

Membrane life in a seeded-slurry reverse osmosis system

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Abstract

Membrane replacement can be a major operating cost of a membrane plant. During the development of a novel desalination technique (the SPARRO process) for treating calcium sulphate scaling mine waters the expected life of tubular cellulose acetate membranes operating in the seeded-slurry mode was investigated.

During four operating phases of the plant over a five-year period more than 9 000 h of operating data were obtained. Performance data showed that each operating phase was dominated by either membrane fouling or membrane hydrolysis. Membrane fouling was observed to begin near the front-end of the membrane stack and proceed towards the back. Hydrolysis, on the other hand, occurred first in the tail end of the stack and moved backwards towards the front end modules. Although two detailed membrane autopsies were carried out no definitive statement can be made in respect of the causes of either membrane hydrolysis or membrane fouling. However, suggestions are presented to explain the observed fouling phenomenon in relation to the turbidity of the pretreated feed water and the presence of chlorine. It is proposed that the presence of radioactive isotopes in the mine water which become concentrated in the process contributes to the observed membrane hydrolysis. A membrane life of up to two years is projected for an improved pretreatment arrangement.

Introduction and background

Desalination of water containing high concentrations of calcium and sulphate presents problems due to the potential to form calcium sulphate scale on process equipment surfaces when the solubility of the salt is exceeded. In membrane desalination processes the membranes themselves can be at risk of being destroyed by scaling. Water containing high concentrations of calcium and sulphate is found in most South African gold mines. Sulphate is introduced to the water by the oxidation of pyrite ores present in the gold bearing reefs (Juby et al., 1986), while elevated calcium levels are often a result of the addition of lime during neutralisation of the mine water underground. The concentration of dissolved calcium and sulphate increases further due to the tendency of mines to re-circulate and reuse most of the mine water. Calcium sulphate scaling water causes major technical and economic problems for the mines, and it contributes a large pollution load to the environment (Mackay et al., 1991).

As a result of the water quality problems experienced by the mines and pressures by the authorities to reduce the pollution load from mines, the Chamber of Mines Research Organisation of South Africa (COMRO) (now CSIR Miningtek) embarked on a research project to assess the viability of existing membrane processes to desalinate calcium sulphate scaling mine water. The project later expanded to the development of a novel seeded reverse osmosis

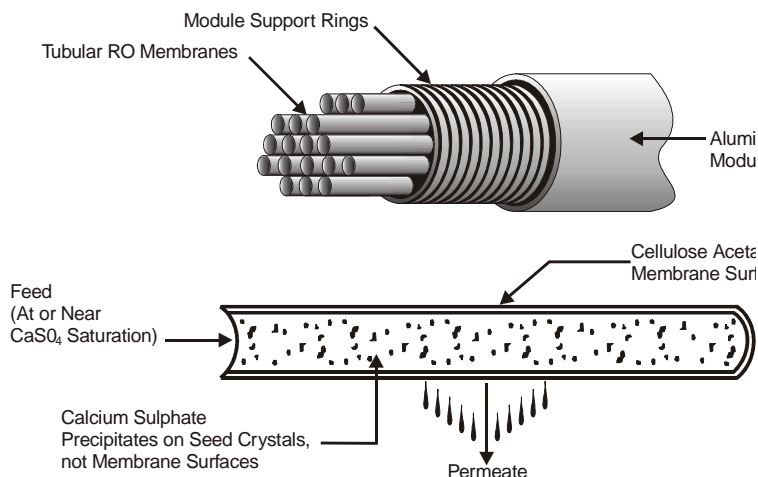


Figure 1
Conceptual illustration of seeded reverse osmosis

(SRO) process, the SPARRO process (slurry precipitation and recycle reverse osmosis) to desalinate calcium sulphate mine water.

The research began in the early 1980s and continued until 1993 in several phases, culminating in the patenting of several of the novel design features of the SPARRO process. Several aspects were investigated in detail during this period and some of these have been published elsewhere (Juby, 1994; Juby et al., 1996).

The SRO concept (Fig. 1) was developed in the late 1970s by Resources Conservation Company (RCC) in Seattle, USA (O'Neil et al., 1981). Basically, the concept involves circulating a slurry of seed crystals within the RO system. The seed crystals serve as preferential growth sites for calcium sulphate and other calcium salts and silicates, which begin to precipitate as their solubility products are exceeded during the concentration process within the membrane tubes (Dibenedetto, 1984). The preferential growth of scale on the seed crystals prevents scale formation on the membrane surface.

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Due to the need to circulate a slurry within the membranes, the process is confined to the use of membrane configurations that will not plug - such as tubular membrane systems.

In South Africa, work with SRO began in the early 1980s. After successfully testing a small (0.05 l/s) SRO pilot plant (Harries 1984; 1985) and limited tests on a larger 0.5 l/s plant, COMRO embarked on a new project in 1986 to develop a modified SRO process. The work of Harries (1985) concluded that the tubular cellulose acetate (CA) membranes had performed satisfactorily in the seeded slurry mode with no evidence of fouling, scaling or damage to the membranes due to recirculation of the seed slurry at concentrations of around 40 g/l.

Despite the positive results, many process and equipment related questions remained unanswered, including the life expectancy of the tubular membranes. The work on the SPARRO process was aimed at answering many of the queries resulting from previous work. The steps in the development of the new SPARRO process as well as design aspects are given in detail by Juby (1994). The new features of the process include:

- a lower linear slurry velocity in the membrane tubes - to reduce energy consumption;
- a significantly lower feed water seed slurry concentration - to reduce the recirculating load and wear on the slurry pumps;
- a dual pumping system incorporating separate pumps for mine water and seed slurry - to allow conventional RO pumps to be used for the mine water feed stream;
- a tapered membrane stack configuration - to improve system efficiency;
- a smaller desupersaturation reactor - to make the process more practical for full-scale operation; and
- separate seed crystal and brine blowdown systems - to independently control the suspended and dissolved solids mass balances in the system.

The focus of this paper is the membrane life in a seeded-slurry RO system. Specifically, this paper deals with the pretreatment received prior to desalination, a summary of membrane performance observed during four operating phases of the SPARRO plant and a detailed account of membrane autopsies carried out during the first operating phase. Suggestions to explain the observed membrane performance are presented.

Experimental

Equipment

In order to evaluate the performance of the new process, a 0.85 l/s pilot plant with a membrane area of 154 m² was designed and constructed. The plant was operated at a test facility at East Rand Proprietary Mines (ERPM) Limited Hercules Shaft complex where a constant supply of underground mine service water was available. Approximately 9 300 operating hours were achieved during four operational phases between March 1989 and February 1993. Tubular CA membranes supplied by Membratex (now Envig (Pty) Ltd) were used throughout the investigations.

Each 2 m long membrane module was a self-contained pressure vessel. The CA membrane was cast onto the inside of 12.5 mm diameter porous tubes. Nineteen tube lengths were connected end to end within each module, with one inlet and one outlet per module, to give an active membrane area of 1.75 m² per module. The typical operating pressure of the modules was 4 000 kPa(g).

The membrane stack of the SPARRO plant was configured in four banks of modules. Three rows of ten modules in parallel made

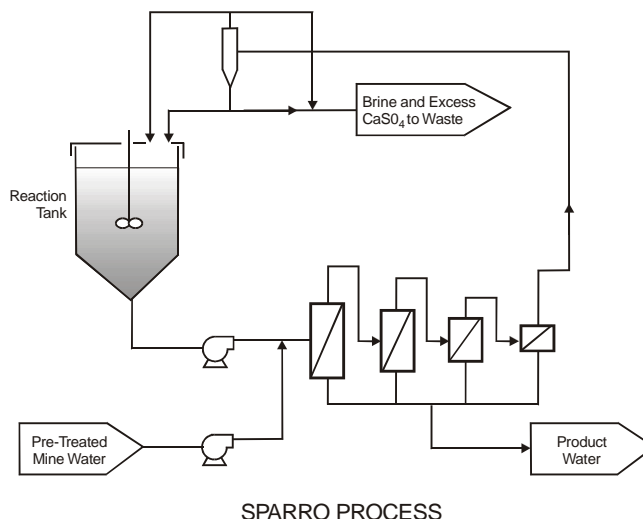


Figure 2
Schematic flow diagram of SPARRO plant

up the first bank, three rows of eight modules in parallel in the second bank, four rows of six modules in the third and two rows of five in the fourth - to give a total of 88 membrane modules. The available membrane area in the plant was not constant for all phases of the work due to modifications that were made to reduce the membrane area. The changes in membrane area were taken into account in assessing the performance of the membranes and the plant as a whole. Details are presented elsewhere (Juby, 1994). The feed stream to the membranes consisted of a mixture of pretreated mine water mixed, just upstream of the membranes, with a stream of recycled brine containing 20 g/l of calcium sulphate crystals. The recycle stream of seed crystals was pumped from a desupersaturation tank (or reactor) positioned downstream of the membranes. Figure 2 is a schematic of the SPARRO plant configuration. The mixing time between the pretreated mine water and the seed recycle stream was less than 10 s prior to the mixture entering the membrane bank.

In an attempt to obtain information on expected membrane life that could be used with confidence in economic evaluations of the process, a membrane lifetime test (MLT) plant was constructed and operated in parallel with the SPARRO pilot plant during the first two operating phases, between March 1989 and August 1990.

The configuration of the MLT plant was different to that of the SPARRO plant, as shown in Fig. 3. For the MLT plant the pretreated mine water was introduced directly into the reaction tank, where it was mixed with the recycled brine stream. The theoretical hydraulic retention time in the reaction tank was 4 h.

The MLT plant used identical membranes to those used in the SPARRO plant, but the MLT plant stack contained only 20 membrane modules, arranged in four parallel rows of five modules in series. The plant had a nominal production rate of 0.23 l/s. The available membrane area was 35 m², which remained constant for the entire experimental period.

The evaluation of the SPARRO process took place during four phases over a period of approximately five years. The MLT plant operated in parallel on the same pretreated feed water during the first two operating phases. During all phases of the work attempts were made to operate the plants on a 24 h per day basis. However, as this was not a laboratory-controlled investigation, operational problems were encountered from time to time which resulted in periods of down time during each of the operating phases.

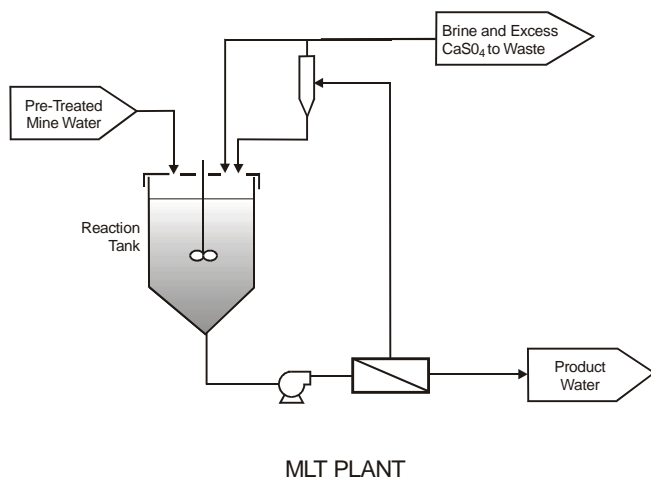


Figure 3
Schematic flow diagram of MLT plant

Pretreatment

Pretreatment during Phase I consisted of the following process steps:

- **Metals precipitation** - in-line flocculation with 0.5 mg/l of polymer (both Anikem 4816 and Magnafloc 1011 were used on separate occasions), the addition of 1 mg/l of potassium permanganate as an oxidant and adjustment of pH to between 9.5 and 10.0 with caustic soda, to promote oxidation and precipitation of heavy metals (particularly iron).
- **Clarification** - removal of the bulk of the flocculated material in a clarifier.
- **pH adjustment** - adjustment of the pH of the clarified mine water to between 5 and 6 with sulphuric acid.
- **Temperature reduction** - a portion of the pH corrected water was recirculated and cooled by passing it over a forced air evaporative cooling tower.
- **Filtration** - the cooled water was filtered through dual media anthracite/sand pressure filters as a final treatment step to reduce the turbidity of the mine water.

For Phases II, III and IV, the high pH metals oxidation and precipitation step was not used. This change was made because of the high cost associated with dosing caustic soda to achieve the high pH conditions. For these three operating phases, the pH of the raw mine water entering the pretreatment plant was determined by the lime neutralisation operations taking place underground in the mine - as part of the normal mining operation. The pretreatment steps of flocculation, clarification, cooling and filtration continued as before.

Chlorination of the cooled pretreated mine water (by the addition of sodium hypochlorite) was introduced as an additional step in Phases II and III as a precaution against biological fouling of the membranes. The redox potential of the pretreated feed water was not measured.

Membrane autopsies

Two sets of operating membranes were removed from the MLT plant during Phase I and sent to the Institute of Polymer Science (IPS) at the University of Stellenbosch, for membrane autopsies.

The purpose of the autopsies was to provide an independent evaluation of the membrane integrity and to establish whether membrane damage or changes to the membrane material had taken place.

First set of membrane samples

In Phase I, after 1 047 h of operation with a full set of new membranes in the MLT plant, the first set of two modules was removed and sent to the IPS for inspection. One module was removed from the first row of modules in the membrane stack. This row received the slurry recycle feed water. The second module was removed from the second row of modules in the membrane stack. The modules that were removed were preserved in a solution of formalin, in accordance with the manufacturers' recommendations. Two new modules were used to replace the ones removed from the stack.

The first set of membranes were examined by reflected-light differential interference contrast (DIC) microscopy, by optical and scanning electron microscope (SEM) analysis and by surface staining techniques (Jacobs, 1989a). The results were compared with those from unused membranes as well as membrane samples taken from other plants.

Second set of membrane samples

A second set of membrane modules was removed from the MLT plant in Phase I after the plant had operated for 1 800 h. The first module in this batch was removed from a position in the third row of modules about halfway through the membrane stack. The second module was removed from a position in the fourth row of modules. Again, two new modules were used to replace the ones that were removed.

At the IPS, the second batch of membranes was examined in a similar manner to the first batch of membranes.

Results

Raw mine water

Table 1 shows a typical analysis of the raw mine water pumped from underground to the test site. As indicated, manganese, nickel, aluminium and strontium all had concentrations of several mg/l. The table also shows average values for turbidity, suspended solids, pH and the temperature of the raw mine water. Guideline values established for certain quality parameters of the pretreated feed water to the SPARRO plant are also shown in Table 1.

The guideline values for pH and temperature were chosen to minimise hydrolysis of the CA membranes. The guideline turbidity value of less than 2.0 NTU was chosen primarily in order to reduce wear on high pressure feed pumps that may be caused by suspended quartzitic particles in the mine water. Guideline values for iron, manganese and aluminium were chosen to reduce the likelihood of membrane fouling due to these metals.

Pretreatment

It is common for mines to neutralise the mine water (usually with lime) before pumping it to the surface. At the Hercules shaft the lime dosage was insufficient to neutralise the water and, as shown by the average raw mine water pH values in Table 2, the water was always acidic. Thus, little or no final pH correction was required during Phases II, III and IV. Table 2 shows a summary of the pretreatment steps carried out in each of the operating phases. The table also presents the operating hours achieved for each phase.

Turbidity

The turbidity of the pretreated mine water varied from phase to phase. Although the SRO system involves high concentrations of suspended solids within the membrane tubes, the turbidity of the pretreated feed water is still considered an important variable. The significance of turbidity will be discussed later.

Table 2 summarises the average turbidity values of the pretreated feed water during the four operating phases. Clearly, suspended solids removal during Phase I was better than during any other phase of the work.

Although Phase III had a high average turbidity, the highest turbidity values only occurred during the first 400 h of operation, as shown in Fig. 4. For the remaining period the average turbidity was significantly better, at 1.6 NTU.

During Phase IV there were excursions to above 30 NTU at times. The period of poorest turbidity started after about 300 h of operation and lasted for about 200 h. During this period the turbidity was consistently above 5 NTU.

Overall quality

The average mine-water quality during Phase II before and after pretreatment is presented in Table 3. The values in the table show that without the initial high pH step, the removal of heavy metals was poor and as a result the SPARRO raw water feed quality guidelines were exceeded. The quality values presented in Table 3 are representative of the quality achieved during Phases III and IV as well.

Removal of radioactive isotopes

In order to assess the effectiveness of membrane desalination for removal of isotopes present in the raw mine water, a series of six chemical analyses were conducted during the

Parameter	Units	Raw mine water quality		SPARRO feed quality guidelines
		Average	Standard deviation	
pH	-	5.35	1.5	5 - 6
Turbidity	NTU	247	130	< 2
Temperature	EC	29	-	< 25
Total dissolved solids	mg/l	2 161	135	-
Calcium	mg/l	306	60	-
Magnesium	mg/l	84	30	-
Sodium	mg/l	116	13	-
Chloride	mg/l	50	3	-
Sulphate	mg/l	1 243	31	-
Iron	mg/l	0.3	0.2	< 0.3
Manganese	mg/l	4.4	2.2	< 1.0
Nickel	mg/l	3.7	1.9	-
Zinc	mg/l	1.1	0.6	-
Aluminium	mg/l	13.4	13.0	< 1.0

Treatment	Phase I (2 615 h)	Phase II (3 316 h)	Phase III (1 361 h)	Phase IV (1 100 h)
Average pH of raw mine water entering pretreatment plant	5.35	4.91	5.97	5.73
Chemicals added	caustic soda KMnO ₄ - 1 mg/l polymer - 0.5 mg/l	polymer: 0.5 mg/l	polymer: 0.5 mg/l	polymer: 0.5 mg/l
pH achieved after chemical addition	9.5 to 10.0	No significant change	No significant change	No significant change
Cooling to 25°C	Yes	Yes	Yes	Yes
Average turbidity after filtration, NTU	0.9	5.0	4.7	2.5
pH after acid addition (as required)	5.0 to 6.0	5.0 to 6.0	5.0 to 6.0	5.0 to 6.0
Chlorination	Nil	1 to 3 mg/l	1 to 2.5 mg/l	Nil
Metals (mg/l)				
Iron	0.3	0.3	Similar to Phase II	Similar to Phase II
Manganese	0.2	4.4		
Aluminium	0.6	4.1		

Phase II operating period. Further samples were taken during Phase IV. Table 4 presents the average retention of various ions by the membranes in the SPARRO plant. In Phase II average rejections of 91% for radium and 88% for uranium were achieved. By comparison, the average rejection of TDS was 94%. Membranes in the MLT plant showed slightly greater rejections in all cases.

During Phase IV the TDS retention of the membranes in the SPARRO plant stack was only 60%, however, the uranium radio-nuclide was rejected at levels of greater than 90%. Thus, although the membrane performance deteriorated sufficiently to allow the smaller low molecular mass ions through the membrane, most of the larger radio-nuclide ions were still retained by the membrane.

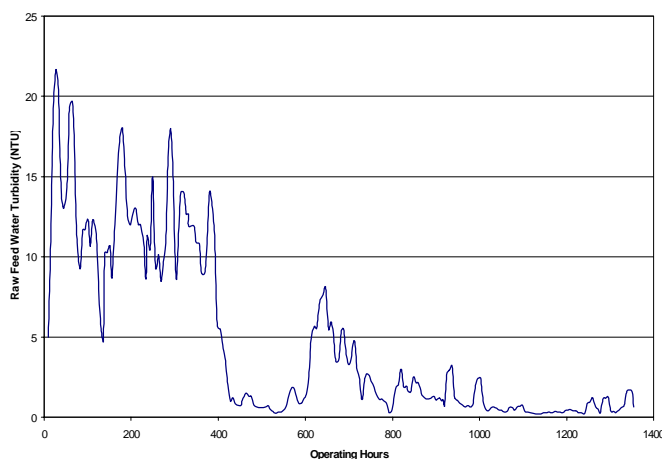


Figure 4

Variation in pretreated raw mine water turbidity for Phase III

TABLE 3
AVERAGE RAW MINE WATER QUALITY FOR PHASE II BEFORE AND AFTER PRETREATMENT

Parameter	Units	Before pretreatment	After pretreatment	SPARRO feed quality guidelines
pH	-	4.91	5.07	5 - 6
Turbidity	NTU	95	5	<2
Suspended solids	mg/l	32	3	NV
TDS	mg/l	2 169	2 204	NV
Conductivity	mS/m	217	222	NV
Sulphate	mg SO ₄ /l	1 214	1 200	NV
Calcium	mg Ca/l	310	303	NV
Magnesium	mg Mg/l	76	78	NV
Sodium	mg Na/l	115	120	NV
Chloride	mg Cl/l	51	57	NV
Iron	mg Fe/l	0.3	0.3	<0.3
Zinc	mg Zn/l	1.0	0.9	NV
Manganese	mg Mn/l	4.7	4.4	<1.0
Nickel	mg Ni/l	3.3	3.1	NV
Aluminium	mg Al/l	4.9	4.1	<1.0
Total chlorine	mg/l	0	1 - 3	NV
Temperature	°C	29	24	<25
(NV - No guideline value given)				

TABLE 4
RETENTION (REJECTION) OF RADIOACTIVE ISOTOPES BY MEMBRANES IN SPARRO PLANT

Operating period	Membrane retention (%)		
	Radium	Uranium	TDS
Phase II	90.9	87.6	93.5
Phase IV	no data	> 90	60

The permeate produced by the SPARRO plant membranes had a uranium (U²³⁸) concentration of less than 30 µg/l. An analysis of the feed (blend of raw mine water and slurry recycle) and brine reject streams from the SPARRO plant during Phase IV showed uranium (U²³⁸) concentrations of 588 µg/l and 920 µg/l respectively.

Membrane performance

The detailed performance of the SPARRO and MLT plants is presented elsewhere (Juby, 1994). However, a summary of the results of the membrane performance for both plants is presented in Table 5.

Briefly, Table 5 presents operating and performance data for each phase of the investigation. As shown, during Phases I and II, the MLT plant operated in parallel with the SPARRO plant. For each operating phase the number of operating hours, the overall plant recovery and the extraction are presented. The extraction is the recovery across the membrane stack itself. It is lower than the overall recovery of the plant due to the effect of the seed slurry recycle. Also shown for each phase of the work is the overall trend of the corrected membrane flux and the overall salt rejection (retention) of the membranes. To give an indication of the overall membrane performance for each phase, the performance trend is summarised as either fouling or hydrolysis. Finally, an indication of the average seed concentration in the feed stream to the membranes is shown.

The main point to emerge from the data that is relevant to this discussion is that both membrane hydrolysis and membrane fouling were observed during the operation of the plants. Furthermore, in Phases I and II when the SPARRO and MLT plants were operated in parallel, the membranes in both plants showed the same overall performances - hydrolysis during Phase I and fouling during Phase II. This is significant because the plant configurations were not the same (as discussed earlier) and the operating conditions were different. But, the plants received the same pretreated feed water. The same overall membrane performance in each plant indicates that the feed water quality had an impact on the performance of the membranes.

In Phases III and IV, when only the SPARRO plant was in operation, membrane fouling dominated during Phase III, whereas membrane hydrolysis dominated during Phase IV.

<p style="text-align: center;">TABLE 5 SUMMARY OF MEMBRANE PERFORMANCE</p>		
Operating phase	SPARRO pilot plant	MLT plant
I - March 1989 to December 1989	<ul style="list-style-type: none"> • 2 615 operating hours • Recovery : > 90% • Extraction : 40 - 50% • Salt rejection : declining • Flux : increasing • Membrane hydrolysis • Seed concentration : 14 g/l 	<ul style="list-style-type: none"> • 4 360 operating hours • Recovery : 93% • Extraction : 20% • Salt rejection : declining • Flux : increasing • Membrane hydrolysis
II - January 1990 to August 1990	<ul style="list-style-type: none"> • 3 316 operating hours • Recovery : 93.3% • Extraction : 50 then 37% • Salt rejection : steady • Flux : decreasing • Membrane fouling • Seed concentration : 25 g/l 	<ul style="list-style-type: none"> • 4 184 operating hours • Recovery : 94% • Extraction : 20% • Salt rejection : steady • Flux : decreasing • Membrane fouling • Seed concentration : 13 g/l
III - December 1991 to February 1992	<ul style="list-style-type: none"> • 1 361 operating hours • Recovery : 80.5% • Extraction : 28% • Salt rejection : steady • Flux : decreasing • Membrane fouling • Seed concentration : 17 g/l 	Not in operation
IV - October 1992 to February 1993	<ul style="list-style-type: none"> • 1 100 operating hours • Recovery : 98 - 99% (est) • Extraction : 37% • Salt rejection : declining • Flux : slightly increasing • Membrane hydrolysis • Seed concentration : 15 g/l 	Not in operation

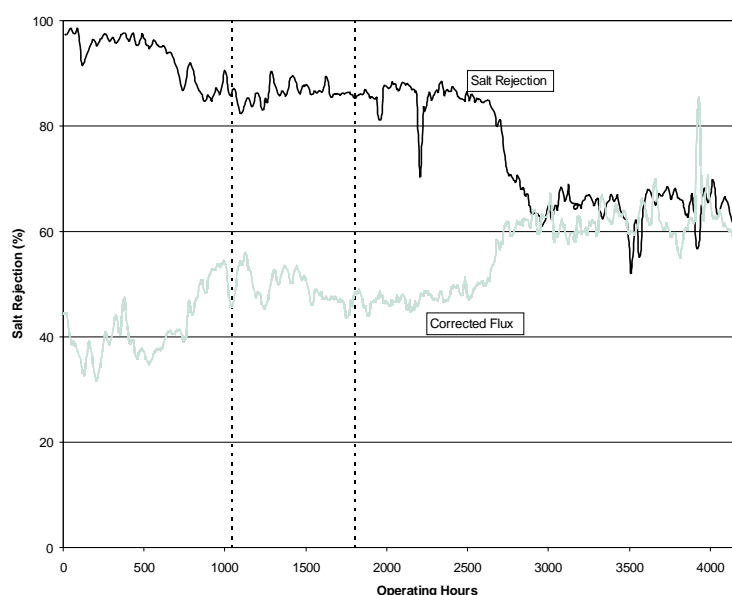


Figure 5
Variation in salt rejection and membrane flux for MLT plant during Phase I

Detailed membrane autopsies

Figure 5 shows the salt rejection and the corrected membrane flux of the MLT membranes for the Phase I operating period. The vertical dashed lines indicate the approximate times at which membranes were removed for membrane autopsies. As shown, the overall salt rejection was around 85%, while the flux was 700 to 800 l/m²-d (29 to 33 l/m²-h or Lmh), at the point at which membrane samples were taken and for the period between samples.

Figure 6 presents results of individual module surveys from selected membrane modules in the MLT plant. The figure presents the results of the salt rejection values obtained for the second row of membrane modules in the stack. The results shown are typical for each row of modules.

The salt rejection curves in Fig. 6 show that three of the four membrane modules exhibited a severe drop in salt rejection, from 90% to around 50%. The trend of declining salt rejection for these three modules appears to show two stages of decline: An initial gradual decline up to 2 300 h followed by a more accelerated rate of decline.

The fourth module in the group (module number 5) showed different performance because three different modules were used in position number 5. The first one was removed and replaced with a new module after 1 047 h, as part of the detailed membrane autopsy investigation. The replacement module was removed after 2 751 h, and a second new module was installed. The new module remained in position number 5 until the end of Phase I.

Figure 6 shows that there was a gradual decline in salt rejection of the new module in position 5 during its 1 600 h of operation. The decline in salt rejection for the module in position number 5 during the last 1 600 h of Phase I, was similar to that observed for the other three membranes during the early part of Phase I. The results suggest that in both cases a similar rate of hydrolysis was occurring.

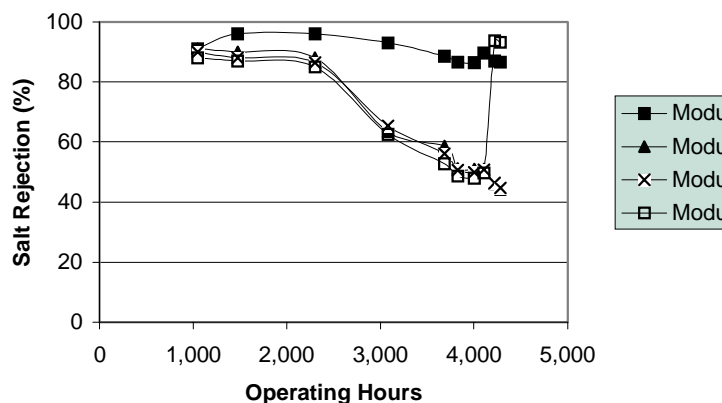


Figure 6
Results of module survey from MLT Plant in Phase I

Examination of first set of membranes

The DIC optical microscopy investigation, showed that there were marked differences between the surface of unused membranes and those of membranes taken from the MLT plant. The membranes from the MLT plant showed considerably more evidence of surface deformation due to impingement of crystals in the feed solution, compared with CA membrane samples from two other RO plants. However, there was no evidence of membrane surface puncturing (Jacobs, 1989a).

The SEM investigation showed that there was presence of non-adhering crystals on the surface of the membrane, but no evidence of fixed deposits or scale was found (Jacobs, 1989a).

The surface dye staining tests showed that the membranes from the MLT plant all had radial indentations, corresponding to the parting line between the plastic membrane tube support disks of the tubular module (Fig. 1). The unused membranes and the MLT membranes both stained a light-yellow colour; however, the MLT membranes also showed a slight red discolouration along some of the radial indentation lines. When compared with the unused membrane, it was not clear whether the red stain could be ascribed to chemical or physical alteration of the membrane surface or membrane material (Jacobs, 1989a).

In summary, the inspection of the first set of membranes from the MLT plant during Phase I showed two things when compared with unused membranes and those from other plants. Firstly, there were surface markings on the membranes, presumably caused by the recirculating seed slurry. Secondly, although not substantiated, there were indications that either chemical or physical alteration of the membrane surface or the membrane material had occurred.

Examination of second set of membranes

The second set of membranes removed from the plant had been in operation for almost twice as long as the first sample set and had also received slightly more concentrated feed water due to their positions in the membrane stack.

The DIC optical microscopy showed that the second batch of membranes had marked differences in appearance to the first batch. Radial bands (thought to coincide with the positions of the radial support rings) of up to 4 mm in width and dull in contrast to the remainder of the membrane surface extended at intervals across the length of the samples analysed (Jacobs 1989b).

As in the case of the first batch of membranes examined, the second batch also showed evidence of erosion marks caused by

particle impingement, although no evidence was found of gross structural damage to the membrane body.

The membrane surface of both modules showed evidence of deposits. Analysis of the surface deposits by EDAX showed that the deposits were not calcium sulphate in origin, but consisted of mainly aluminium and silicon (probably aluminium silicates) (Jacobs, 1989b).

When compared with the first batch of membranes examined, the results of the staining tests that were carried out on the second batch indicated some differences in the way in which the membrane stained. This was regarded as an indication that the chemistry of the membrane may have been altered (Jacobs, 1989b).

An additional test was carried out in an attempt to check whether the membrane chemistry had been altered. Unfortunately, the use of the Fourier transformed infrared (FTIR) analysis was unsuccessful due to the low emission levels obtained for the spectra. However, during preparation of the membrane samples and the control samples for the tests other observations were made. Sample preparation involved dissolving membrane films from the second batch of MLT modules, and it was observed that there were differences in solubility between the MLT membranes, freshly produced CA membranes and virgin CA 398-10 cellulose diacetate powder.

New CA membrane films and virgin CA powder dissolved in acetone and swelled in chloroform. The MLT membrane films, on the other hand, only swelled in acetone and were unaffected by chloroform (Jacobs, 1989b). This was viewed to be further evidence that the chemistry of the membranes had been modified during their 1 800 h of operation, although the extent of the modifications could not be quantified.

Discussion

Membrane autopsies

The observations made during the examination of two sets of membrane samples from the MLT plant, have two points of significance.

- The observations of surface “marking” on the MLT membrane samples, thought to be caused by the impingement of gypsum crystals on the membrane surface, was the first recorded evidence of physical contact between the slurry crystals and the membrane surface. In all previous work carried out by COMRO on seeded RO systems, microscopic examinations of membrane surfaces had shown no evidence of surface erosion. This observation may be related to the lower operating velocity of the slurry in the SPARRO-type configuration, which may enable larger crystals to get closer to the membrane surface.
- The overall performance of the MLT plant was relatively stable during the period between sampling for the two sets of membranes (Fig. 5). The average turbidity of the pretreated feed water entering the MLT plant during this period was also stable. Measurements of the performance of individual membrane modules in the MLT plant (Fig. 6), however, showed a gradual decline in the module salt rejections between 1 000 and 2 000 h of operation. This indicated that some membrane hydrolysis was occurring.

The observations by Jacobs (1989a; b), suggest that the chemical structure of the MLT membranes was different to that of new membranes and virgin CA powder. However, it is not

clear if the difference in the membrane structure was the same for both sets of membrane samples. The overall performance of the plant was more or less stable during the approximately 800 h period between taking membrane samples. The results suggest that the chemical change thought to have occurred could either have happened prior to the sampling period, or, more likely, was gradually happening at a relatively slow rate, as suggested by the measurements of the salt rejection of the individual membranes (Fig. 6).

Membrane performance

From a detailed analysis of membrane performance during the four phases of SPARRO operation and two phases of MLT operation, it is concluded that overall two opposite types of membrane performances were observed. These were performance predominantly affected by membrane hydrolysis and performance predominantly affected by membrane fouling. This is not to say that at certain times there was no fouling or no hydrolysis taking place. Rather, it seems that both were occurring simultaneously, but pretreatment and operating conditions resulted in one phenomenon dominating over the other.

No definitive statement in respect of the cause(s) of fouling and hydrolysis observed during this study could be made. However, possible causes are presented below and are discussed in more detail by Juby (1994). The suggestions below are provided in order to identify further possible research needs.

Membrane fouling

The membrane fouling that was observed and which dominated the membrane performance in Phases II and III is thought to have been caused in some way by the presence of turbidity in the pretreated mine water and the presence of free chlorine in solution. The guideline turbidity value for the pretreated raw feed water (less than 2 NTU) was selected primarily to protect the high pressure feed pumps against highly abrasive quartzitic material present in the mine water. In the initial work by Harries (1984) a nominal 50 micron cartridge filter had been used for this purpose. A turbidity of less than 2.0 NTU was chosen as a reasonable guideline value to indicate that most of the quartzitic material had been removed from the water.

However, the results of this study indicate in fact that raw feed water turbidity in tubular RO systems may be a significant factor influencing membrane fouling. Contrary to previous feed water quality requirements for tubular RO membranes operating in a slurry mode, a turbidity of greater than 1.0 NTU in the raw feed water appears to be unacceptably high. The effects of excess turbidity in the SPARRO configuration may be made worse by the high water recovery values at which the process operates.

The mechanism by which colloidal material (present as turbidity) influences fouling in the SPARRO and MLT plants, in the presence of chlorine, is proposed in the following hypothesis:

- The effects of colloid destabilisation by colloid concentration, a high positive ion concentration and concentration polarisation tends to result in an accumulation of destabilised colloidal particles near the membrane wall.
- Although the larger diameter agglomerates are positively influenced by the hydraulic shear forces of the cross-flow feed solution (Wiesner and Chellam, 1992), the oxidising environment caused by the presence of free chlorine in the water (Phases II and II when fouling dominated) results in a surface attraction phenomenon occurring between the hydrophilic

cellulose acetate membrane and the agglomerated colloidal particles.

- As product permeation continues, portions of the agglomerate are driven into the membrane, permanently blocking the pores and resulting in irreversible fouling of the membrane.
- The observed membrane fouling occurs first at the front-end of the membrane bank where the ionic concentration polarisation and the seed slurry concentration are lower than at the tail end of the plant. These conditions enable the agglomerates to accumulate near the membrane surface more easily. However, with time the probability of the agglomerates reaching the membrane surface in the tail-end regions increases and gradually the fouling "front" moves through the membrane stack.

A constituent of the slurry recycle stream which was noticeable during all four phases of operation of the SPARRO plant, and which supports the above fouling hypothesis, was a layer of light brown gelatinous solids. The gelatinous solids were observed in samples of the slurry recycle stream. When a sample of the slurry recycle stream was allowed to settle the gelatinous layer was visible on top of the white gypsum crystals. These gelatinous solids were not noticeable in the raw feed water entering the plant and were probably agglomerates formed from the colloidal material in the raw feed water.

Further evidence of colloidal fouling was the identification of a silicate deposit on the surface of a membrane taken from the MLT plant during Phase I. This was in spite of the lowest pretreated feed water turbidity of the entire study during this period.

Membrane hydrolysis

Chlorination of the pretreated feed water was started at the beginning of Phase II as a precaution against bacterial attack of the membranes. However, the membrane hydrolysis observed during Phase I was not considered to be specifically caused by bacterial action. Firstly, there was no microscopic evidence of biological matter on the membranes, and secondly a far steeper decline in salt rejection would have been expected if bacterial attack of the cellulose acetate had occurred.

Nonetheless, when chlorine was added to the pretreated feed water, the membrane performance was dominated by fouling (as discussed above), rather than hydrolysis. When chlorine was not present hydrolysis dominated.

Measurements of the performance of individual membrane modules in the MLT and SPARRO plants showed that when membrane fouling was occurring it tended to start at the front end of the membrane stack and move through the modules progressively towards the tail end, as mentioned above. On the other hand, when hydrolysis was dominating it appeared to manifest in the tail end modules and then work its way back towards the front of the membrane bank.

These observations tend to support the view that hydrolysis was caused as a result of the concentration of certain substances within the membrane stack. However, the fact that the membrane deterioration spreads towards the front of the plant suggests that it is the combination of both operating time and concentration effects that result in hydrolysis. The results indicate that if the front-end membranes were given enough exposure time at the lower concentrations near the front of the plant, they would also hydrolyse. Figure 6 provides a good illustration of how hydrolysis seems to accelerate with operating time.

The "usual" causes of membrane hydrolysis (such as wide pH variation, high temperature and bacterial attack) have been ruled out as possible major causes of the hydrolysis observed in this

study. Damage caused by cleaning solutions is not possible because the membranes were hardly ever washed. Mechanical damage, while a possibility, is not considered to be a realistic option in this case. This is because firstly, although the membrane inspections carried out by the IPS indicated that physical contact between the seed crystals and the membrane surface had occurred, the IPS observations did not show evidence of mechanical damage. Secondly, mechanical damage would have given rise to severe and sudden salt and seed leakage, which was not observed.

The only pretreatment chemicals that were used were sodium hydroxide and sulphuric acid (for pH control), potassium permanganate (as an oxidant during Phase I) and polyelectrolyte solution to aid flocculation. None of these chemicals are considered to have been a cause of membrane hydrolysis.

One possible explanation of the observed membrane hydrolysis is the presence of radioactive material in the mine water, which is discussed below.

Effect of radioactivity

Ali and Clay (1979) report that cellulose acetate is susceptible to degradation by radioactivity. The type of degradation expected could be either a significant loss of acetate groups or polymer chain scission leading to the membrane failure. Their results showed that as exposure to a radioactive source increased, both the salt passage and solute flux increased. These are the same performance changes which identify membrane hydrolysis.

The presence of radioactive isotopes in the underground workings of the South African gold mines in particular, is of concern to the mining industry. During the mining operation the radioactive isotopes are leached from the gold-bearing ores into the mine service water and they become part of the circulating salt load within the mine-water reticulation system.

The results of the sampling to assess the removal efficiency of radioactive isotopes by the membranes show two important things. Firstly, that the tubular cellulose acetate membranes operating in a seeded slurry type configuration were able to reject the radio-nuclides at high levels even when the salt rejection in terms of TDS was poor. This indicates that this process can be used effectively to reduce the concentration of radio-nuclides in mine water.

Secondly, because only a small concentration of radio-nuclides pass through the membranes, the radio-nuclides become concentrated within the RO process.

The concentration of radio-nuclides within the process to levels about five or more times greater than the raw mine water, increases the effect that their radioactive output may have on the membranes. The concentration polarisation effects that occur during RO could increase the concentration of the radio-nuclide species close to membrane by a further three to five times. It is possible that this could be a high enough concentration to have a detrimental effect on the chemical integrity of the membrane.

Based on the above, Juby (1994) carried out a theoretical calculation to establish what radioactive dose the membranes could receive. Using the assumption that concentration polarisation effects would bring the radio-nuclides close enough to the membrane surface to enable their α -radiation to penetrate the concentrated boundary layer and the membrane skin, it was shown that it would take 2 500 h for the membranes to receive a dosage of 1 rad. Taking into account that different types of radiation have different effects (Hodges, 1977), a dose of 1 rad is approximately equivalent to the amount of whole-body radiation dose received from 140 diagnostic x-ray examinations (National Academy of Sciences, 1972).

Because charged particles lose energy continuously along their paths (Friedlander et al., 1981), and because of the low penetrating power of α -radiation, most, if not all of the radioactive energy would be released within the membrane. It is reasonable to conclude that no matter how low the dose, the radiation energy would be expected to have some impact on the chemical make-up of the membrane material. The autopsies carried out by Jacobs (1989 a; b) indicated that alterations to the chemical make-up of the CA material had occurred. It will be recalled that the membranes in which the changes were noticed had only been in operation for 1 000 to 1 800 h.

Furthermore, the theoretical calculation by Juby (1994) only considered uranium (U^{238}) and not the other isotopes. Radium was definitely present in the water as well as U^{234} . Both of these isotopes have higher particle energy levels than uranium and they also emit α -radiation.

The organophilic properties of radium (Tsezos and Keller, 1983), may also be an important consideration. Adsorption of radium onto the membrane surface could increase the concentration of the radio-nuclides at the membrane surface even more than could be achieved by concentration polarisation alone. The presence or absence of free chlorine may also influence the organophilic properties of radium and may help to explain why the hydrolysis was not as severe during Phases II and III.

Based upon the results available there is no clear indication of what caused the membrane hydrolysis; however, the following issues have emerged as contributing factors:

- The hydrolysis experienced seems to be exacerbated by the **absence** of free chlorine in the raw feed water, although biological growth on the membranes was never found.
- Radio-nuclide species of uranium (U^{238}) and radium were identified in the feed water to the membranes and shown to become concentrated within the process.
- With the presence of radio-nuclides in the process water, the high operating recoveries of the treatment process and the good ionic rejection of radio-nuclides by the CA membranes, it is highly likely that the membranes received some dose of high-energy α -radiation.

Other membrane materials

Screening studies using other tubular membrane materials (such as polyamide) were started. However, due to physical problems with the apparatus these investigations were not completed.

Conclusions

SRO systems appear to offer significant advantages for the desalination of calcium sulphate scaling type waters. One of the objectives of the studies described in this paper was to determine the life expectancy of membranes in SRO systems. However, questions regarding the performance of the CA membranes have not been answered quantitatively. The work has also identified areas in which additional research may be needed in order to fully understand the fouling and hydrolysis mechanisms influencing membrane performance and useful membrane life.

The nature of the feed water used in these studies, viz. underground mine service water, introduced additional factors which might have an effect on membrane performance and membrane life. For example the presence of radioactive isotopes. Conclusions from these studies may therefore not be directly applicable to other types of feed water.

The following specific conclusions and recommendations should be considered in any potential application of the SPARRO process:

- (i) Both fouling and hydrolysis of the membranes occurred to varying degrees during the different phases of the study. A definitive statement on the causes of fouling and hydrolysis which resulted in poor membrane life expectancy cannot be made in spite of the extensive tests that were done to establish the exact causes.
- (ii) Pretreatment plays an important role in controlling fouling and hydrolysis. In order to improve the membrane life beyond that obtained in this work, removal of turbidity from the raw mine water to less than 1 NTU and chlorination to ensure a free residual of 0.5 mg/l are recommended, in addition to the other requirements of the membrane manufacturers.
- (iii) No evidence of abrasion or mechanical damage as a result of contact between the recirculating seed crystals and the membrane surface could be found. Autopsies of used membranes only showed surface markings presumably caused by the seed crystals.
- (iv) The effect on membrane structure of radioactive materials concentrated by membranes is an unknown factor that may be contributing to membrane hydrolysis and should be investigated further.
- (v) Membrane performance and the predicted membrane life of the tubular CA membranes achieved in these studies were rather disappointing. The life expectancy of the membranes under the conditions of the tests is limited to about one year. However, the membrane life of tubular CA membranes employed for SRO applications is projected to be between one and two years if optimum pretreatment of the feed water is maintained as described in (ii).
- (vi) Membrane materials other than CA may be more suitable and should be investigated.

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References

- ALI SM and CLAY PG (1979) Radiolysis of Cellulose Acetate. *J. Appl. Polym. Sci.* **23** 2893-2897.
- DIBENEDETTO PJ (1984) Options for industrial effluent control. *Proc. Int. Conf. Water Re-use Desalination*. Johannesburg, November.
- FRIEDLANDER G, KENNEDY JW, MACIAS ES and MILLER JM (1981) *Nuclear and Radiochemistry* (3rd edn.), New York: John Wiley and Sons. Chapters 3 and 6.
- HARRIES RC (1984) A Feasibility Study of the Use of Seeded Reverse Osmosis to Desalinate Mine Service Water. COMRO Research Report No. 50/84.
- HARRIES RC (1985) A field trial of seeded reverse osmosis for the desalination of a scaling-type mine water. *Desalination* **56** 227-236.
- HODGES L (1997) *Environmental Pollution* (2nd edn.) New York: Holt, Rinehart and Winston. Chapter 15.
- JACOBS EP (1989a) Analysis of COMRO Tubular CA Membranes. Unpublished contract report to COMRO.
- JACOBS EP (1989b) Analysis of Membrane Samples - Second Module Sample Set. Unpublished contract report to COMRO.
- JUBY GJG (1994) Development of a Novel Membrane Desalination Technique for Treating Calcium Sulphate Scaling Mine Water: The SPARRO Process. Ph.D. Thesis, Dept. of Chem. Eng., Univ. of Pretoria, Pretoria.
- JUBY GJG, HARRIES RC and GREIG JD (1986) Improving the quality of mine service water in gold mines in South Africa. *Proc. 2nd Int. Mine Water Assoc. Congress on Mine Water*. Grenada, Spain. Vol 1, 353-363.
- JUBY GJG, SCHUTTE CF and VAN LEEUWEN J (1996) Desalination of calcium sulphate scaling mine water: Design and operation of the SPARRO process. *Water SA* **22** (2) 161-172.
- MACKAY JG, WIECHERS HNS, PULLES W, HOWARTH D, BUSBY RW and COMBRINCK C (1991) Water quality and associated cost implications for the South African gold mining industry. *Proc. 2nd Bienn. Conf. WISA*. Johannesburg.
- NATIONAL ACADEMY OF SCIENCES (1972) Advisory Committee on the Biological Effects of Ionizing Radiations - The Effects on Populations of Exposure to Low Levels of Ionizing Radiation. National Academy of Sciences, Washington DC.
- O'NEIL TM, KIRCHNER OE and DAY WJ (1981) Achieving high recovery from brackish water with seeded reverse osmosis systems. *Proc. 42nd Annu. Meeting Int. Water Conf.* Pittsburgh, Pennsylvania, October.
- TSEZOS M and KELLER DM (1983) Adsorption of radium-226 by biological origin absorbents. *Biotechnol. and Bioeng.* **25** 201-215.
- WIESNER MR and CHELLAM S (1992) Mass transport considerations for pressure-driven membrane processes. *J. AWWA* **48** (1) 88-95.