ケーキ含水率41.0%、ろ過速度14kg/m²・dであり、圧搾有りの場合とほぼ同じ含水率であった。

4. おわりに

海水淡水化逆洗排水を小型の凝集槽、沈殿槽、濃縮槽を用いて連続処理し、実施設計の際に必要なデータを得た。また、濃縮槽から排出される汚泥の脱水試験を行い、概略の脱水性能を把握した。

付属資料 7.1.5-2

海水淡水化用逆浸透膜装置の最新分析データ

海水淡水化用逆浸透膜装置の最新分析データ

Table 1 水質分析結果 (TOYOBO)

		原海水	供給水	透過水	濃縮水	採水日
Cl ⁻	mg/l	23,800	24,100	65	30,880	
SO ₄ ⁻	mg/l	3,100	3,226	5	4,270	
M-alk	mg/l	132	88	7	118	
Na ⁺	mg/l	13,050	13,230	35	17,650	
K ⁺	mg/l	490	496	1	745	
Ca ⁺⁺	mg/l	496	480	0.4	560	
Mg ⁺⁺	mg/l	1,506	1,482	2.3	1,749	
TDS	mg/l	48,060	46,600	120	63,281	
COD _{Cr2}	mg/l	200	166	ND	114	
Borne	mg/l	3.2	2.9	ND	3.1	
Cu	mg/l	4.0	1.5			
Fe	mg/l	8				
Co	mg/l	0.5	ND			
Cr	mg/l	0.1	ND			
Ni	mg/l	1	ND			
THM	ng/l	0.102	1.539	3.234	1.422	
CHCl ₃	ng/l	0.001	0.007	0.007	0.002	
CHBrCl ₂	ng/l	0.012	0.092	0.207	0.093	
CHBr ₂ Cl	ng/l	0.006	0.116	0.254	0.115	
CHBr ₃	ng/l	0.083	1.325	2.766	1.212	
EC	μS/cm		61,200	248	76,000	

試験日 : 1994年11月19日

モジュール名 : HM 8255FI (中空糸型、東洋紡製)

エレメント数 : 2 エレメント (製造番号#1: #2:)

運転圧力 : 56.0 kg/cm²、 供給水量 : 2.35 m³/h、 回収率 : 22.8 %

供給水 : SDI 3.61

水温 25.5 °C

残留塩素 Nil mg/l

pH 6.5

Table 2 水質分析結果 (NITTO)

	原海水	供給水	透過水	濃縮水	採水日
Cl ⁻ mg/l		23,788	125	27,500	
SO ₄ ⁻² mg/l		3,187	12	3,645	
M-alk mg/l		97	8	111	
Na ⁺ mg/l		13,120	55	15,370	
K ⁺ mg/l		455	3.5	579	
Ca ⁺⁺ mg/l		484	2	520	
Mg ⁺⁺ mg/l		1,533	5.8	1,792	
TDS mg/l		45,980	229	54,432	
COD _{Cr2} mg/l		100	ND	1	
Borne mg/l		3.1	ND	> 3.4	
Cu mg/l		1.4			
Fe mg/l					
Co mg/l		ND			
Cr mg/l		ND			
Ni mg/l		ND			
THM ng/l		0.937	0.172	1.468	
CHCl ₃ ng/l		0.002	0.002	0.001	
CHBrCl ₂ ng/l		0.063	0.044	0.087	
CHBr ₂ Cl ng/l		0.051	0.009	0.086	
CHBr ₃ ng/l		0.821	0.117	1.294	
EC μS/cm		61,000	526	68,000	

試験日 : 1994年12月 4日

モジュール名 : NTR-70SWC-S8 (スパイラル型、日東電工製)

エレメント数 : 1 エレメント (製造番号、リード側#13080155)

運転圧力 : 60.0 kg/cm²、 供給水量 : 3.5 m³/h、 回収率 : 11.4 %

供給水 : SDI 3.54

水温 24.1 °C

残留塩素 0.0 mg/l

pH 6.6

Table 3 水質分析結果 (TORAY)

		原海水	供給水	透過水	濃縮水	採水日
Cl ⁻	mg/l	23,800	23,750	172	29,760	
SO ₄ ⁻	mg/l	3,100	3,260	3.2	4,050	
M-alk	mg/l	132	73	10	95	
Na ⁺	mg/l	13,050	13,128	112	17,240	
K ⁺	mg/l	490	571	7.8	621	
Ca ⁺⁺	mg/l	496	472	0.4	632	
Mg ⁺⁺	mg/l	1,506	1,482	1.5	1,701	
TDS	mg/l	48,060	47,000	380	60,926	
COD _{Cr2}	mg/l	200	110	ND	20	
Borne	mg/l	3.2	2.9	ND	3.0	
Cu	mg/l	4.0	1.7			
Fe	mg/l	8				
Co	mg/l	0.5	ND			
Cr	mg/l	0.1	ND			
Ni	mg/l	1	ND			
THM	ng/l	0.102	1.147	0.437	1.154	
CHCl ₃	ng/l	0.001	0.002	0.002	0.002	
CHBrCl ₂	ng/l	0.012	0.098	0.120	0.082	
CHBr ₂ Cl	ng/l	0.006	0.113	0.038	0.101	
CHBr ₃	ng/l	0.083	0.934	0.277	0.969	
EC	μS/cm		61,300	665	76,700	

試験日 : 1994年11月19日

ND=Not detected

モジュール名 : SU-820 (スパイラル型、東レ製)

エレメント数 : 2 エレメント (製造番号、リト側#1:40250213, #2:40250256)

運転圧力 : 56.0 kg/cm²、供給水量 : 2.8 m³/h、回収率 : 21.8 %

供給水 : SDI 3.61

水温 25.5 °C

残留塩素 0.0 mg/l

pH 6.5

付属資料 7.2.3-1

逆浸透膜前処理用精密ろ過膜の適用状況

Literature Survey

The pre-filtration of the RO desalination process with MF and UF membranes is a possible method for pretreatment of oil-polluted seawater, and small-scale experiments on this process are now being carried out in Japan.

On the other hand, various equipment with separation membranes are already in practical use for the treatment of water supply and wastewater.

The results achieved with these devices can be used as reference for evaluating the practicality, on the basis of performance and cost, of separation membrane equipment. It was for that purpose that we investigated the practical use of MF and UF membranes for pretreatment in RO systems.

Also, in the desalination treatment of seawater, the effects of trihalomethane pose a problem when the product water is used for drinking, so investigations were carried out on the current methods used in Japan to suppress the generation of trihalomethane.

In addition, since the disposal of sludge created by pretreatment filtration equipment in reverse osmosis seawater desalination systems was a problem, we investigated the measures that were available to counteract this problem.

We report herewith the results of our investigations of the above three subjects.

I. Treatment of water supply and Waste Water with MF and UF Membranes

1. Application of MF Membranes to the Treatment of Water Supplies

The Ministry of Health and Welfare started the Membrane Aqua Century 21 Project (MAC-21 Project), an advanced water treatment project involving membrane separations to establish counter-measures to the contamination of drinking water.

Various local governments, including more than seven cities such as Yokosuka, Kobe and Nagoya, are running independent proving trials with similar membrane separation.

The background to this is the increasing demand from the people for palatable drinking water and the fact that the benefits of membrane separation are recognized by many people.

Membrane treatment systems have the following advantages over conventional systems for treating water by flocculation, sedimentation and filtration:

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The background to this is the increasing demand from the people for palatable drinking water and the fact that the benefits of membrane separation are recognized by many people.

Membrane treatment systems have the following advantages over conventional systems for treating water by flocculation, sedimentation and filtration:

- (1) Easy operation. Completely closed system with no need to add flocculent means less pollution at the water purification plant. Can be automated and unmanned.
- (2) Reduced area of installation. Can be prefabricated, occupies less space.
- (3) Reduced chlorination. Simultaneous clarification and removal of bacteria allows reduced chlorination.
- (4) Reduced sludge treatment. Less added chemicals means less sludge production.
- (5) Reduced operating costs. It was said to be more expensive but dead end filtration with microfiltration membrane operating at 1kg/cm^2 is said to be less expensive.
- (6) Shorter construction time.

In Japan there are more than 12,000 water works (although 80% of them are small-scale systems operated by 0.5 worker per installation) and there is a demand for labor-saving water treatment technology such as membrane separation. Also, the fact that many existing water purification plants are nearly 50 years old and needing replacement is a factor in the desire for membrane systems.

In order to introduce the membrane system into water purification, I believe progress will only be made after the safety and reliability of membrane technology has been proved and clear solutions to the following problems have been found.

- (1) Membrane life. Chemical cleaning methods for membrane surface contamination and membrane deterioration with time are still being studied/developed.
- (2) Membrane cost.
- (3) Emergency back-up technology.

In a conventional water purification system, the feed water flows into a receiving sump and several hours are required for it to reach the clean water pond. When the feed water is contaminated, time and distance can be varied accordingly, but with a membrane system it will be necessary to develop a method of detecting minute leaks.

Japan is currently conducting pilot plant tests for technical confirmation of these points. Some current areas of Japanese research and development are:

- (1) Submerged separation membrane system.
- (2) Energy-saving vacuum leg system of membrane filtration.
- (3) Ceramic membrane.
- (4) Rotary type system with circular plate membrane.

The following is detailed technical information on membrane plants for the treatment of drinking water in Japan.

3.1 MAC-21 (A National Project)

As mentioned previously, MAC-21 is a project which has been sponsored by the Ministry of Health and Welfare. The proving trials of Step 1 have been completed and presently the proving trails to improve water quality with nanofiltration membranes, etc., which constitute the Step 2 experiments are about to begin.

I summarize the results of Step 1 by quoting from the paper of Dr Kunikane, which is a comprehensive summation of the results³.

(1) Outline of the Project

Sponsor: Department of Water Supply and Environmental Sanitation, Ministry of Health and Welfare (MHW), Japan.

Research period: FY 1991-1993

Research initiative: Institute of Public Health, MHW

Participants in demonstration experiment: 18 companies in collaboration with the Water Purification Association.

Mode of operation: Three six-monthly periods of continuous operation of the Project's plant with different methods using microfiltration or ultrafiltration.

Experimental facility: Kita-Chiba Regional Water Supply Authority, located in Matsudo City, Chiba Prefecture.

Source of experimental feed water: Edo River

Flow diagram of the experimental facility: Fig. 3

Capacity of each plant: $30\text{m}^3/\text{d}$

Classification of plants in 1st and 2nd runs: Table 1

(2) Summary of Results

Net water production (filtrate less membrane cleaning water):

Fig. 4

Net water flux: 0.27 to $1.93\text{ m}^3/\text{m}^2/\text{d}$ for microfiltration, 0.39 to $1.80\text{ m}^3/\text{m}^2/\text{d}$ for ultrafiltration as a mean of the six months' operation.

Water recovery for all membrane plants: 80% to more than 99%

Rejection of contaminants: Table 2

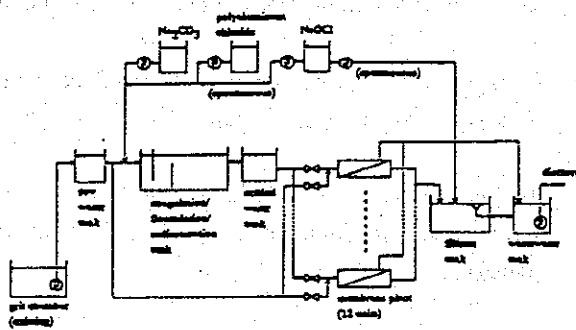


Figure 3. Schematic flow diagram of the experimental facility

The following shows some technical information on membrane plants for the treatment of drinking water in Japan.

1.1 MAC-21 (A National Project)¹⁾

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using microfiltration or ultrafiltration

Experimental facility: Kita-Chiba Regional Water Supply Authority,
located in Matsudo City, Chiba Prefecture

Source of experimental feed water: Edo River

Flow diagram of the experimental facility: Fig. 1

Capacity of each plant: 30 m³/d

Classification of plants in 1st and 2nd runs: Table 1

2) Summary of Results

Net water production (filtrate less membrane cleaning water): Fig. 2

Net water flux: 0.27 to 1.93 m³/m²/d for microfiltration, 0.39 to 1.80 m³/m²/d
for ultrafiltration as a mean of the six months' operation

Water recovery for all membrane plants: 80% to more than 99%

Rejection of contaminants: Table 2

There was no significant difference in membrane filtrate quality between MF and UF membranes. Coliform removal was excellent, that is, no coliforms were found in any of the 100 ml filtrate samples taken weekly throughout the operation period from nine of the membrane plants in the first run and ten plants in the second run.

Fig. 3 shows estimated energy consumption based on the experimental data, assuming that a real plant with a capacity of 1,000 m³/d would be constructed.

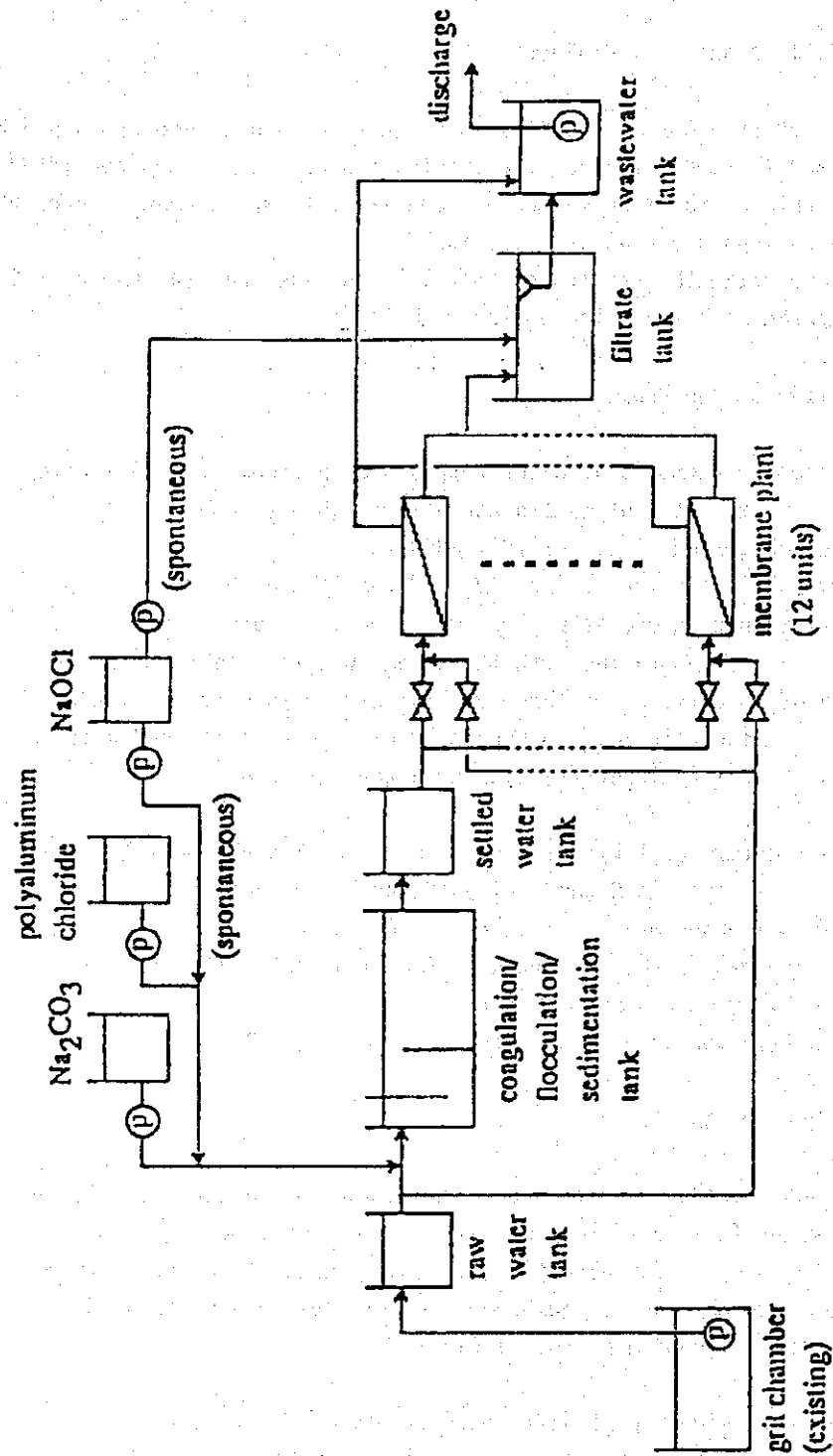
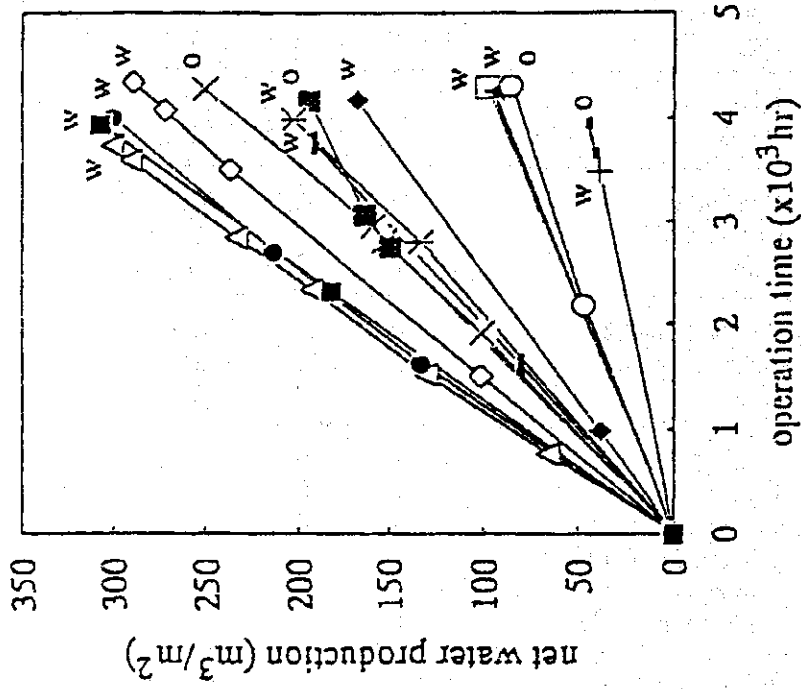


Fig. 1 Schematic flow diagram of the experimental facility

Table 1 Classification of the twenty-four membrane plants used in the first and second runs of the experiment

Classification		first	second	total	
Module	Kind	MF(0.01-0.4 μ m)	9	5	14
		UF(1.3 $\times 10^4$ -2 $\times 10^6$ Dalton)	3	7	10
	Material	Organic	10	10	20
		Inorganic	2	2	4
	Type	Hollow fiber	10	9	19
		Tube	1	1	2
		Multitube	1	1	2
		Bag	0	1	1
	Skin	Inside	5	7	12
		Outside	7	5	12
Operation method	Flow type	Crossflow	5	8	13
		Deadend	5	4	9
		Both	2	0	2
	Flow control	Constant flow rate	10	11	21
		Constant pressure	1	1	2
		Both	1	0	1
	Pretreatment	None	2	0	2
		None or common	1	0	1
		Individual	8	10	18
		Individual or common	0	1	1
		Common	0	1	1
		Common+individual	1	0	1
	Others	Housing-pressure	10	10	20
		Tank-pressure	0	1	1
		Tank-suction	2	1	3

Note) In the "pretreatment", chlorination is not taken into account; "common" pretreatment means coagulation and sedimentation by the common pretreatment facility; "individual" pretreatment means the one in each membrane plant; six cases of pretreatment by coagulation with polyaluminum chloride in each run of the experiment are included in the account of "individual" pretreatment.

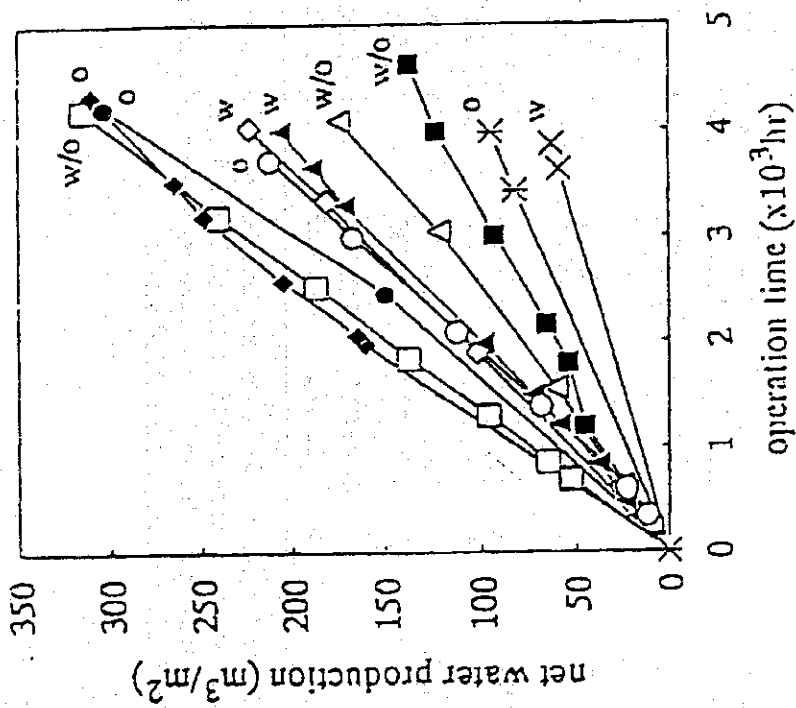


(a) MF membrane

Fig. 2 Net water production per unit surface area of membrane

Plots denote chemical cleaning in six months' operation;

"w"—with polyaluminum chloride and "o"—without polyaluminum chloride.



(b) UF membrane

Fig. 2 Net water production per unit surface area of membrane

Plots denote chemical cleaning in six months' operation;

"w"—with polyaluminum chloride and "o"—without polyaluminum chloride.

Table 2 The result of contaminant rejection on physical and chemical parameters in the first and second runs of the experiment

Parameter	Run	Raw water	Clarified water	Membrane filtrate
Turbidity (unit)	1	16.1 (100)	1.60 (9.9)	0.01 - 0.17 (0.1 - 1.1)
	2	15.8 (100)	1.14 (7.2)	0.00 - 0.02 (0.0 - 0.1)
Color (unit)	1	10 (100)	4 (40)	1.6 - 4 (16 - 40)
	2	11 (100)	4 (33)	3 - 4 (25 - 32)
Permanganate value (mg/L)	1	7.3 (100)	2.8 (38)	1.7 - 2.8 (23 - 42)
	2	7.7 (100)	2.8 (36)	1.4 - 3.1 (16 - 41)
E260, 50mm (-)	1	0.174 (100)	0.134 (77)	0.1 - 0.172 (59 - 96)
	2	0.161 (100)	0.117 (73)	0.074 - 0.150 (46 - 93)
Ammonia nitrogen (mg/L)	1	0.06 (100)	0.05 (83)	0.01 - 0.06 (16 - 100)
	2	0.22 (100)	0.22 (100)	0.09 - 0.30 (42 - 92)
Total manganese (mg/L)	1	0.049 (100)	0.020 (48)	<0.005 - 0.016 (0 - 32)
	2	0.054 (100)	0.029 (54)	<0.005 - 0.024 (0 - 49)
Total iron (mg/L)	1	0.83 (100)	0.03 (4)	<0.01 - 0.01 (0 - 2)
	2	0.94 (100)	0.09 (10)	0.00 - 0.01 (0 - 1)
Aluminum (mg/L)	1	1.10 (100)	0.34 (31)	0.01 - 0.09 (1 - 8)
	2	0.91 (100)	0.33 (37)	0.00 - 0.05 (0 - 5)
THMFP (mg/L)	1	0.046 (100)	0.027 (59)	0.021 - 0.036 (45 - 78)
	2	0.045 (100)	0.024 (53)	0.017 - 0.045 (34 - 100)

Note) "Clarified water" means the water after coagulation using polyaluminum chloride and sedimentation by the common pretreatment facility. The figures in the column of "membrane filtrate" show the range of mean values obtained in the twelve membrane plants. The figure in parentheses is residual per cent.

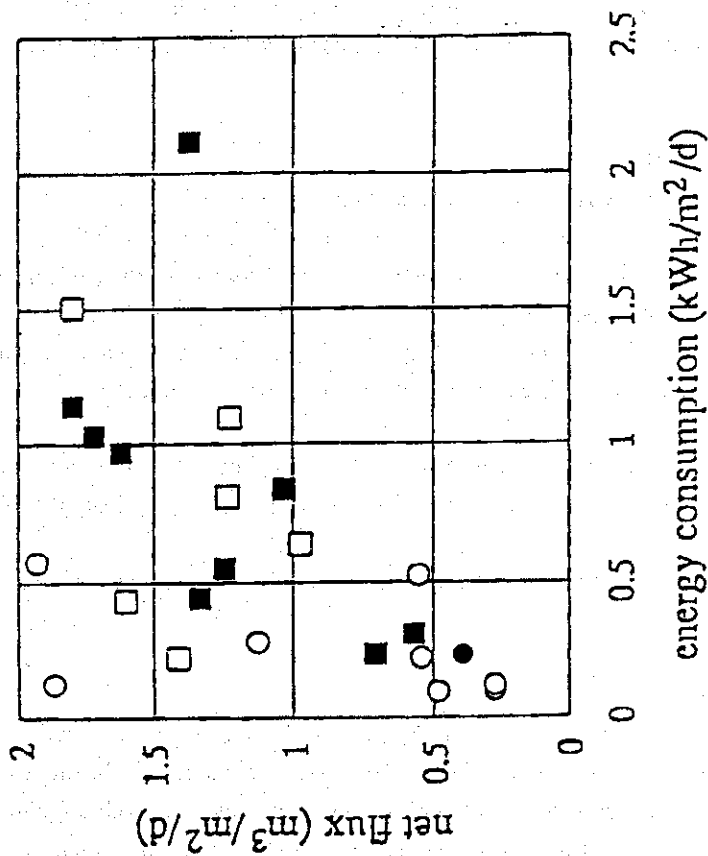


Figure 3 Relationship between energy consumption per unit surface area of membrane and net flux

Symbols: white--MF membrane and black--UF membrane;
square--crossflow and circle--deadend.

It is clear that dead end filtration was more efficient than cross-flow filtration and no difference in energy consumption could be detected between MF and UF membranes.

1.2 Technical aspects of membrane performance in the treatment of drinking water

(1) Selection of membrane type

Before deciding on a system, feed water quality should be evaluated in order to select the optimum type of membrane.

Flocculation followed by microfiltration is effective for removing organic substances and it is clear that flocculation contributes to reduced clogging of the MF membrane by foulants.

Ultrafiltration is suitable for filtering raw feed which is low inorganic substances such as well water. In the future, nanofiltration will be available for improving water quality.

(2) Selection of flow mode pattern

Two types of flow modes are available for membrane systems.

Cross flow mode is usually applied to prevent membrane fouling but it requires higher energy to maintain a high velocity over the membrane. Dead endflow mode is an option which requires less energy.

With the dead end flow mode, there is a high tendency for suspended solids to accumulate on the membrane and frequent back-washing is necessary to remove the suspended solids.

Pilot plant test results show that for tertiary treatment of sewage by membrane separation, with a back-wash cycle every 15 minutes, energy consumption is less than 0.5 kwh per cubic meter of product.

Flow mode selection must be determined by the design of a system to suit the water quality.

(3) The role of flocculation

Eventhough flocculation generates more sludge, it will remove dissolved organic matter and discoloration which are difficult to remove with a membrane system. In any case, it is clear that membrane separation systems have a high potential for improving the quality of drinking water and have a very promising future.

2. Application of Membrane Separations to the Treatment of Waste Water

2.1 Advanced treatment of sewage

More than 9.8 billion cubic meter of sewage is treated annually in Japan and it is expected to become a valuable resource.

With the stringent supply and demand for water, treated sewage is gradually becoming more widely recognized as a convenient, constantly available water resource which is beginning

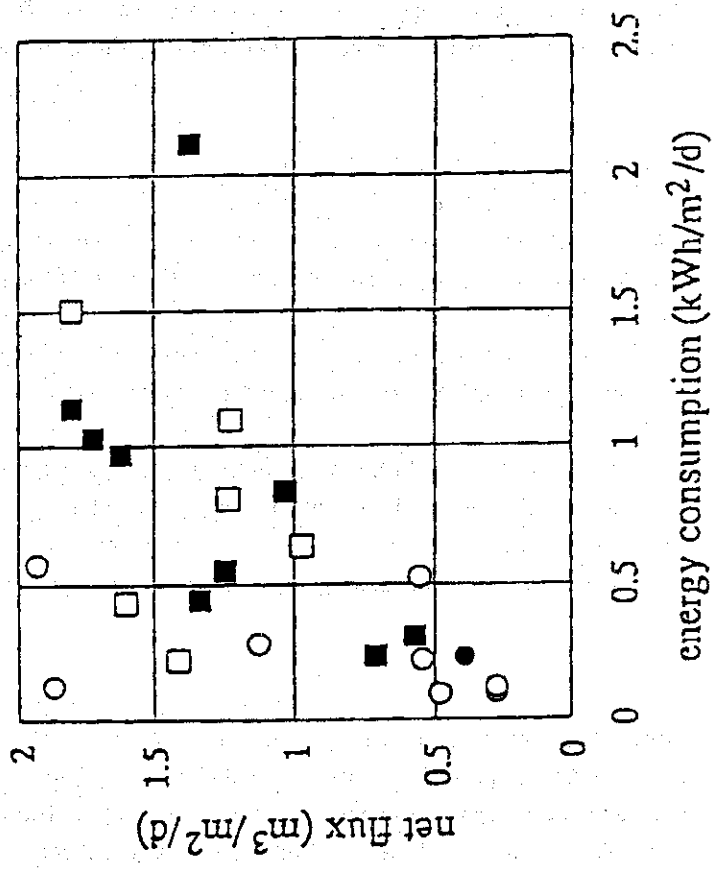


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to be reused in a variety of applications.

Here I shall introduce some composite MF membrane and RO membrane systems as one of the advanced treatment of sewage.

2.1.1 The Tokyo Metropolitan Government's Ochiai Waste Water Treatment²⁾

(A sewage waste water reclamation plant for scenic and recreational purposes)

(1) Summary of facilities

Plant site : The Tokyo Metropolitan Government's Ochiai Waste Water Treatment Facility

Commencement of operations: April 1993

Feed water : Sand filtered sewage waste water

Treatment method: MF membrane and RO membrane

Plant capacity : 50 m³/d

Usage of treated water: To feed the source of a brooklet and a fountain at the main entrance to the treatment facility

MF membrane specifications

Type: Hollow fiber Membrane pore diameter: 0.2 micron

Applied pressure : 1.0 to 1.5 kgf/cm²

External pressure mode, Cross-flow

Membrane area : 30 m²

Membrane cleaning: Automatic backwash with compressed air each 15 minutes and semi-monthly chemical cleaning

RO membrane specifications

Type: Spiral wound type

Applied pressure : 15 to 20 kgf/cm²

Membrane area : 84 m²

Membrane cleaning: Bi-monthly chemical cleaning

System flow diagram: Fig. 4

(2) Treatment capacity

Both quantity and quality are in accord with design capacity.

Water quality : Table 3

This plant is easily operated. Maintenance involves daily inspections and membrane cleaning several times monthly.

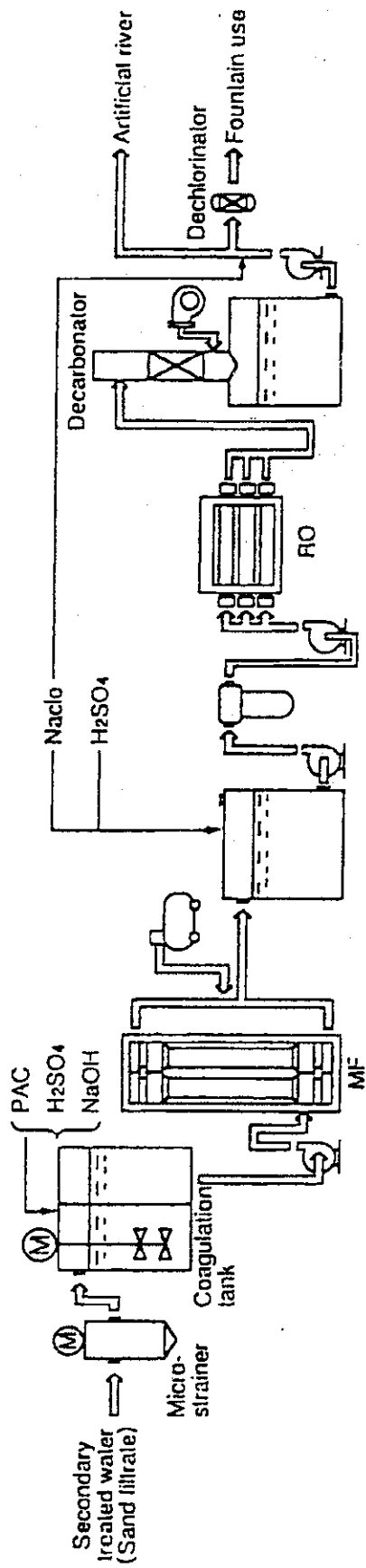


Figure 4 Flow-diagram of membrane separation plant.