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THE AUTHOR

Gilbert F. Froment received his Ph.D. at the State University in Gent, Belgium, and became a member of the Faculty there in 1961, after postdoctoral work at the Technische Hochschule Darmstadt, Germany, and the University of Wisconsin. He was appointed Full Professor and Director of the Petrochemical Engineering Laboratory in 1968. A frequent visitor to the United States, he taught as a Visiting Professor at Yale University in 1969 and at the University of Houston in 1973.

Extensive industrial consulting in kinetics and reactor design of both catalytic processes and olefins production by thermal cracking has oriented his research towards the application of fundamental principles to problems of practical importance.

When he is not working or traveling, he is fervently hunting, horseback riding or playing soccer . . . . with really old veterans.

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Membrane Ultrafiltration of a Nonionic Surfactant and Inorganic Salts from Complex Aqueous Suspensions: Design for Water Reuse

Complex aqueous suspensions containing a nonionic surfactant, phosphates, silicate, hypochlorite, oil, and kaolinite particulates are subjected to continuous flow membrane ultrafiltration with noncellulosic membranes. The ultrafiltrate water flux and the rejections by the Millipore PSAL membrane of total organic carbon, surfactant, and total phosphate are related by stepwise, multiple linear regression analysis (logarithmic model) to transmembrane pressure difference, thin channel velocity, membrane resistance, and feed solution concentration. The variables are adjusted to eliminate gel polarization and to minimize concentration polarization.

The data are extended, by the development and use of a computer simulation scale-up procedure, to a 1 000 cm^3/s (23 000 gal/day) laundry waste treatment and water recovery unit. The procedure considers banks of modules in series, banks in parallel, and a parallel-series-tapered arrangement. Membrane area requirements per unit ultrafiltrate water flux and solute rejections are predicted for water recoveries up to 95% of the inlet flow rate.

DIBAKAR BHATTACHARYYA,
K. A. GARRISON,
A. B. JUMAWAN, JR. and
R. B. GRIEVES

Department of Chemical Engineering
University of Kentucky
Lexington, Kentucky 40506

SCOPE

Membrane ultrafiltration has been used successfully as an effective process for the treatment of a large number of industrial wastes. The process is appropriate for applications requiring water recycle and reuse and particularly for systems in which the very high rejection of low-molecular-weight solutes is not warranted. Ultrafiltration is a pressure-activated process and is generally carried out at low pressures of 10^5 to 10^6 N/m^2. The use of ultrafiltration for the separation of low-molecular-weight ionic solutes with charged membranes (Bhattacharyya et al., 1974*a*), modest-molecular-weight (size) organic solutes (Grieves et al., 1973; Bhattacharyya et al., 1974*b*), and organic macromolecules and colloids (Porter and Nelsen, 1972) has been reported in the literature. Some of the water reuse applications involving ultrafiltration include electrodeposition primers (Goldsmith et al., 1970), oil-water separation in metal cutting operations (Goldsmith, 1974), and the renovation of sewage effluents (Witmer, 1974). Porter and Nelsen (1972) have reviewed applications of ultrafiltration in the chemical, food processing, and pharmaceutical industries. High-pressure membrane processes such as reverse osmosis and hyperfiltration with dynamic membranes have also been utilized in many water reuse and solute recovery systems (Okey, 1972; Rozelle et al., 1973; Brandon et al., 1972).

Excellent discussions and mathematical formulations of the ultrafiltration process, including considerable detail on concentration polarization, have been presented by Michaels et al. (1971), Porter (1972) and de Filippi and Goldsmith (1970). The concentration polarization caused by a nonionic surfactant during ultrafiltration has been discussed by Grieves et al. (1973).

The treatment of commercial laundry wastes by membrane processes for the purpose of water reuse is a very promising application. The use of reverse osmosis (Koenst et al., 1973) and ultrafiltration (Bhattacharyya et al., 1974*b*) for the treatment of laundry wastes containing anionic surfactants has been reported in the literature. The present study primarily involves complex aqueous suspensions containing nonionic surfactants. The objectives of this investigation are the establishment of operating conditions to minimize concentration polarization and membrane fouling, the achievement of adequate rejections of selected solutes, and the development of a unique scale-up procedure involving membrane module arrangements to obtain the high water recovery essential in waste treatment. From the experimental data obtained at very low water recovery, predictive design equations, relating ultrafiltrate flux and the concentration of selected constituents in the ultrafiltrate stream to the key independent variables, are generated by multiple linear regression analysis. These equations are used to estimate membrane area requirements for laundry waste treatment and ultrafiltrate water quality at water recoveries ranging up to 95% of the inlet feed rate.

CONCLUSIONS AND SIGNIFICANCE

The feasibility of membrane ultrafiltration is established to obtain adequate solute rejection and high water recovery for complex aqueous suspensions containing a nonionic surfactant; inorganic salts including hypochlorite, polyphosphates, and silicates; oil; and clay particulates. Most of the experiments were conducted in a continuous flow, thin channel unit, containing Millipore PSAL noncellulosic membranes. Experiments were carried out over a broad range of channel Reynolds numbers (4 800 to 36 000), of average transmembrane pressure differences (1.4×10^5 to 6.9×10^5 N/m^2), and of concentrations of the simulated waste constituents (tenfold). The extreme flux decline due to gel polarization could be consistently avoided by maintaining the channel velocity above the threshold value of 400 cm/s ($Re = 9\,600$) for transmembrane pressure differences between 2.8×10^5 and 6.0×10^5 N/m^2.

Empirical equations were developed to enable the prediction of the effect of the independent variables on the ultrafiltrate water flux and on the concentrations of the key solutes in the ultrafiltrate. Above the threshold channel velocity, the water flux and the concentrations in the ultrafiltrate of total organic carbon, surfactant, and phosphate were related to the average transmembrane pressure difference, the average channel velocity, the bulk stream solute(s) concentration, and the membrane resistance by stepwise, multiple linear regression analysis, by using a logarithmic model, with multiple regression coefficients of the order 0.7 to 0.8.

Limited data were also obtained with a commercially available, tubular module (UOP 225) containing 1.3 cm I.D. tubes. Higher flux drops and lower solute rejections were observed, compared to the Millipore PSAL membranes in the thin channel unit.

A detailed procedure was developed for scale-up of the thin channel unit to obtain the membrane area required and resultant solute(s) rejections for any specified water recovery. The computer simulation considered three module arrangements: banks of modules in series, a single bank of parallel modules, and a tapered arrangement of banks of modules in series with each bank containing the same or a fewer number of parallel modules than the preceding bank. The tapered configuration, because of the more limited recycle requirement, consistently required the least membrane area and provided the highest solute(s) rejections at high water recoveries.

For a synthetic laundry waste containing 186 mg/l of total organic carbon (58 mg/l from the nonionic surfactant), 100 mg/l of phosphate, and oil, clay, bleach, etc., at an inlet flow rate of 1 000 cm^3/s (23 000 gal./day) and utilizing a PSAL membrane of resistance 2.8×10^8 N/m^2/cm/s, 90% water recovery and greater than 90% rejections of total organic carbon, surfactant, and phosphate could be achieved with an average ultrafiltrate flux of 1.5×10^{-3} cm^3/cm^2 s (30.5 gal./ft.^{2} day), at a channel Reynolds number of 14 000 and average transmembrane pressure difference of 5.6×10^5 N/m^2 (5.4 atm.).

The approach using empirical equations developed from laboratory scale data at very low water recoveries together with the computer simulation for multiple configurations at high water recoveries can be extended to any waste treatment and water reuse system involving ultrafiltration. The tapered arrangement should consistently be the optimum.

EXPERIMENT

A schematic diagram of the experimental unit is shown in Figure 1. The ultrafiltration cell was constructed of clear Lucite and the feed channel (high pressure side) height, width, and length were 0.152, 1.28, and 40.0 cm, respectively. The effective membrane area was 51.2 cm^2. All experiments were conducted until steady state was reached; this generally required from 6 to 10 hr., and in a few experiments the ultrafiltration time was extended to 30 hr. At the termination of each run, the membrane was thoroughly flushed with tap water at high flow rate and low pressure.

The inlet stream temperature was maintained at 24 ± 1°C. The flow regime was always in the turbulent region, and the channel velocity U was varied between 170 cm/s ($Re = 4\,800$) and 1 300 cm/s ($Re = 36\,000$). The transmembrane pressure difference Δp, defined as $p_{\text{inlet}} - 0.5\ \Delta p_{\text{loss}}$, ranged between 1.3×10^5 and 6.9×10^5 N/m^2. The pressure loss (Δp_{loss}) in the channel due to friction and due to entrance and exit effects was proportional to $U^{2.0}$.

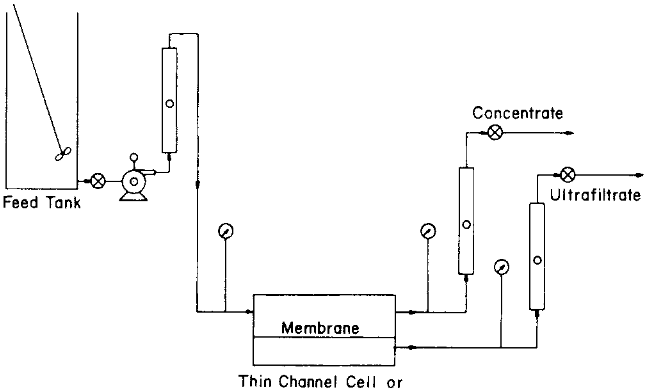

Fig. 1. Schematic diagram of experimental apparatus.

Synthetic Laundry Wastes

The composition of a normal feed solution (designated as $1x$) used in the ultrafiltration experiments was

	Concentration, mg/l	Organic carbon concentration, mg/l
Surfactant (nonionic)	100	58
CMC	5	2
Vegetable oil	200	124
Ca^{2+} ($CaCl_2 \cdot 2H_2O$)	50	—
P ($Na_5P_3O_{10}$)	100	—
SiO_3^{2-} ($Na_2SiO_3 \cdot 9H_2O$)	100	—
Bleach (NaOCl-5% solution)	10	—
Clay (kaolinite; 0.2 μm)	100	—

The surfactant used in this study was a linear, C_{12}-C_{15}, primary alcohol ethoxylate (Neodol 25-9, Shell Chemical Co.) containing nine moles of ethylene oxide. Neodol 25-9, of molecular weight 603, was 100% active. These laundry waste constituents at these concentrations are typical of commercial laundry wastes. Type I military detergents contain nonionic surfactants similar to Neodol 25-9. The tap water used to prepare the feed solutions was of conductivity approximately 240 μmho/cm, contained a calcium concentration between 20 and 35 mg/l, and contained organic carbon ranging from 2 to 5 mg/l. All experiments were conducted between pH 8.0 and 8.5. The concentration of total organic carbon (C_i, mg/l) in a normal ($1x$) feed solution was 186 mg/l.

The concentrations of total organic carbon, phosphate, and total dissolved solids in the inlet stream and in the ultrafiltrate were monitored. Organic carbon (total carbon—inorganic carbon) concentrations were measured by a Beckman, Model 915 carbon analyzer, and the reproducibility of the carbon analysis was ± 5% of full scale. In a few experiments, the ultrafiltrate surfactant concentration was measured by the molybdophosphoric acid colorimetric method and by the sodium tetraphenylborate titration method (Nadeau and Siggia, 1967), and it was shown that the organic carbon concentration of the ultrafiltrate was primarily surfactant ($<$ 2 mg/l was nonsurfactant organic carbon). Phosphate (expressed as mg/l P) concentrations were measured by the vanadomolybdophosphoric acid colorimetric method after acid hydrolysis (Anon., 1971). Calcium concentrations were measured by the EDTA titrimetric method, and total dissolved solids were determined after evaporation at 104°C (Anon., 1971).

Membranes

The membranes used in this study were tight, noncellulosic type, commercially available ultrafiltration membranes. Most of the experiments were carried out with negatively charged Millipore PSAL (noncellulosic skin on cellulosic backing) membranes. These membranes were obtained in sheet form. The recommended maximum operating pressure and temperature of the PSAL membrane is 9.0×10^5 N/m^2 and 35°C. A few preliminary experiments were also conducted with the recently developed, UOP 225, tubular minimodule (Universal Oil Products) containing 980 cm^2 of membrane area.

WATER FLUX AND SOLUTE REJECTION

Water transport through charged and uncharged ultrafiltration membranes follows a viscous flow mechanism. The ultrafiltrate water flux J_w in the absence of concentration polarization can be related to the effective transmembrane pressure difference:

$$J_w = \frac{\Delta p}{K\mu} = \frac{\Delta p}{R_m} \tag{1}$$

The water flux-temperature dependence, and thus the variation of R_m with temperature, can be completely accounted for by the variation of the viscosity of water with temperature (Grieves et al., 1973). The phenomenon of concentration polarization, and particularly gel polarization (water flux invariant with Δp), is a major process limitation on ultrafiltration units. For many waste streams containing macromolecules, surfactant micelles, and particulates, the observed J_w is considerably lower than the J_w obtained [Equation (1)] with solute free water, and thus it is necessary to generate an equation relating J_w to the independent variables C, Δp, R_m, and U (or Re).

For single solute systems of known diffusivity, the film theory model has been used for evaluating concentration polarization (Porter, 1972; Blatt et al., 1970). The following relation at steady state operation has been derived by several investigators:

$$J_w = K_s \ln \frac{C_w}{C} \tag{2}$$

According to Derzansky and Gill (1974), at high Reynolds numbers the Deissler analogy for K_s is most appropriate:

$$\begin{aligned} J_w &= 0.023 \frac{D}{d} Re^{0.88} Sc^{0.25} \ln \frac{C_w}{C} \\ &= 0.023 \frac{U^{0.88} D^{0.75}}{d^{0.12} \nu^{0.63}} \ln \frac{C_w}{C} \end{aligned} \tag{3}$$

In the pre gel (transition) region, because C_w/C and D (for mixed solute systems) are not known, only the relative effects of U and d at constant C_w/C can be predicted from the above equation. In the gel polarization region, C_w becomes constant (no longer a function of U), and

$$J_w \alpha \frac{U^{0.88}}{d^{0.12}} \text{ or } \frac{Re^{0.88}}{d} \tag{4}$$

The validity of Equation (4), in terms of J_w variation with U, has been demonstrated in turbulent flow for most macromolecular systems. In the present study with laundry wastes, because all experiments were performed in a channel of constant hydraulic diameter d, the velocity-flux relation, at a fixed C_w/C, could be evaluated at other channel heights by using Equations (3) and (4).

The parameter which determines the ultrafiltrate water quality is the rejection (R):

$$R = 1 - \frac{C_f}{C} \tag{5}$$

Solute rejection by a membrane is due to a combination of several factors, such as simple sieving action, differences in diffusion rates through membrane pores, Van der Waals' forces, the Donnan exclusion of ionic solutes for charged membranes, and the effect of concentration polarization. Because theoretical equations cannot be derived to predict solute(s) concentration in the ultrafiltrate from multisolute industrial wastes, the effects of the variables Δp, R_m, U, and C on C_f must be determined experimentally.

RESULTS AND DISCUSSION

Ultrafiltration with PSAL Membranes

Membranes from different batches supplied by the manufacturer had to be utilized. The membrane resistance (R_m) varied from 1.1×10^8 to 4.1×10^8 N/m^2/cm/s. Some of the low R_m values were produced by membrane swelling due to deliberate operation at adverse conditions. The average representative membrane supplied by the manufacturer yielded $R_m = 2.8 \times 10^8$ N/m^2/cm/s.

By using the ninety-three continuous flow, steady state experiments, the water flux J_w can be correlated with C,

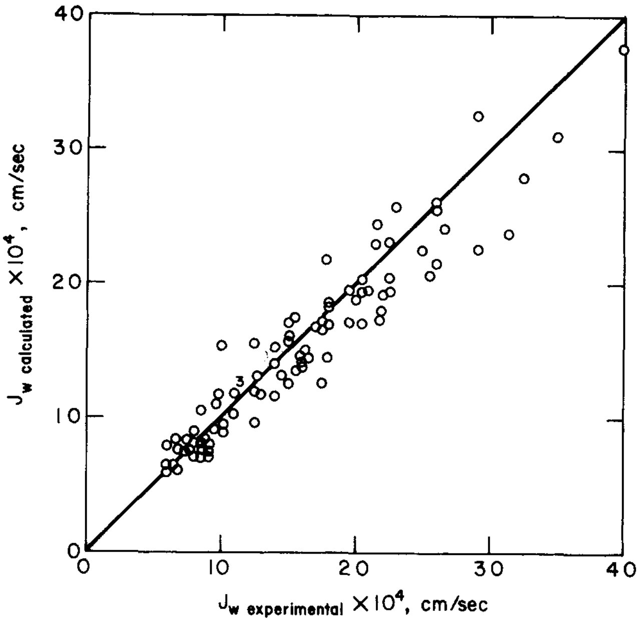

Fig. 2. Values of J_w calculated with Equation (6) vs. experimental values.

Δp, R_m, and U by stepwise, multiple linear regression analysis, utilizing a logarithmic model:

$$J_w = 0.083\,\frac{\Delta p^{0.81}\,U^{0.44}}{C^{0.04}\,R_m^{0.89}} \qquad (6)$$

The multiple regression coefficient, defined as

$$\frac{\Sigma(J_{w\ \text{calculated}} - J_{w\ \text{mean}})^2}{\Sigma\ (J_{w\ \text{experimental}} - J_{w\ \text{mean}})^2}$$

was 0.80. The average percent deviation, defined as

$$\Sigma\,\frac{100\ |\,J_{w\ \text{experimental}} - J_{w\ \text{calculated}}\,|}{J_{w\ \text{experimental}}}/\text{no. of points}$$

was 12.9%. Figure 2 presents values of J_w calculated from Equation (6) vs. experimental values. The increase in J_w with increase in Δp and U and with decrease in C and R_m is to be expected. The power on U would have been higher than 0.44 only if all experiments were carried out in the gel polarization region [Equation (4)]. Witmer (1974), in his ultrafiltration studies with sewage effluents, found J_w to be proportional to U to the 0.5 power. The high power of 0.8 on Δp indicates that in the range U = 427 to 1 000 cm/s, gel formation was not a limiting factor.

The experimental values and calculated lines [Equation (6)] showing the effects of Δp and R_m on J_w at two extreme concentrations (1 x and 10 x) are presented in Figure 3. At $\Delta p = 5.5 \times 10^5$ N/m² and for a concentrated feed solution (C_i = 2 000 mg/l), the flux drop (compared to $C_i = 0$) was about 38% at the lower channel velocity. The approximate linear increase of J_w with $1/R_m$ is shown in Figure 3 (top) for a relatively dilute feed solution C_i = 186 mg/l (1 x). Even for the dilute solutions, some concentration polarization was observed; and similar behavior was also noted at other feed concentrations. Data for a PSAL membrane with a thicker backing are also shown for comparison.

Figure 4 shows the effect of the channel velocity U on J_w for the cases of a large transmembrane pressure difference (high initial water flux) and 10 x feed solution concentration, and for a moderate Δp and 1 x feed solution concentration. In both cases, an extensive flux decline occurred below a critical threshold velocity. The critical threshold velocity increased substantially at the very high Δp of 6.9 × 10⁵. For all concentration ranges and Δp between 2.8 × 10⁵ and 5.6 × 10⁵, operation at $U \geqq 400$ cm/s prevented an excessive flux drop. Below the threshold velocity, the power dependence on U was 0.8 or higher and agreed reasonably well with the gel polarization model. Because actual ultrafiltration operation should not be conducted below the critical threshold velocity, limited data

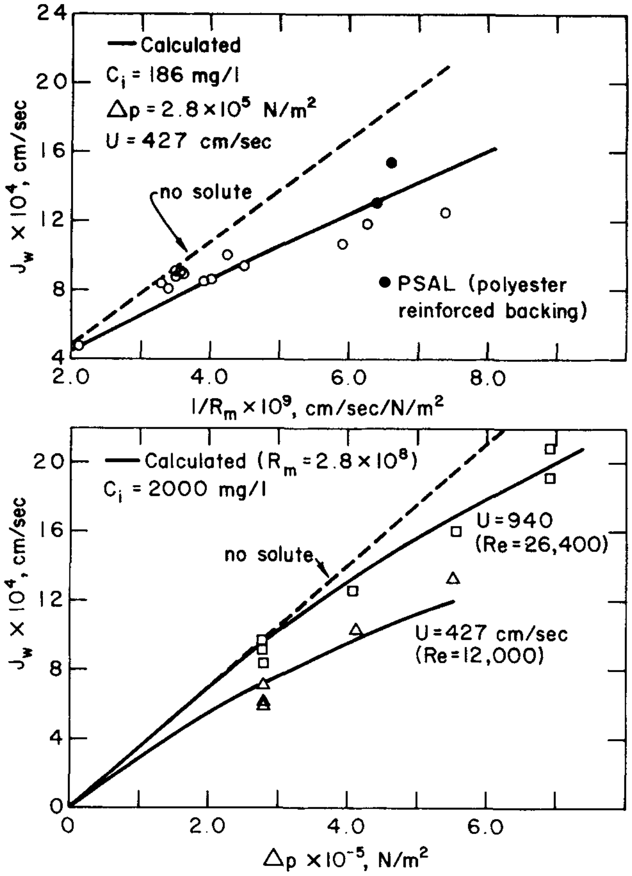

Fig. 3. Calculated [Equation (6)] and experimental values of water flux vs. transmembrane pressure difference and vs. reciprocal of membane resistance.

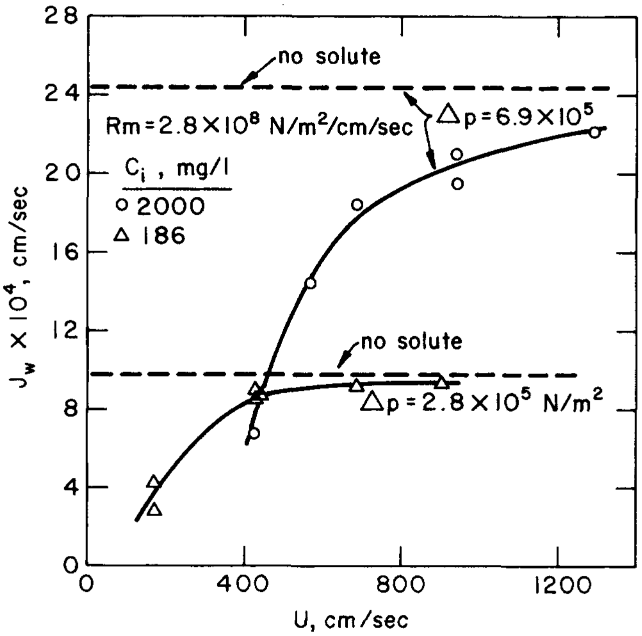

Fig. 4. Effects of average channel velocity on water flux.

TABLE 1. REJECTION CHARACTERISTICS OF LAUNDRY WASTES

$\Delta p = 2.8 \times 10^5$ N/m², $R_m = 2.8 \times 10^8$ N/m²/cm/s

Feed concentration, C_i, mg/l	Rejection					
	Organic carbon	Surfactant	Phosphate	Total dissolved solids	Conductivity	Calcium
186	0.98	0.98	0.98	0.72	0.51	0.95
186	0.97	0.94	0.98	—	0.50	0.95
186	0.97	0.95	0.97	—	0.50	—
2,230	0.99+	0.98	0.96	0.80	0.57	0.99+
2,230	0.99+	0.97	0.95	0.81	0.54	—
2,230	0.99+	0.98	0.95	—	0.46	—
3,532	0.99+	0.98+	0.89	—	0.20	—

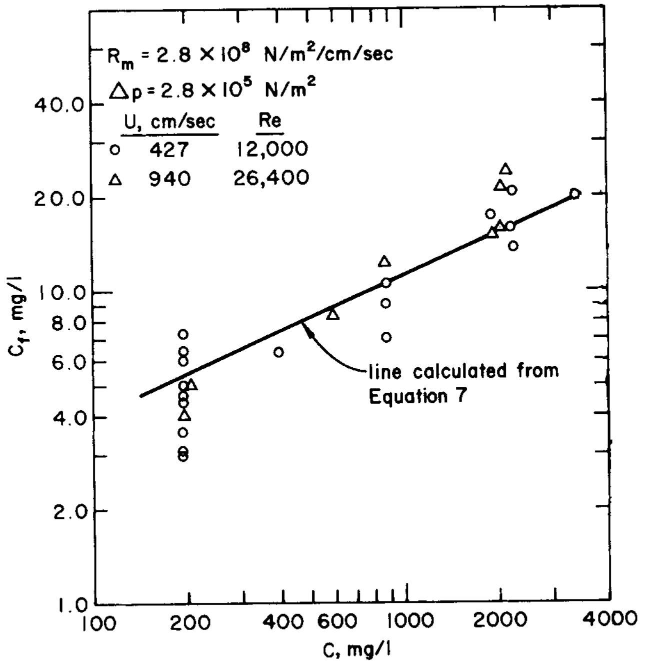

Fig. 5. Calculated and experimental [Equation (7)] relation between organic carbon concentration in ultrafiltrate stream and inlet stream for an average PSAL membrane.

were taken in this range. The existence of a critical threshold velocity for other waste treatment systems has been verified by Witmer (1974) and by Thomas and Mixon (1972). A flux drop of 30% or less is considered reasonable in most membrane operations.

The concentrations of total organic carbon (C_f) and total phosphate (P_f) in the ultrafiltrate stream were correlated with the respective bulk solute concentrations (C and P), Δp, and R_m. The regression eliminated U as being a variable of significance. This could be predicted because the species that were primarily built up in the polarized layer at the membrane surface were oil, particulates, and some surfactant micelles; the rejections of these species were always unity (1.0). The resultant regression equations are

$$C_f = 9.3 \times 10^8 \, (C)^{0.45} \, (\Delta p)^{-0.21} \, (R_m)^{-0.96} \qquad (7)$$

$$P_f = 1.8 \times 10^8 \, (P)^{1.2} \, (\Delta p)^{-0.14} \, (R_m)^{-1.1} \qquad (8)$$

For Equations (7) and (8), the multiple regression coefficients were 0.68 and 0.82, and the average percent deviations were 30.7 and 39.5. For membrane studies with complex wastes, errors in ultrafiltrate concentration correlations in the range 30 to 40% are not unexpected, particularly because many experiments result in very low values of the dependent variables.

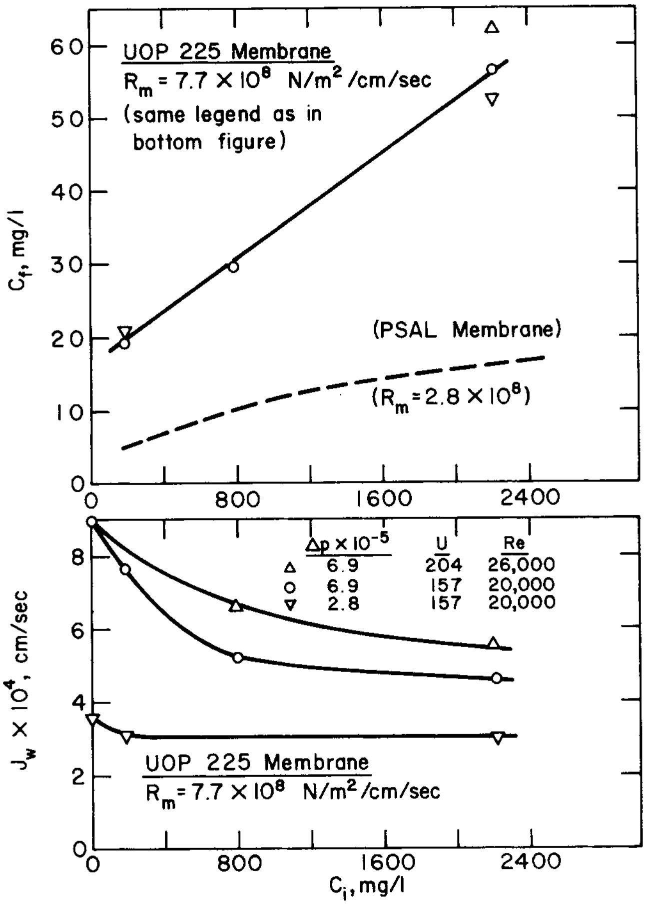

Fig. 6. Dependence of water flux and ultrafiltrate organic carbon concentration on inlet stream concentration, with UOP 225 minimodule.

Experimental values of C_f vs. C for an average membrane at $\Delta p = 2.8 \times 10^5$ N/m² and at two channel velocities are shown in Figure 5. One experimental point at a very high (20 x) feed solution concentration is included and shows excellent agreement with the line calculated from Equation (7).

As a summary of the rejection behavior of a typical membrane, Table 1 indicates rejections for three feed solution concentrations. The high rejection of calcium was due primarily to the presence of calcium-polyphosphate complex ionic species. The rejection of the kaolinite clay particulates was always 1.0.

Ultrafiltration with UOP 225 Tubular Module

A short series of ultrafiltration experiments was performed with a tubular module (1.27 cm I.D. tubes) supplied by Universal Oil Products. The UOP 225 membrane was also noncellulosic. According to the manufacturer, the module could be operated at a maximum operating pressure and temperature of 14×10^5 N/m² and 50°C, respectively. Results in terms of J_w and C_f are presented in Figure 6. In terms of J_w at $C_i = 0$, the UOP membrane performance at $\Delta p = 6.9 \times 10^5$ N/m² was comparable to the PSAL performance at $\Delta p = 2.8 \times 10^5$ N/m². At $C_i =$ 2 200 mg/l ($\approx$ 10 x concentration), at $\Delta p = 6.9 \times 10^5$ N/m², and at $U = 204$ cm/s, the drop in J_w was 39% compared to only an 8% drop with the thin channel system and the PSAL membrane (Figure 3). This trend agrees with the effect of hydraulic diameter d as shown in Equation (3). At $U = 157$ cm/s, the flux drop was 49%, and gel polarization was probably controlling. At $\Delta p =$ 2.8×10^5 N/m², although the flux drop was small (< 13%), the practical usefulness would be limited because of the low J_w.

The UOP 225 also performed considerably worse with respect to C_f, compared to the PSAL (Figure 6, top). At $C_i = 186$ mg/l, the rejections of surfactant, phosphate, TDS, and conductivity by the UOP membrane were 0.73, 0.67, 0.30, and 0.18, respectively, and a comparison with Table 1 shows generally poorer solute(s) rejection.

Scale-up Procedure: Computer Simulation Results

The membrane ultrafiltration unit design for any water reuse system depends on the fractional water recovery r required, which in turn depends on the requisite degree of solute(s) separation and on concentrate disposal requirements. The fractional water recovery, defined as the total ultrafiltrate flow rate per unit inlet flow rate, can be increased by means of multiple membrane module arrangements in series, in parallel, or in series-parallel (tapered) combinations. For ultrafiltration to be a feasible waste treatment method, fractional recoveries of the order of 0.8 to 0.9^+ must be achieved.

The design of a membrane ultrafiltration unit for a multicomponent waste system in terms of the objectives mentioned above has not been reported in the literature. The estimation of membrane area and solute separability for solutions containing surfactant only has been reported by Grieves et al. (1973). The optimization of reverse osmosis system design, involving low-molecular-weight solutes (particularly desalination), has been given considerable attention (McCutchan and Goel, 1974; Murkes and Bohman, 1972).

In the present study, a generalized computer program for the case of a module of arbitrary membrane area A, hydraulic diameter of the channel (or tube) d, and cross-sectional area A_x, was developed. For numerical calculations it was necessary to divide the length of the module into small sections (inner stages) N, each containing membrane area A/N. The inner stages were assumed to be connected in series, and because the water recovery in each of these stages was small, the desired precision by an iterative method was obtained. Recursive equations were derived to simulate the actual conditions at the end of each inner stage and at the end of each module. For the computation of J_w, C_f, and P_f, average values of Δp, C, P, and U in each inner stage were utilized in the empirical Equations (6), (7), and (8).

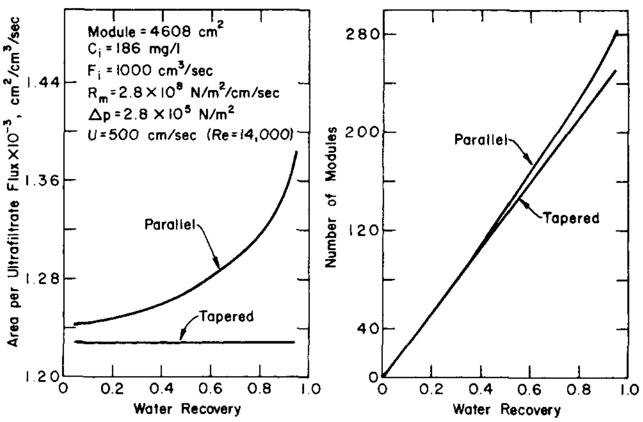

Fig. 7. Predicted membrane area per unit ultrafiltrate flow rate and number of modules required to obtain specified water recoveries for parallel and tapered operation.

Inlet conditions of $F_i = 1\,000$ cm³/s, $C_i = 186$ mg/l, $S_i = 58$ mg/l, and $P_i = 100$ mg/l (composition shown in experimental section table) were assumed for the calculations. The ranges of operating conditions were: $400 \leqq U \leqq 900$, $2.5 \times 10^5 \leqq \Delta p \leqq 6.0 \times 10^5$, $1.4 \times 10^8 \leqq R_m \leqq 3.0 \times 10^8$, and the constraints were $J_{w\,\max} = \Delta p / R_m$ and $r =$ 0.95. The selected membrane module parameters were A $= 4\,608$ cm² ($\approx$ 5 ft.²) $N = 90$, and $d = 0.27$ cm. The module area is typical of a production unit, and N and d were selected primarily on the basis of the experimental channel used in this study. As long as N is large enough to produce insignificant water recovery in each inner stage, the results obtained will be independent of N. For values of d greater than 0.27, and to maintain the same C_w/C and thus J_w, proportionately higher U must be used as shown in Equation (3). The solute rejection (for example, in terms of total organic carbon) is defined as follows:

$$\text{Solute rejection} = 1 - \frac{C_{f\,\text{avg}}}{C_i} \tag{9}$$

$$C_{f\,\text{avg}} = \frac{\sum_{1}^{n} J_{wn}\, A\, C_{fn}}{F_i\, r} \tag{10}$$

Results of membrane area requirements and solute rejection at $\Delta p = 2.8 \times 10^5$ N/m² and $U \approx 500$ cm/s ($Re =$ 14 000) for parallel and tapered (series-parallel) module arrangements are shown in Figures 7 to 9. The performance of modules in series (with no tapering) operation, not shown, was consistently in between those of the other two arrangements. The membrane area requirements (with average $R_m = 2.8 \times 10^8$) for parallel (one bank of parallel modules) and for tapered (multiple banks in series with each bank consisting of the same or a fewer number of modules in parallel) arrangements are shown in Figure 7, both in terms of the number of modules required and in terms of the area required per unit ultrafiltrate flow rate.

The computer program was written to maintain the channel velocity (or Reynolds number) to within a narrow range. For parallel operation, as the number of modules was increased, recirculation of a fraction of the concentrate stream would have to be employed in order to maintain the proper U. Because the average bulk concentration in the modules would be higher with recirculation, Figure 7 (left, note the expanded scale) shows that the area per unit ultrafiltrate increased at higher recoveries because of concentration polarization. With the tapered arrangement, the velocity could be maintained as the water recovery increased by increasing the number of banks in series and by decreasing the number of modules in parallel in each bank, and thus recycle would only be necessary at very high recovery when the number of modules in the final bank reached one. The invariance of membrane area per unit ultrafiltrate flow rate for tapered operation in Figure 7, or the linear increase of the number of modules, signifies constant total membrane flux per unit area as additional modules were added to increase the recovery r.

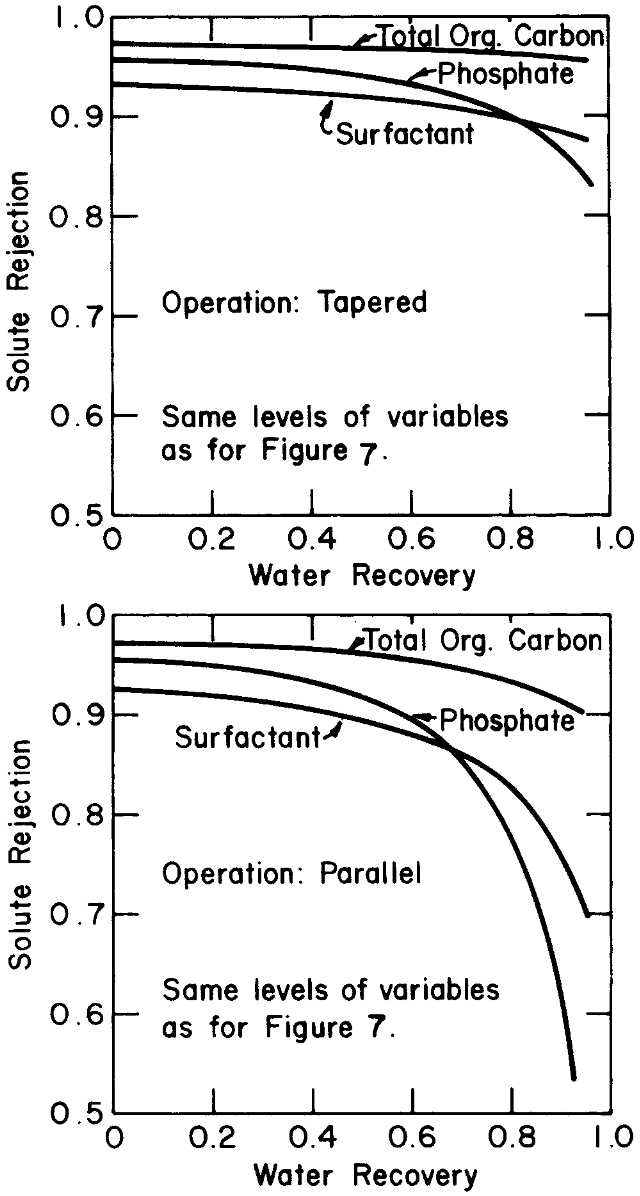

Fig. 8. Predicted rejections of total organic carbon, phosphate, and surfactant for specified water recoveries for parallel and tapered operation.

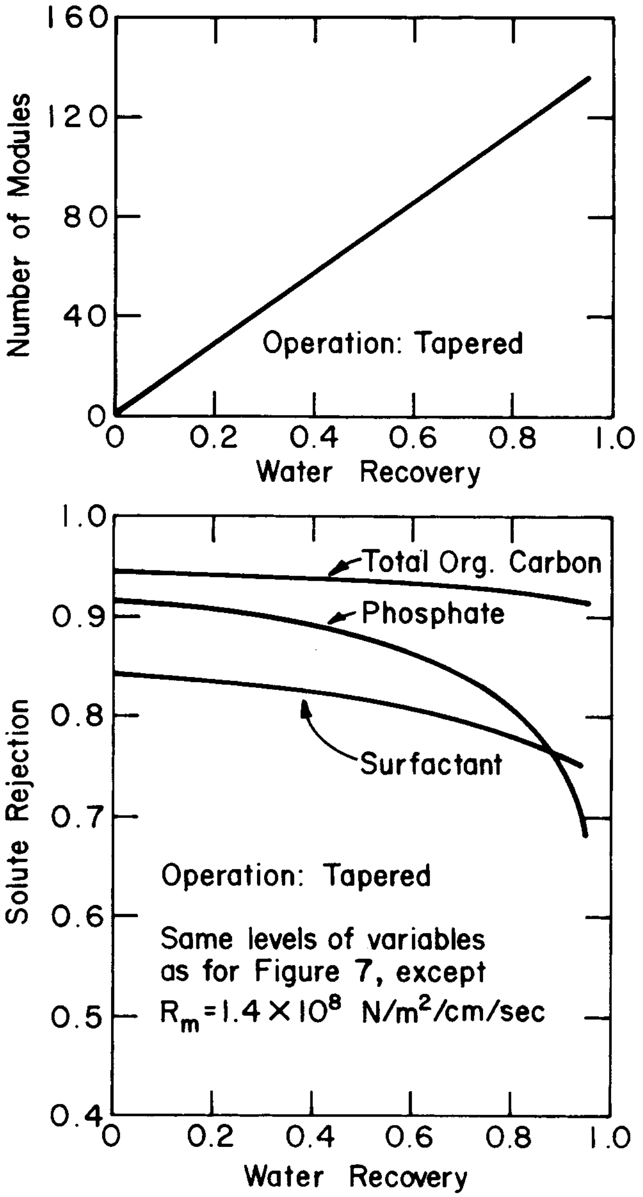

Fig. 9. Predicted number of modules required and rejections of total organic carbon, phosphate, and surfactant for specified water recoveries for tapered operation with comparatively open membranes (R_m = 1.4 × 10^8 N/m^2/cm/s).

The solute separation in terms of total organic carbon, phosphate, and surfactant are shown in Figure 8. In this case, the surfactant concentration in the ultrafiltrate stream was also included, because at high water recoveries, although the rejection of total organic carbon (which includes both oil and surfactant) might still be relatively high, the rejection of the surfactant itself might fall off. An equation for S_f, similar to Equations (7) and (8) and generated from the experimental data, was used in the computations. With the tapered arrangement, the rejection was always greater than with the parallel arrangement. In the case of the latter, the sharp drop in both surfactant and phosphate rejections above a water recovery of 0.7 was primarily due to the increase in S and P produced by recirculation. The solute removal trends were similar for operation at higher pressures.

Figure 9 shows the number of modules required and the solute rejection obtained with a comparatively open membrane (low $R_m = 1.4 \times 10^8$). The number of modules required for a specified water recovery was, of course, significantly lower than in the case of $R_m = 2.8 \times 10^8$. With the parallel arrangement (not shown), the solute removal dropped sharply. For example, to obtain 80% rejection of all solutes (carbon, phosphate, surfactant), only 40% water recovery could be obtained with parallel operation, but with the tapered mode, about 80% water recovery would be feasible.

Table 2 summarizes some of the results that may be achieved with PSAL membranes ($R_m = 2.8 \times 10^8$) at $\Delta p = 2.8 \times 10^5$ N/m^2 (2.7 atm.) and at $\Delta p = 5.6 \times 10^5$ N/m^2. Solute rejection and module requirements are tabulated for high recoveries. J_w^D is the water flux at $C_i = 0$ (no solute). The membrane area required for a specified water recovery was, of course, lower at higher Δp as long as the gel polarization region was avoided. At the high Δp, 90% water recovery could be achieved with only 56% of the number of modules required at $\Delta p = 2.8 \times 10^5$ N/m^2. The higher Δp also gave somewhat better solute rejection; note the negative power on Δp in Equations (7) and (8). Table 2 shows improved solute separation and module requirements with the tapered mode in all cases. For parallel operation, a high recycle ratio α (defined as the flow rate

Table 2. Module Operation

$Re \approx 14{,}000$, Single module area $= 4.6 \times 10^3$ cm^2 (≈ 5 ft.^{2}),
$F_i = 1{,}000$ cm^3/s (23,000 gal./day)

Mode	$\Delta p \times 10^{-5}$, N/m^2	$J_w^D \times 10^4$, cm/s	$r = 0.8$					$r = 0.9$				
			α	N_T	R_c	R_s	R_p	α	N_T	R_c	R_s	R_p
Tapered	2.8	9.8 (20.5 gal./ft.^{2}/day)	0	212	0.96	0.90	0.91	0	238	0.96	0.88	0.87
Parallel	2.8	9.8	22	228	0.94	0.82	0.78	25	262	0.92	0.76	0.62
Tapered	5.6	19.6 (41.0 gal./ft.^{2}/day)	0	121	0.97	0.91	0.92	0	134	0.97	0.90	0.89
Parallel	5.6	19.6	12	129	0.95	0.86	0.81	14	149	0.94	0.81	0.67

of the recirculated stream divided by the inlet flow rate) of 12 to 25 would be required to maintain the proper U. Recycling would also be necessary for banks of modules in series operation.

As a summary of the unit process that could be realized for a typical laundry waste at an inlet flow rate of 1 000 cm^3/s, 90% water recovery and more than 90% removal of organic carbon, surfactant, and phosphate could be achieved with 6.2×10^5 cm^2 (670 ft.^{2}) of membrane area with operation at $\Delta p = 5.6 \times 10^5$ N/m^2 (5.4 atm.), $U \approx 500$ cm/s ($Re = 14\,000$), and by utilizing the tapered mode. At these conditions, and assuming a 2 yr. membrane life, the membrane replacement cost ($20.00/ft.^{2} membrane area) per 1 000 gal. of product water would be equal to $0.89.

At this high velocity, the pumping cost would be quite significant. The pressure loss would depend on the type of commercial module which is used; assuming a 4.1×10^5 N/m^2 pressure drop in each module, the overall pumping cost per 1 000 gal. of water would be $1.20. Because the pressure loss is proportional to $U^{2.0}$, the optimum operation must be a compromise between pumping costs and membrane replacement costs.

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NOTATION

A = membrane area of a module, cm^2

A_x = cross-sectional area of a module, cm^2

C = average concentration of organic carbon in channel on high pressure side, $(C_i + C_o)/2$, mg/l

C_f = concentration of organic carbon in ultrafiltrate stream, mg/l

$C_{f\,\mathrm{avg}}$ = average concentration of organic carbon in ultrafiltrate stream [Equation (10)], mg/l

C_{fn} = concentration of organic carbon in ultrafiltrate from the n^{th} module, mg/l

C_i = concentration of organic carbon in inlet stream, mg/l

C_o = concentration of organic carbon in concentrate steam (effluent from high pressure side), mg/l

d = hydraulic diameter of channel, cm

D = solute diffusivity, cm^2/s

F_i = flow rate of inlet stream, cm^3/s

J_w = water (ultrafiltrate) flux, cm^3/(s cm^2 membrane area)

J_{wn} = water (ultrafiltrate) flux from n^{th} module, cm^3/(s cm^2 membrane area)

J_w^D = ultrafiltrate flux in solute free system, cm^3/(s cm^2 membrane area)

K_s = mass transfer coefficient, cm/s

N = number of inner stages in a module

N_T = total number of modules

Δp = average transmembrane pressure difference, N/m^2

P = average phosphate concentration in channel on high pressure side, mg P/l

P_f = concentration of phosphate in ultrafiltrate stream, mg P/l

P_i = concentration of phosphate in inlet stream, mg P/l

r = fractional water recovery (total ultrafiltrate flow rate per unit inlet flow rate)

R = solute rejection

R_c = removal (rejection) of organic carbon, Equation (9)

R_m = resistance of ultrafiltration membrane to water flux, N/m^2/cm/s

R_p = removal (rejection) of phosphate

R_s = removal (rejection) of surfactant

S = average surfactant concentration in channel on high pressure side, mg carbon/l

S_f = concentration of surfactant in ultrafiltrate stream, mg carbon/l

S_i = concentration of surfactant in inlet stream, mg carbon/l

U = average channel velocity, $(U_i + U_o)/2$, cm/s

U_i = velocity of inlet stream, cm/s

U_o = velocity of concentrate stream, cm/s

α = recycle ratio (flow rate of recirculated stream divided by the inlet rate)

μ = viscosity of water, N m/s^2

ν = kinematic viscosity of water, cm^2/s

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Thermal Cracking of Propane and Propane-Propylene Mixtures: Pilot Plant Versus Industrial Data

The product distribution and kinetics of the thermal cracking of propane and propane-propylene mixtures were investigated for a temperature range of 700° to 850°C, exit total pressures from 1.2 to 2 atm. absolute, and steam dilutions of 0.4 and 1.0. The reaction kinetics were determined by two methods. The first uses the equivalent reactor volume concept to reduce the data to isothermicity before attempting the kinetic analysis. The second determines the parameters directly from the nonisothermal data by means of a search routine. Both methods led to a reaction order of 1. The effect of propylene addition was also investigated. Finally, a detailed molecular reaction scheme was derived from a nonisothermal and nonisobaric simulation of the cracking experiments. This scheme was used in the simulation of an industrial cracker and led to excellent agreement, in particular of the product distribution.

P. S. VAN DAMME,
S. NARAYANAN, and
G. F. FROMENT

Laboratorium voor Petrochemische Techniek
Rijksuniversiteit
Gent, Belgium

SCOPE

The major fraction of the scientific literature on propane cracking deals with radical mechanisms and kinetics of elementary steps, generally studied under conditions which bear little relation to those used in industry. In recent years only a few bench scale studies in flow equipment focused more on directly practical objectives. In spite of this, the design of industrial cracking coils still faces a lack in reliable basic data obtained on a scale large enough to possess the essential characteristics of industrial operation, in equipment sufficiently versatile to permit wide variations in operating conditions and sufficiently instrumented to permit rigorous analysis of the data. The present paper is an attempt to fill this gap.

S. Narayanan is with Kinetics Technology International B.V., The Hague, The Netherlands.