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Development of reverse osmosis desalination membranes composition and configuration: future prospects

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Abstract

The most common reverse osmosis (RO) membranes which attained the stage of economic application in desalination plants are made of cellulose acetate (CA) or polyamide (PA), in either hollow fiber (HF) or spiral wound (SW) configurations. The first application problem of CA membrane is its sensitivity to hydrolysis being both a polysaccharide and polyester. The resulting deacetylation of the surface film explains the observed loss of selectivity and reverse osmosis failure. In the hot countries of the Middle East this problem acquires particular dimensions in view of the accelerated rate of hydrolysis together with the usually higher frequency of biofouling and chemical cleaning. Failure of CA membrane is also due to the inadequate mechanical and thermal stability of CA polymer which result in progressive decline of RO performance due to membrane compaction and shrinkage. Results of comparative testing and experience in application of PA membranes in plants originally designed to use CA ones of capacities ranging between 25,000 to 66,000 m^3/d are reviewed. With only minor system modifications, this replacement led to generally more steady performance at a higher salt rejection and for a longer life time. Furthermore, a remarkable energy saving is achieved by the operation of RO plants at less than the half of the original operational pressure of CA membranes. On the other hand, the reported replacement of CA membranes by the PA ones is not as straightforward as would be indicated by the oversimplified system design projection programs of membrane producers. Aspects of the mentioned replacement are discussed in detail. Despite their higher surface charge and surface roughness, PA composite membranes did not show excessive biofouling susceptibility. Biofouling was investigated by destructive RO element autopsy, cell test of fouled sheet membranes, surface analysis by scanning electron microscopy and energy dispersive X-ray. The RO element configuration determines the hydrodynamic conditions inside the RO element. Due to this effect, the HF configuration, whether with PA or CA membranes, requires more critical pretreatment and has a lower response to cleaning. Recently introduced modifications to elements of the plate-and-frame configuration enabled successful treatment of high organics, wastewaters. Further

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systematic studies are required to optimize the performance of the now-available RO membrane polymers as well as to develop new ones. Membranes suitable to operate at high temperatures will enable higher process energy efficiency together with control of biofouling. Membranes of promoted hydrophobicity will need only low operational pressures and will have minimized fouling susceptibility by organics for application in industrial wastewater treatment. Chlorine-tolerant membranes will enable easier and more efficient treatment of water contaminated with microorganisms or sewage water.

Keywords: Membrane; Retrofitting; Cellulose acetate; Hollow fiber; Thin film composite

1. Introduction

Performance in reverse osmosis (RO) is determined by several variables which can be classified into three categories, namely: variables concerning the membrane, variables concerning the feed water; and variables concerning the conditions of operation. The RO membrane hydraulic permeability, selectivity, structural configuration and the chemical characteristics of its base polymer are the main membrane parameters which determine RO process efficiency and mechanism [1].

Since the discovery in the mid-sixties of the flat CA RO membranes [2] and the development of the spiral wound configuration to replace the tubular or the plate-and-frame ones, a great volume of research work was devoted to develop the RO membranes. The modified asymmetric blend cellulose di- and tri- acetate membranes [3] enabled a remarkable improvement of performance. The polyamide membranes were introduced in the hollow fiber (HF) configuration, in 1970. Significant development occurred in the mid-seventies with the introduction of the thin film composite membranes of polyurea and polyamide (TFC,PA) [4].

Mechanistic aspects of RO (by CA membranes) were investigated by several authors [5]. We have established a procedure [6,7] for characterization of these membranes and evaluation of permeation and selectivity coefficients, fixed change density, electroosmotic flux and streaming potential, through easier and more precise electrochemical mearsurements. The effect of variation of preparation procedure, chemical composition, annealing temperature and pre-pressurization on the properties and performance of CA membranes has been the subject of study of several contributions [8–11].

The sensitivity and failure of CA membranes in presence of oxidizing agents, microorganisms, acid or alkaline pH values is confirmed [12,13] as compared to the TFC,PA membranes [15,16].

The claimed higher bacterial adhesion to the TFC,PA membranes and the possible higher susceptibility to biofouling has been evaluated [14]. A mechanism is proposed for membrane biofouling in RO which is the most important application problem in the hot countries of the Middle East [15,16]. In view of their higher resistance to feed temperatures, high-temperature-reverse osmosis [17] was shown to be a promising solution to biofouling of TFC,PA membranes parallel to the increase of permeation rate.

As for the application of RO in industrial wastewater treatment, rejection of heavy metal cations at a high efficiency was realized by CA and TFC,PA membranes as compared to the HF elements on which such cations would deposit and foul the membrane surface [9]. Khedr et al. [18] introduced a thin film cellulosic membrane supported by a microporous polysulphone film which showed superior performance for low-pressure RO treatment of wastewaters containing heavy and transition metal cations. These components, besides being health hazardous, would cause severe corrosion cases in water desalination plants [19].

TFC composite membranes are subject to continuous development. Membranes of chlorine resistance, low energy, low fouling were produced.

Recently, extra high rejection TFC membranes enabled to desalt seawater by brine conversion up to a recovery of 60% [20].

The present work reports on twelve-year experience in production, application, research and develop-ment related to RO membranes and systems by SIDMAS Ltd. Particular emphasis is made on the retrofitting of RO systems originally designed to use CA or HF membranes to use the TFC,PA membranes. Encountered problems and realized advantages are discussed.

2. Experimental

The study of membrane elements' performance for the purpose of retrofitting included:

1. *Destructive RO element autopsy*: Collection of sheet membrane sample for the "Cell Test" and "Dye Test" for determining the salt rejection and permeation rate. Surface analysis by scanning electron microscopy and energy dispersive X-ray is performed.

2. *Inspection of plant performance*: Over long operation periods, normalized variation of salt rejection and product rate were represented.

3. *Pilot testing* is performed to enable comparative testing of membrane types, pretreatment and operation pretreatments.

4. *RO system design*: This was based on the standard software of Osmonics/Desal (Probrain and Winflow) and of FilmTec Dow (ROSA).

3. Results and discussion

The most common flat CA membrane subject of retrofitting in the present work is the modified, asymmetric, blend cellulose of di-tri acetate membrane, of 2.60–2.86 acetyl group per anhydrous glucose unit. The active desalting layer is of about 2000 Å thick, dense layer supported by a spongy porous substrate layer.

3.1. *Typical performance of CA membranes*

Typical performance of CA membranes (in hot countries) is summarized as follows:

1. The maximum useful membrane life time is mostly ≤ one year.

2. After a successful startup at the design salt rejection and permeate rate, most of the units suffered from progressive decline of salt rejection usually accompanied by parallel increase in permeate rate, Fig. 1.

3. For the hazardous failure of adjustment of feed pH and the consequent exposure of the membranes to pH values out of the narrow tolerated range of 4.5–6.5, loss of salt rejection took place in the form of an irreversible down jump.

In such big RO facilities of several tens of thousands of m^3/d, pH re-adjustment may need several hours since acid dosing is usually done several steps ahead of huge RO feed tanks. An

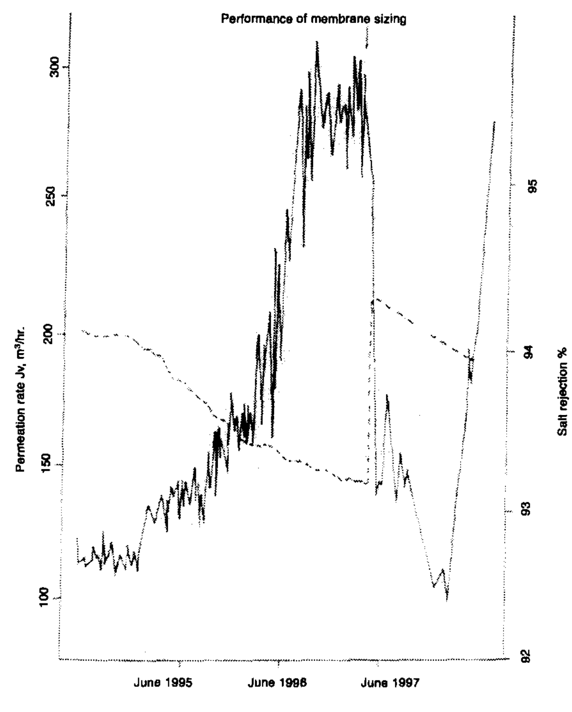


Fig. 1. Variation of the permeation rate, m^3/h and salt rejection of CA membrane in RO units with time.

RO membrane of wide tolerance to feed pH is a must for safe operation.

Similar, more or less, abrupt loss of membrane salt rejection takes place after alkaline or acid cleaning to recover the decline of permeate rate caused by fouling or scale deposition.

4. "Sizing" of CA membranes was sometimes performed, trying to regain such rapid decline of performance due to surface hydrolysis (Durma and Mozahmia plants, and RC plant, Jubail, Saudi Arabia). This is a CA membrane chemical surface treatment inside the RO system which aims to plug the holes caused by partial hydrolysis of the dense active surface film through the use of a vinyl copolymer. Only partial recovery of salt rejection was realized which was viable only for few months.

5. Exposure of CA membranes to feed tempera-tures above 30°C resulted in decline of salt rejection (KKIA International Airport RO plant) rather than what would be expected about CA membrane thermal shrinkage followed by increase of rejection and decrease of permeation [1].

3.2. Retrofitting of CA membranes by TFC,PA membranes

This was first realized by SIDMAS Ltd. in Buwaib plant, Buwaib, Saudi Arabia (1993–94). This plant includes 13 RO skids in which 1950 membranes are arrayed in three stages. Each skid produces 3,600 m^3/d with a permeate high purity which enables to raise the total RO product rate (46,800 m^3/d) by blending with cooled, filtered and preconditioned feed to a total plant product rate of 66,000 m^3/d.

After the success of this retrofitting the same was extended to Majmaah plant (2,000 m^3/d), Durma (25,000 m^3/d), KKIA (13,440 m^3/d) and Unaizah plant (35,000 m^3/d), Saudi Arabia. All these plants were designed to be operated by flat, spiral wound CA membranes and are now successfully operated by TFC,PA membrane.

1. The retrofitting work starts by full re-design of the RO system, based on the TFC,PA membranes but sticking to the previously existing array of stages of the CA RO system in order to avoid the expenses of system modification.

Control of feed water rate and pressure had to be re-adjusted in view of the differences in internal resistance and operation pressures of the two types of membranes. While CA membrane operates at 350–450 psi, the normal TFC,PA membrane operates at 200–225 psi. Currently, low energy TFC membranes are available which operate at 100–150 psi. Such reduction of the operation pressure enabled realization of an important saving energy consumption of $\geq 40\%$.

2. In case where it is required to avoid the cost of replacement of the high pressure pumps, in big RO desalination facilities, but to profit from the other advantages of the retrofitting, we have developed a high-pressure brackish spiral wound RO element TFC,PA which is designed so as to enable the direct replacement of the CA membranes. Fig. 2 shows the specifications of this element, the SB30-330HP. This element is successfully used in Unaizah Water Treatment Plant (1368 membrane elements), Unaizah, Saudi Arabia for almost two years.

3. The pretreatment includes chlorination for sanitization. It had to be followed by dechlorination, e.g. by dosing of meta bisulphite before attaining the TFC membrane. Free chlorine is known to induce oxidation-dissolution to the thin film which would lead to irreversible damage of the selective permeability [21]. However, despite the claimed higher chlorine tolerance of CTA membranes, oxidation was reported as the main reason of their deterioration [22]. Also, while a trace of heavy metal cations strongly catalyses the oxidation of the CA or HHF-CTA membranes [23], our results showed that TFC,PA is not influenced by the presence of these cations and rejects them efficiently in sewage water or industrial wastewaters.

4. The higher compaction of CA membrane and the consequent higher decline in the permeation

SIDMAS/FILMTEC

Membranes

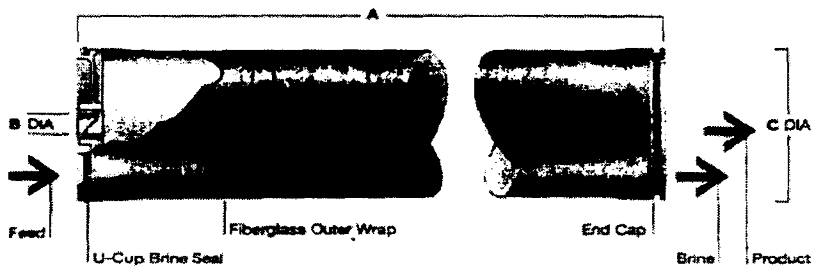
8" High Pressure Brackish Water RO Element

Technical Bulletin

Product	Nominal Surface Area (ft^2)	Product Flow (gpd)	Optimum Operating Pressure (psi)	Salt Rejection (%)
SB30-330HP	345	9000	400	99.5

Permeate flow and salt rejection based on the following standard conditions:
2000 ppm NaCl, 400 psi, 25 °C (77 °F), pH 8, and 15% recovery.

- Flow rates for individual elements may vary but will be not more than 15% below the value shown above.
- Minimum salt rejection for individual elements is 98.0%.
- This element is SIDMAS' standard 8" element for 400 psi application and/or CA element REPLACEMENT.



Operating Limits			
Membrane Type	Thin Film Composite	pH Range:	
Maximum Operating Pressure	600 psi	Continuous Operation	2-11
Maximum Operating Temp.	45°C (113°F)	Short-term (30 min.), Cleaning	1-12
Maximum Feed Turbidity	1 NTU	Maximum Feed Flow	70 gpm
Free Chlorine Tolerance	< 0.1 mg/L	Maximum Feed SDI	5

Single Element Recovery (Permeate Flow to Feed Flow)	Recovery	Dimensions (inches) A	B	C
SB30-330HP	0.15	40.0	1.125	7.9

- Consult the recent DESIGN GUIDELINES for multiple element applications and recommended element recovery rates for various feed sources
- Element to fit 8.00 inch I. D. pressure vessel.

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Fig. 2. Specifications of the high-pressure brackish TFC,PA membrane designed for direct replacement of CA membranes with system modifications.

rate is due to the fact that CA is a porous RO membrane. The permeation of porous membranes is a function of the pore diameter as shown by the scanning electron microscopy in Fig. 3 where the surface carries some scaling deposit.

On the other hand, the TFC membrane is a tough, non-porous RO membrane through which the permeation is a function of the diffusion rate of various species as shown by SEM in Fig. 4, at the same magnification as in Fig. 3.

Fig. 4 shows the progressive development of the biofouling film on the TFC,PA membrane surface with time over 15 days. The study of this phenomenon [15,16] revealed that despite the claimed higher susceptibility of this membrane

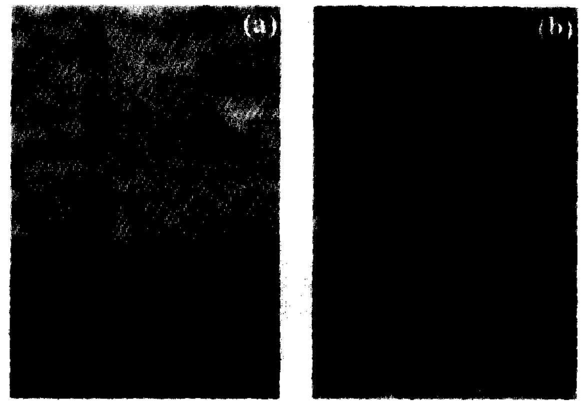

Fig. 3. Scanning electron micrograph of CA membrane surface for fresh and fouled membrane coupons.

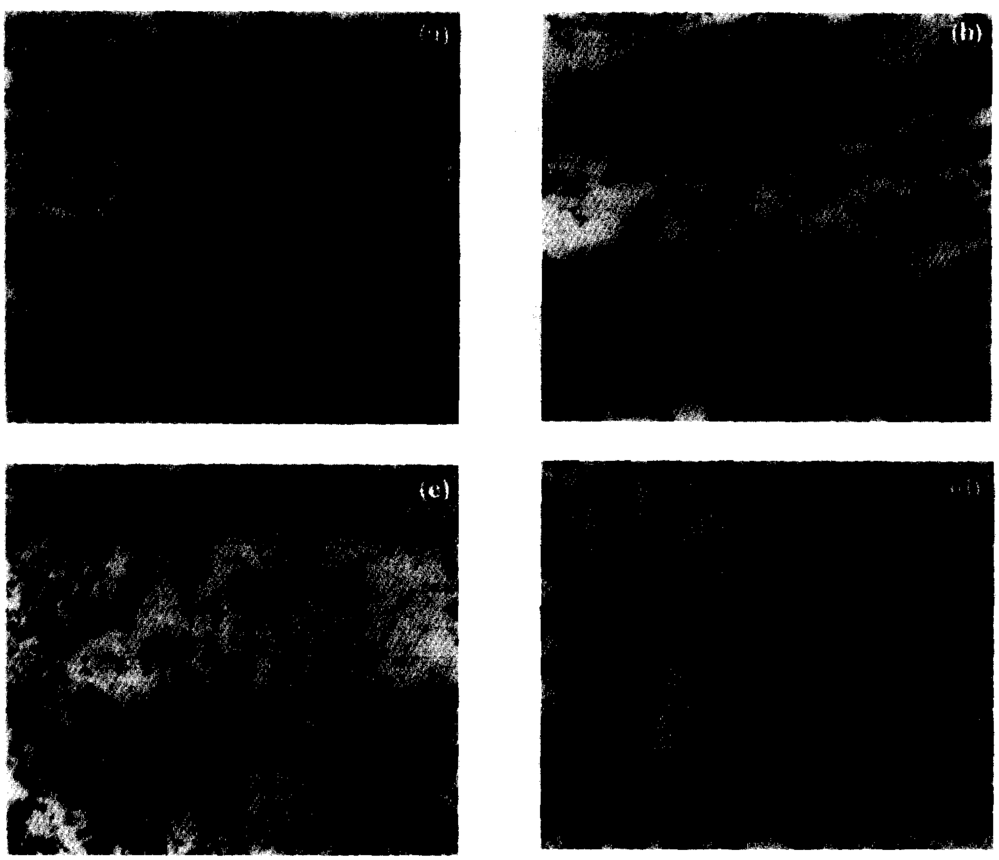

Fig. 4. Scanning electron micrograph for TFC,PA membrane surface fresh and fouled membrane coupons.

to biofouling [14] which is usually attributed to its higher surface roughness and electric charge as compared to the CA membrane, we did not observe lower plant availability than with the CA membrane. While biofouling remains the first application problem in the hot countries of the Middle East, correctly designed pretreatment normally enables steady performance with minimized shutdowns for cleaning.

5. Results of laboratory testing [18] confirmed that the enhanced hydrolysis of CA membrane at operation temperatures ≥ 35°C overcame the simultaneous shrinkage of this membrane which is known to induce increase in salt rejection and decline of permeation [1]. Similarly, the detrimental effect of biofouling on cellulosic membranes is also mainly attributed to the partial hydrolysis of the dense active surface film in contact with the extracellular life product of bacteria. The microscopic examination of the dyed membrane surface upon the element autopsy showed batches of the CA absorbing the dye.

3.3. Typical performance of the HF RO membranes

Survey of the HF membrane performance is based upon inspection of the operation data of several HF plants in comparison with those of the TFC,PA membrane working under the same design conditions (percent recovery) with similar feed water composition.

Fig. 5 shows the typical variation of the product rate and salt rejection as a function of the operation time. The number of membrane modules in operation is marked on the corresponding operation period.

The initial permeation rate declines rather rapidly in the beginning followed by a slow but progressive decline accompanied, in most cases, by decline in salt rejection. After several months, additional modules had to be included in each skid in order to stabilize the product rate and salt rejection of the plant. Despite the repeated inclusion of new modules the permeation rate continued to decline. This represents, in fact, a rather high rate of

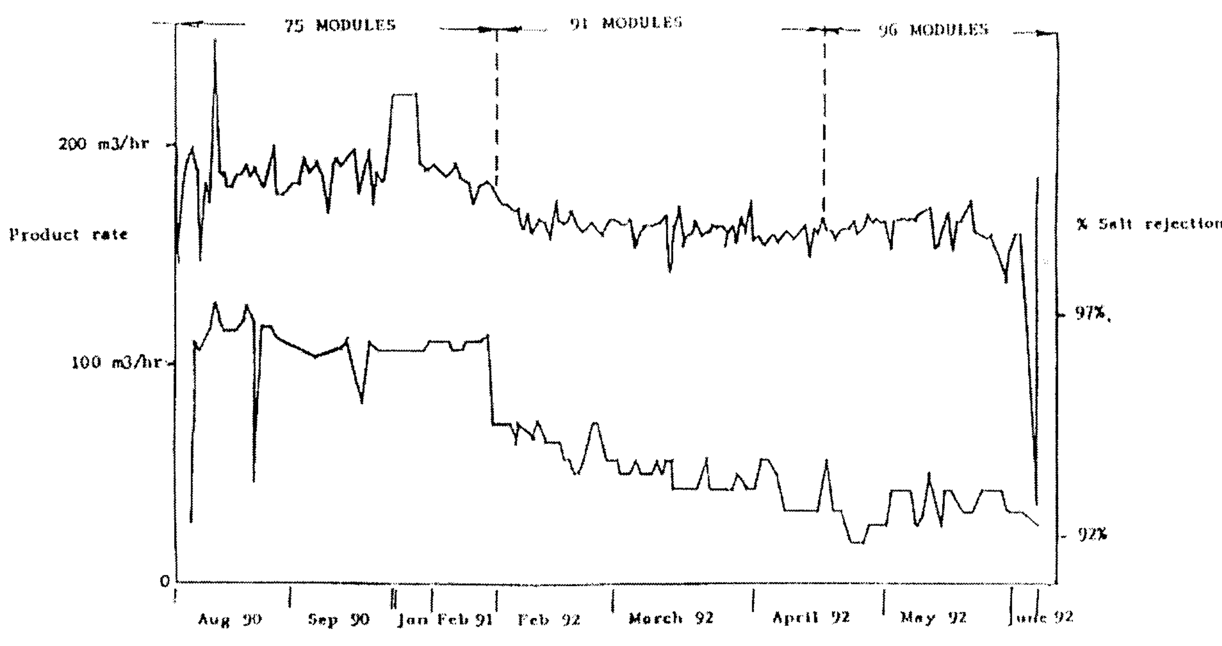

Fig. 5. Variation of the permeation rate, m³/h and salt rejection of the HF membrane in RO units with time.

membrane failure and replacement with new ones. The old modules which were not removed from the skids end by becoming completely blocked and out of operation.

The progressive decline in permeation of the HF element is attributed to its relatively high compressibility. The hollow fiber configuration, under the operational pressures, much higher than those needed for the TC element, undergoes progressive compaction with consequent loss in product rate despite the rise in pressure. Mechanical compaction of the HF element was reported to be equivalent to that of CA membrane [24].

The observed decline of permeation and rejection of the HF element with time is partly due to biofouling, as confirmed by RO element autopsy and feed water bacterial count. However, the comparison of fouling behavior (set up) for HF and TFC membranes revealed that biofouling has a much higher impact on the performance of the HF element. The observed decline in performance — under same biofouling conditions — included, with HF elements, both the product rate and salt rejection, while it is manifested only by decline of product rate for TFC elements.

While adequate cleaning recovers the performance pf the TFC membranes without addition of new ones, it is much less efficient with HF elements. It recovers only partly the salt rejection. The product rate is seldom improved. Furthermore, cleaning of HF elements should usually be followed by regeneration of the active film. This is achieved through an additional post-treatment by polyvinyl methyl ether in case of brackish HF elements or by tannic acid in case of seawater HF elements. Cleaning of TFC membrane, on the other hand, has no effect on the stability of active film.

3.4. Retrofitting of the HF membrane by TFC,PA membranes

This was first realized by SIDMAS Ltd. in GID plant, Mozaihmia, Saudi Arabia (1,000 m^3/d) in the year 2000 with remarkable improvement in performance. Currently the retrofitting of Al Shemaisy plant, Saudi Arabia (28,800 m^3/d) is finalized. SIDMAS is also awarded the retrofitting of Manfouha I and II plants (67,200 m^3/d).

1. Retrofitting resulted in more steady performance over much longer life time. The design permeation rate is stabilized at the design pressure after few hours of start up (Fig. 6). In Buwaib plant, as an example, the TFC,PA membranes are still operated for more than 7 successive years under conditions where the previous CA membranes failed to complete one year of correct performance. Over this period the average decline of salt rejection is 3.8%, and of product rate is 6% and rise in ΔP is of 1 bar which is still very satisfactory and permits a blending rate $\geq$ 30%.

The longer life time of TFC membranes is relevant to the higher chemical, mechanical and thermal resistance of polyamide polymer as compared to the cellulose di- and tri- acetate blend. The much wider pH tolerance of polyamide membrane of 2–11 for permanent operation and 1–12 for short period of acid or alkaline clean reflects the high chemical stability of polyamide. CA, on the other hand, being a polysaccharide and polyester, is sensitive to hydrolysis in both acid and alkaline ranges of pH.

2. The wider pH tolerance of the TFC,PA membrane enables a certain ease in RO system design. The lower feed pH values help to attain higher percent recoveries at safe values of LSI with minimized risk of deposition of $CaCO_3$ scale.

3. Higher salt rejection by the TFC membranes enables higher blending rates with the pretreated feed water and consequently increasing the process cost-effectiveness. On the other hand, the higher TFC membrane rejection for some of the problem-making components like SiO_2 (scale deposition), NO_3^- (results from pollution of well water by fertilizers. Above the WHO norms, it causes bad taste and health problems), organics and heavy metal cations (determine the validity of RO for tertiary wastewater treatment and industrial wastewater treatment) widens the useful application scope of RO (Table 1).

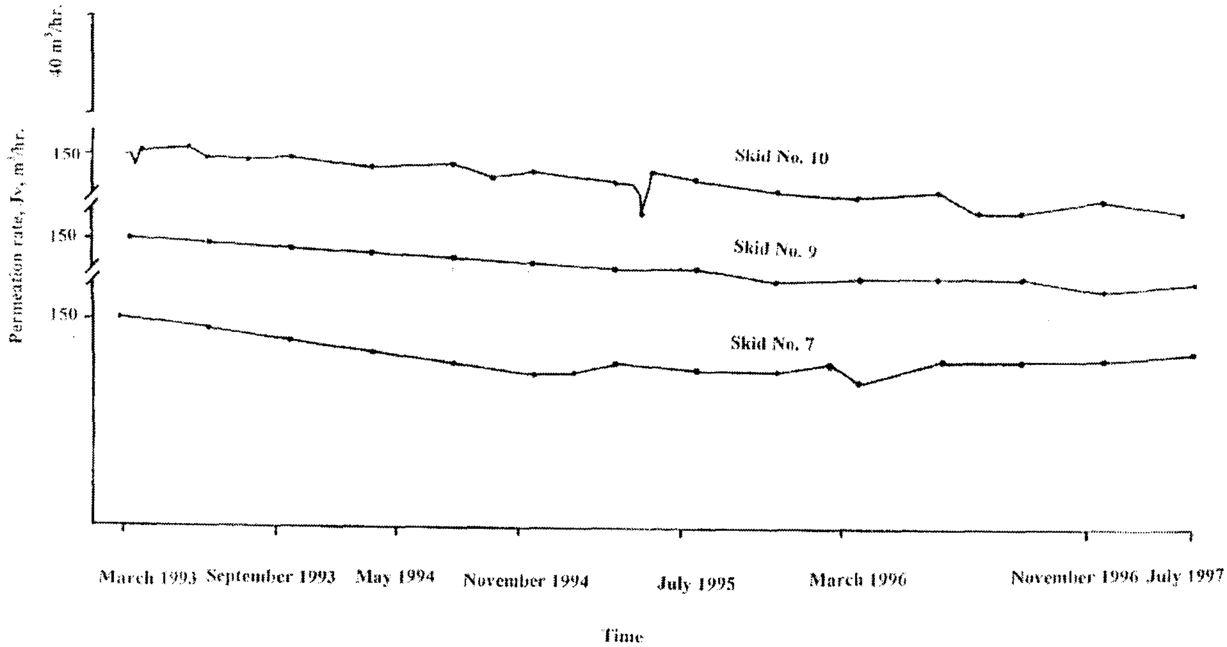

Fig. 6. Variation of the permeation rate, m^3/h with time of the TFC,PA membrane in RO units.

Table 1
Rejection of individual components from feed water upon retrofitting of HF by TFC elements

Dissolved component	Rejection by HF membrane, %	Rejection by TFC,PA membrane, %
System salt rejection	97	99
SiO_2 rejection	85	94
NO_3^- rejection	83	92
Organics rejection (decrease of TOC)	90	98

4. Operation by the TFC membrane is performed is performed at almost half of the pressure of the HF one resulting in important energy saving.

Retrofitting can be done with low-energy TFC membranes, however special care should be taken in the RO system re-design in this case. In view of the high permeation of these membranes at low pressures some difficulty is encountered in stabilizing the operating percent recovery when there is a wide temperature variation between the different seasons, sometimes in the same day. In some cases, the application of controllable back pressure on the first stage(s) was helpful.

4. Conclusions

The replacement of the RO flat CA and the HF membranes by TFC,PA ones positively contributed to the advance of the technology and the solution of the main problems which determine the RO process efficiency and cost-effectiveness. These problems are:

1. Sophisticated pretreatment

- RO feed pretreatment is becoming easier and less expensive with the wider chemical and physical tolerance ranges of TFC,PA membranes.
- Feasibility of operation at higher temperatures led to lower cooling requirements and higher permeation rates.
- The higher SDI tolerance of the TFC membranes led to lower water clarification requirements.

- The higher pH-tolerance enabled lower acid dosing and consequently lower degasification for CO_2 removal from the permeate in post-treatment.

2. Membrane fouling and plant availability

Reverse osmosis is more susceptible to fouling, especially biofouling, than MSF distillation. However, the introduction of the TFC,PA membrane enabled to better combat biofouling and to raise the effective plant availability in view of the higher resistance of the spiral wound configuration to mechanical blocking and of the PA polymer to biodegradation.

3. Process recovery rate

While the maximum permissible recovery is mainly a water composition issue, higher RO process efficiency and recovery rates are realized, particularly in seawater desalination, by the development of the very-high rejection TFC membranes. These are resistant to compaction at high applied pressures and enable brine recovery in two-stage systems.

4. Running cost

- Lower energy consumption is realized by operation at much lower pressures with the TFC membranes. Big brackish RO plants are now designed to operate at <12 bar.
- The steady performance for longer life time of the TFC,PA membrane decreased the projected cost of membrane replacement.

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