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Report to the

WATER RESEARCH COMMISSION

on

DETERMINATION OF THE REACTION KINETICS IN A SPARRO SEED REACTOR

by

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by

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Report to the Water Research Commission on the Project
"Determination of the reaction kinetics in
a sparro seed reactor"

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PREFACE

The importance of water within the mining industry is well known. In an attempt to limit water usage, the mining industry has increased the degree to which mine service water is recycled and re-used. This has considerably reduced consumption of regional board water, but has also resulted in poorer quality of the mine service water.

The Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) process has been demonstrated to be technically feasible for improving the quality of mine service water that contains high concentrations of dissolved calcium and sulphate ions, which is the case for the majority of gold mine service waters.

The work described in this report was aimed principally at identifying the reactions occurring within the seed reactor in the SPARRO pilot plant at the COMRO test site, East Rand Proprietary Mines, Ltd (ERPM). This was in an attempt to find the reasons for the unacceptably poor membrane performance that had been observed in previous work.

The limited test work which it was possible to carry out suggests that the deteriorating membrane performance (which continued to occur) was caused rather by a combination of phenomena associated with the increasing concentration of dissolved and suspended solids as the feed slurry passed through successive rows of membrane modules. Radioactivity may be one such phenomenon. However, the work was insufficient to positively and conclusively identify the cause of deteriorating membrane performance. Further work to so identify this cause, and hence modify plant design to achieve acceptable membrane life, is essential if the SPARRO process is to be applied in full-scale plants to improve service water quality on mines.

ERPM has continued to provide support and assistance throughout the project. Stewart Scott Inc., consulting engineers, were commissioned to provide assistance with recommissioning the SPARRO plant, analysing experimental data and compiling the report.

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EXECUTIVE SUMMARY

In previous work during 1990 at the COMRO test site, East Rand Proprietary Mines, Ltd, two pilot water-desalinating plants were operated in parallel on the same pretreated raw mine water. Both plants employed the seeded reverse osmosis principle. While not identical in capacity, their configuration differed in only one respect. In the first plant, known as the MLT plant, the raw mine water was fed into the seed reactor. In the second plant, known as the SPARRO plant, the raw mine water was instead fed into the slurry recycle stream, leaving the reactor and entering the modules of tubular membranes. The membranes in the MLT plant were able to maintain a stable flux rate at the design value; however, persistent membrane fouling, indicated by flux deteriorating to unacceptably low levels, occurred in the SPARRO plant.

It was postulated that this fouling was inherently due to the difference in configuration between the two plants. Accordingly, the "contaminants" in the raw mine water causing this fouling in the SPARRO plant would not do so in the MLT plant, because the raw mine water was fed into the seed reactor. There, these "contaminants" would be encapsulated in growing seed crystals as the reject stream, also entering the reactor, desupersaturated.

The present study was undertaken to determine the reaction kinetics within the reactors, and thereby ascertain the influence of these reactions upon observed membrane performance. The above postulate would be verified by operating the SPARRO plant in the "MLT mode" (by changing the configuration accordingly), and then in the SPARRO mode under otherwise identical conditions.

Due to various delays, it was only possible to carry out limited test work. The SPARRO plant was converted to operate in the MLT mode, and two experimental analyses of reaction kinetics were performed. Upon reflection, their results pointed to a logical conclusion. This was that, in the MLT mode of operation, blending of the supersaturated reject stream with unsaturated raw mine water results in a mixture of lower supersaturation, and consequently a far slower precipitation rate. Therefore, the likelihood that any "contaminants" in the raw mine water would be trapped within the matrices of growing crystals and be removed from suspension or solution is considered to be remote. Accordingly, there appears to be little merit in pursuing the study of reaction kinetics further.

During operation of the SPARRO plant in the MLT mode, membrane performance was monitored through detailed surveys of 30 individual modules. Over 1300 hours, overall salt rejection decreased, and flux increased, gradually. Of more significance was that, of all Three Banks, the modules in Bank 1 of the tapered module stack showed the best performance; while those in Bank 3 showed the worst performance. Although there was no time available to convert the plant back to the SPARRO mode, records of operation in the SPARRO mode during early 1992 showed similar membrane degradation. Therefore, this degradation does not appear to be due to mode of operation (plant configuration), but rather to a combination of phenomena associated with the increasing concentration of dissolved and suspended solids in the feed to successive rows of membrane modules.

Radioactivity may be one such phenomenon; radionuclides appear to be almost totally rejected by the membranes, even when their overall salt rejection is poor. This is an encouraging finding, suggesting that SPARRO systems may find application in removal of radionuclides from chilled service water for drinking by workers underground.

The work done to date nevertheless remains insufficient to conclusively identify the causes of the various forms of unacceptable membrane performance that have been observed on the SPARRO plant in all tests since 1989. If the SPARRO process is to be applied in full-scale improvement of water quality on mines, further work is essential to so identify these causes and modify plant design appropriately. Accordingly, it is suggested that, as the first phase of future work, an intensive, short-duration investigation be conducted with the following aim:

> To develop a conclusive statement with regard to the effects of the presence of radioactive isotopes in the feed water on membrane degradation in particular and on the performance characteristics of locally produced tubular cellulose acetate membrane modules in general.

It is envisaged that this investigation be carried out at the existing test facility at ERPM using a modified version of the SPARRO plant with a reduced number of membrane modules. The plant need to be operated in a manner to allow for detailed monitoring of selected modules within the membrane stack, in order to establish a pattern of membrane performance relating to the degree of concentration of radionuclides and other dissolved and suspended species in the feed water, over on operating period of about 15 000 hours.

ACKNOWLEDGEMENT

The research in this report emanated from a formal collaboration between COMRO (Division of Mining Technology, CSIR) and the Water Research Commission. The title of the project was:

DETERMINATION OF THE REACTION KINETICS IN A SPARRO SEED REACTOR.

The financing of the project by the Water Research Commission and the contribution by members of the Commission and the mining industry are acknowledged.

DETERMINATION OF THE REACTION KINETICS IN A SPARRO SEED REACTOR

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1. INTRODUCTION

In 1992, the Water Research Commission (WRC) agreed to provide funds to the Chamber of Mines Research Organisation (COMRO)* to carry out a project to determine the reaction kinetics in a slurry precipitation and recycle reverse osmosis (SPARRO) seed reactor.

The reason for this study was that in previous work during 1989 and 1990 - also partially funded by the WRC, and carried out by COMRO - it had been found that there was a significant difference in the membrane performance of two different reverse osmosis (RO) pilot plants operating in the seed slurry mode. [1,2]

A review of this previous work is given in Appendix A. Briefly, the two plants were operated simultaneously on the same pretreated raw mine water. In the first plant, termed the MLT plant, the raw mine water (RMW) was fed into the desupersaturation reactor together with the highly concentrated brine leaving the membrane modules. In this reactor, there was approximately a 3-4 hour hydraulic retention time before the slurry mixture was pumped into the RO modules. In the second plant, termed the SPARRO plant, the RMW was fed directly into the slurry recycle stream pumped from the desupersaturation reactor, allowing less than one minute of mixing time before entering the RO modules. The only stream in the plant returning to the reactor was the concentrated brine stream.

The membranes in the MLT plant were able to maintain a stable flux rate at the design value of 500-600 $l/m^2.d$. However, over an operating period of approximately 3 000 hours, the flux of the membranes in the SPARRO plant persisted in dropping off to about 300 $l/m^2.d$. This indicated membrane fouling.

It was postulated[1,2] that the essential difference in configuration between the two plants - the point of feed of the raw mine water** - was in some way responsible for the significant difference in membrane flux observed. The long hydraulic retention time in the MLT plant reactor allowed "contaminants" in the mine water to be intimately mixed with the supersaturated brine. So, as desupersaturation occurred, it was thought that these "contaminants" were captured within the gypsum crystal matrix, thereby removing them from solution and preventing them from degrading membrane performance.

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** It is worth noting even here that this was by no means the only major difference between the two plants. Table A-3 in Appendix A lists five other major differences. Some of these, as discussed later, could also have contributed to the unacceptable performance of the SPARRO plant.

If such a mechanism operated in the MLT plant, there would have been no chance for it to operate in the SPARRO plant. The reasons are twofold. First, the recycled slurry into which the raw feed was mixed would already have been desupersaturated. Second, the contact time between the seed and the "contaminants" would have been too short.

It was therefore proposed that further research be conducted to determine the reaction kinetics within the reactors used, and thereby provide information that could be used to explain the differences in membrane performance observed.

2. AIMS OF RESEARCH PROJECT

In accordance with the proposal submitted to the WRC, the aims of this research project were:

(a) to determine the reactions which occur in the SPARRO seed reactor and the applicable reaction rate kinetics, through a study on a pilot seed reactor.

(b) to establish the effects of those reactions on the performance parameters (flux rate and salt rejection profiles) of tubular reverse osmosis membranes.

(c) to define the appropriate design considerations for a SPARRO seed reactor which will maximise the life of tubular reverse osmosis membranes.

Not all these aims were achieved. The kinetics of the reactions taking place within the pilot seed reactor employed could not be quantified adequately, but sufficient information was obtained to draw reasonable conclusions. The effects of the reactions in the seed reactor on membrane performance were observed for the plant operating in the MLT mode, but there was insufficient time to change operation back to the SPARRO mode and repeat these observations. It was not possible, therefore, to make a conclusive statement on appropriate reactor designs for future SPARRO plant configurations.

Nevertheless, valuable additional information emerged from the results obtained. This comprised the comparative performance of individual membrane modules within the stack, and encouraging information on the ability of the membranes to remove and concentrate radionuclides.

3. EXPERIMENTAL WORK

3.1 Pilot Seed Reactor (Kinetic Study)

3.1.1 Description

The pilot seed reactor consisted of a 500-litre plastic container mounted above the main reactor on the SPARRO plant at the COMRO test site, East Rand Proprietary

Mines, Ltd (ERPM). A variable-speed mixer was obtained and mounted above this 500 l container, and various systems of pipework were installed to allow raw feed water and brine reject to be directed to the container.

3.1.2 Monitoring

The variables that were identified as probably having the most significant effect on the kinetics and crystal growth within the reactor were:

(i) the mixing ratio between the raw feed water and the brine reject. Changing this variable would change the concentration of "contaminant" relative to the seed concentration.

(ii) the seed concentration itself, because this would determine the surface area available for crystal growth to occur.

(iii) the degree of mixing within the reactor, because this could influence the degree of contact between growing crystals and any "contaminant" in solution.

(iv) the contact time in the reactor, because this would influence the probability of the "contaminants" being held within the growing crystal matrix.

It was decided that the many other variables within the brine stream and the raw mine water would be ignored, such as the major dissolved species (Ca, SO_4, Na, Cl). The reason for ignoring these species is that in an operational plant it would be impossible to precisely control them, as the quality of the raw mine water fed to the plant constantly changes.

One variable that was altered to within a set range was the pH of the final mixture.

A problem with deciding upon a protocol for the experimental work was how to determine whether observed or reported changes in quantitative data were significant.

As each of these problem areas was addressed, it became clear that at the micro level, where changes in "contaminants" were thought to be taking place, it would be very difficult to assess such changes by observing differences in the quality of the solutions before and after crystallisation. The accuracy of the available analytical methods was just not sufficient to permit such comparisons.

Therefore, although the experimental procedure put forward in the WRC proposal stated that detailed analyses, including those of the micro constituents, would be carried out on the aqueous phase, this was found to be impracticable in the context of this study, and was therefore not done.

3.1.3 Method

Even working with four main variables poses problems with regard to the statistical significance of results. Therefore, a protocol was drawn up to establish the variance that could be expected in the study, and hence determine the number of experimental runs that would be required to provide data from which meaningful conclusions could be drawn.

According to the protocol, the determination of this variance required conducting 11 experiments in which the following were to be varied:

(i) mixing ratio (of feed to brine reject) - between 0,9:1 and 1,5:1, to simulate the variation achievable in the plant at different pass conversion levels.

(ii) seed concentration - between 5000 mg/l and 15 000 mg/l, again to simulate the possible variation over which such systems could be designed.

(iii) mixing intensity in the reactor - between 150 s^{-1} and 300 s^{-1}.

(iv) contact time in the reactor - between five minutes and 60 minutes.

The procedure proposed for these 11 variance experiments is outlined in Appendix C. The experimental procedure was complicated, and each experiment would produce five liquid samples and four solid samples for chemical analysis.

3.1.4 Delays

There were several delays with getting this experimental procedure underway. It was originally planned to operate the SPARRO plant in parallel with the Water Reclamation Plant (a project at the same site which received considerable funding from the WRC). Unfortunately, this was not possible for several reasons, two of the most important being:

- initial problems with commissioning the 500 litre pilot reactor at the SPARRO plant, and

- a shortage of mine water at the site. There was very little that COMRO could do about this, being totally reliant on the mine for water.

As the project involving the Water Reclamation Plant had the much greater funding, it was given priority at the site in terms of personnel and available water. It was only towards mid-1992, when work on this project was almost over, that water became available for the SPARRO plant and a concerted effort was made to render that plant operational again.

In contrast to previous tests in 1990 and early 1992, the plant was operated with the incoming raw mine water unchlorinated, as the chlorination stage in the Raw Mine Water (RMW) pretreatment plant was inoperative.

Even within the operating period there were delays, due primarily to mechanical failures of the pumping equipment. Upon start-up of the plant, the operating pump was one manufactured by Crown Chrome. After approximately 300 hours, this pump broke down. Investigations revealed that to overhaul the pump and restore it to working condition would cost about R7 000. The less expensive option (about R3 000) was to recommission the standby pump, manufactured by National Pumps. This, however, was not straightforward, mainly due to serious problems with the pump seals and plungers. It took approximately one month to render the plant operational again and stoppages were experienced approximately every 300 hours afterwards, when the pump had to be fitted with new seals and plungers replaced when necessary.

As a result of these delays, only two of the 11 proposed variance experiments were conducted. Nevertheless, apart from confirming the difficulty of carrying out test work of this type on an operational plant, the two experiments yielded results which appeared to be logical. The findings are discussed later.

3.2 Performance of Tubular Membrane Modules

3.2.1 SPARRO plant converted to MLT mode

Once the kinetic study had shown which variables were the most important, it was planned to operate the plant with those variables in controlled ranges, and observe the resulting effect on membrane performance.

In the interim period, until the results of the kinetic study were available, it was decided to operate the SPARRO plant in two modes - the MLT mode and then the SPARRO mode - and compare the overall performance of the plant and membrane modules.

The reason was that, as mentioned previously, the work in 1990 had led to the postulate that the unacceptable performance of the SPARRO plant might have been due to its essential difference in configuration from the MLT plant (the point of feed of the pretreated raw mine water). However, there were other major physical and operating differences between these two plants, as listed in Table A-3 of Appendix A. In the light of these other differences, this postulate had to be regarded as unverified (some of these other differences could also have contributed to the SPARRO plant's unacceptable performance in 1990).

The logical way to verify this postulate was as follows. If *one and the same plant* (here, the SPARRO plant) were operated first in MLT and then in SPARRO modes, but otherwise identically, significant differences in performance would be uniquely attributable to these two different modes of operation. Such information would be extremely valuable, enhancing the results obtained from the kinetic study.

Accordingly, the SPARRO plant was converted to operate in the MLT mode. This was a fairly simple modification which required repiping the raw mine water feed line to the reactor, and fitting a float valve onto this line to control the reactor liquid level. The plant was operated in this mode and performance data were gathered continually on a six-hourly basis. Again, it must be noted that the raw mine water fed to the plant was unchlorinated.

3.2.2 Individual module performance

In addition to monitoring the overall plant performance, 30 membrane modules in the tapered module stack were identified for closer monitoring of performance. These were nine modules each from the first and second banks, and 12 modules from the third bank.

Each module in the stack was numbered starting with the inlet row of modules in the first bank. The selected module numbers and their positions in the stack are listed in Table 1.

Table 1: Modules Selected for Detailed Monitoring, with their Positions in SPARRO Plant

MODULE NUMBER	POSITION IN MODULE STACK
2, 5, 8	Bank 1 - row 1
12, 15, 18	Bank 1 - row 2
22, 25, 28	Bank 1 - row 3
34, 36, 37	Bank 2 - row 1
42, 44, 45	Bank 2 - row 2
50, 52, 53	Bank 2 - row 3
55, 56, 57	Bank 3 - row 1
61, 62, 63	Bank 3 - row 2
67, 68, 69	Bank 3 - row 3
73, 74, 75	Bank 3 - row 4

It was aimed to carry out a survey of the performance of these modules two or three times per week. However, it was not possible to adhere to this schedule, because of the aforementioned mechanical pumping problems. Nevertheless, 11 module surveys were conducted on the selected modules, the data being used to obtain the salt rejections and fluxes of each membrane module.

All data obtained were for the SPARRO plant operating in the MLT mode. There was no time available to convert the plant back to the SPARRO mode.

4. RESULTS

4.1 Pilot Seed Reactor - Kinetic Study

As discussed above, only two of the 11 planned experiments for determining the expected variance in the study were undertaken.

Table 2 presents a summary of the experimental conditions for the two experiments, and the chemical analyses of the liquid samples are tabulated in Tables 3 and 4.

Table 2: Summary of Experimental Conditions in Kinetic Study

DESCRIPTION	EXPERIMENT NO.1	EXPERIMENT NO.2
Mixing Ratio (RMW: brine reject)	1, 2	0, 9
Seed Concentration (mg/1)	10 000	5 000
Mixing Speed (rpm)	225	300
Reactor Volume (1)	400	400
Brine Reject:		
Solids Concentration (mg/1)	8 852	8 852
Temperature (°C)	28, 5	29, 2
pH	6, 30	5, 98
Volume of Sample (ml)	500	500
Volume of dilution (ml)	500	500
Volume of filtrate (ml	990	995
Raw Mine Water (RMW):		
Temperature (°C)	26, 0	23,3
pH	5,23	6,06
Reaction Mixture:		
Volume RMW (1)	220	190
Volume Brine (1)	180	210
Mass of seed to be added (kg)	3, 7	0, 22
Volume acid to be added (ml)	5, 0	10,0
Time to add Brine (min)	4, 33	3, 87
Actual pH	6, 40	5,86
Actual solids concentration (mg/1)	17 988	4 569
Actual temperature (°C)	27, 0	26,9
Time of 1st sample (min)	5	5
Volume of filtrate (ml)	995	995
Time of 2nd sample (min)	17, 33	17, 33
Volume of filtrate (ml)	1 005	995
Time of 3rd sample (min)	45, 0	45, 0
Volume of filtrate (ml)	1 010	1 002

Table 3: Kinetic Study: Chemical Analyses of Samples Taken during Experiment 1

				Pilot Reactor		
Determined	Units	Raw Mine Water	Brine Reject	After 5 minutes	After 17, 3 minutes	After 45 minutes
pH		5,52	6,86	6,65	6,59	6,88
Conductivity	mS/m	164	319	271	264	284
TDS	mg/l	1 452	3 265	3 092	3 053	3 075
Ca	mg/l	170	412	467	467	467
Mg	mg/l	54	111	60	61	61
Na	mg/l	100	127	86	87	88
Cl	mg/l	39	38	28	28	28
NO_3	mg/l	6,6	4,7	4,7	3,7	3,8
SO_4	mg/l	781	1 994	1 787	1 775	1 809
Fe	mg/l	<0,01	< 0,01	<0,01	< 0,01	< 0,01
Mn	mg/l	2,13	3,59	2,27	2,27	2,30
SiO_2	mg/l	6,8	8,4	5,2	5,6	4,40

Table 4: Kinetic Study: Chemical Analyses of Samples Taken during Experiment 2

				Pilot Reactor		
Determined	Units	Raw Mine Water	Brine Reject	After 5 minutes	After 17, 3 minutes	After 45 minutes
pH		6,89	6,81	6,76	6,51	6,63
Conductivity	mS/m	159	310	270	274	273
TDS	mg/l	1 372	3 325	2 995	2 860	2 871
Ca	mg/l	160	422	444	429	417
Mg	mg/l	52	100	71	70	70
Na	mg/l	97	117	88	88	87
Cl	mg/l	40	37	30	30	30
NO_3	mg/l	8,5	4,7	4,7	4,7	3,8
SO_4	mg/l	854	1 938	1 798	1 742	1 725
Fe	mg/l	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Mn	mg/l	1,98	3,24	2,38	2,36	2,33
SiO_2	mg/l	8,0	6,4	6,4	7,2	6,8

4.1.1 Discussion

Bearing in mind the different mixing ratios and seed concentrations used in the two experiments (see Table 2), the results presented in Tables 3 and 4 indicate very few differences. Before discussing the results in detail, however, three factors need to be considered.

(i) The time taken for the brine reject stream to return to the reaction vessel is significant relative to the expected precipitation rate of highly supersaturated solutions. Work carried out by the CSIR for COMRO in 1987[3] revealed that the precipitation rate of highly supersaturated $CaSO_4$ solutions is very fast in the presence of seed growth sites, and that the bulk of the desupersaturation reaction is complete within a period of 2-3 minutes.

(ii) The greatest supersaturation concentration achieved in the brine reject is as it leaves the last module bank in the plant. From that point onwards it is conceivable that desupersaturation would commence and that this would be occurring at the highest possible rate. Therefore, even in the time taken for the brine stream to return to the desupersaturation vessel (less than a minute), a significant amount of precipitation could already have occurred. This does not include the time taken for the brine to pass through the last membrane modules, where precipitation could also be occurring.

(iii) It will be recalled that the SPARRO plant was operating in the MLT mode during these experiments. Thus, once the brine reject entered the reactor, it was diluted with the raw mine water. This would reduce the degree of supersaturation in the mixture, resulting in a far slower rate of reaction.

Upon reflection, therefore, *the effect of mixing raw mine water with brine reject in the reactor* (which occurs in the MLT mode of operation) *would be expected to result in a mixture with a relatively low potential for precipitation and therefore a slow precipitation rate.* The chemical constituents in solution would change only slightly, as indicated by the results.

By mass balance the expected TDS of the reaction mixture in Experiments 1 and 2 should have been approximately 2 270 mg/l and 2 400 mg/l respectively. In both cases the TDS in the sample taken after five minutes was significantly higher (3 092 mg/l and 2 995 mg/l respectively). This could indicate that possibly some seed material had even dissolved rather than precipitated. This possible indication is strengthened by the observation that both the calcium and sulphate concentrations in the reaction mixture were greater than mass balance calculations predict.

In Experiment 1, comparing the results obtained after 5, 17,3 and 45 minutes of reaction time indicates that the concentrations of the main constituents (TDS, calcium and sulphate) were virtually unchanged. This suggests that it is unlikely that any significant changes would occur at longer reaction times. In fact, it appears that the system is close to chemical equilibrium.

In Experiment 2, the results (except for the TDS) show a consistent drop in the concentration of the main constituents between the first and third samples, indicating that precipitation could still have been occurring.

These results appear to be logical, as for Experiment 1 the mixing ratio (feed:brine reject) was 1,2:1, and for Experiment 2 it was 0,9:1. In Experiment 2, therefore, the dilution effect of the raw mine water was less, and so the saturation concentration of the mixture remained high enough for precipitation to continue, albeit slowly.

Experiment 1 corresponds to the conditions in an MLT-mode plant operating at 95 per cent water recovery and a pass conversion of just over 50 per cent. Experiment 2 corresponds to the same plant operating at the same water recovery, but with a lower pass conversion of approximately 45 per cent.

These experiments throw additional light on the previous work of 1989 and 1990, when the old, separate MLT plant was operating. The pass conversion which could be achieved on that plant averaged 20 per cent; therefore, the degree to which the brine reject stream could become supersaturated was limited to about 125 per cent, which is not particularly high. The dilution effect of raw mine water being added to the brine reject stream would have reduced the saturation still further. Therefore, in hindsight it could be expected that in this old MLT plant - which operated in the MLT mode at low pass conversion rates - the rate of crystal growth in the reactor was small, and therefore the potential for the growing crystals to encapsulate "contaminants" in the mine water was also small.

The third mixing ratio that was to be tested was 1,5:1. The results obtained for Experiment 1 (mixing ratio 1,2:1) suggest that the rate of crystallisation for a mixing ratio of 1,5:1 would be even slower. Therefore, it appeared that further experiments would not alter the conclusion suggested by Experiments 1 and 2. This was that within the operating range for full scale plants - i.e. pass conversions of greater than 30 per cent - the effect of mixing the raw feed with the brine reject in the MLT mode of operation is to dilute this brine reject, and hence to significantly decrease the rate of crystallisation in the reactor. At this slower rate of crystallisation, the change in the macro constituents of the liquid phase would only be small (as shown by the results) and consequently the change in the micro constituents could be expected to be even smaller.

In summary, in a seeded RO plant where firstly a significant amount of precipitation is likely to occur before the brine reject stream mixes with the raw mine water, and secondly where the mixing of these two streams results in a lowering of the rate of precipitation, it is unlikely that growing gypsum crystals would encapsulate a significant amount of "contaminants" from the mine water.

4.2 Performance of Tubular Membrane Modules

Since 1989, the SPARRO plant has achieved a total of 9 300 hours of operation, approximately 1 300 hours of which has been related to the present study. Throughout this latter period, the plant was operated in the MLT mode with raw feed water entering the reactor vessel.

4.2.1 Overall plant performance

The variation in overall membrane flux for the entire plant is shown in Figure 1. This flux is corrected to 4 000 kPa and 25°C. As can be seen, the high overall flux in the plant at the start of the period (800 - 1000 $l/m^2.d$) indicates the generally poor quality of the membranes. The general trend in plant flux was fairly stable, varying between 800 - 1000 $l/m^2.d$, until about 9 200 hours, when a distinct drop in flux is shown. This drop in flux corresponds to the removal of the last two rows of membrane modules from the plant because their salt rejection was unacceptably low.

The product recovery for this period averaged approximately 98 - 99 per cent.

The variation in overall membrane salt rejection, calculated from the six-hourly conductivity readings, is shown in Figure 2. As can be seen, there was a gradual decrease in the overall salt rejection of the plant over the 1 300-hour operating period. The rejection started at approximately 65 per cent and dropped to approximately 60 per cent.

The flux and salt rejection values for the plant indicated fairly stable operation over the last 1 300 hours, albeit at a decreasing salt rejection and a high overall flux. Such conditions point to the occurrence of membrane hydrolysis or structural damage.

4.2.2 Individual module performance

At the start of the present investigation, the SPARRO plant had a total of 78 modules, in three banks, in its tapered module stack. However, only 64 modules were operational; the remainder had been valved off due to blockages or poor performance. As already mentioned, 30 operational modules were selected for detailed observation during the study. These were nine modules each from the first and second banks of the stack and 12 from the third bank.

Figure 3 presents the variation in salt rejection of a selected membrane module in each row of the membrane stack. As can be seen from the figure, there was a trend of decreasing salt rejection for all modules. Furthermore, the salt rejection dropped between each bank of membranes in the stack, being between 80 and 95 per cent in the first bank, between 60 and 85 per cent in the second bank and below 75 per cent in the third bank.

Figure 1 : Variation in Corrected Membrane Flux

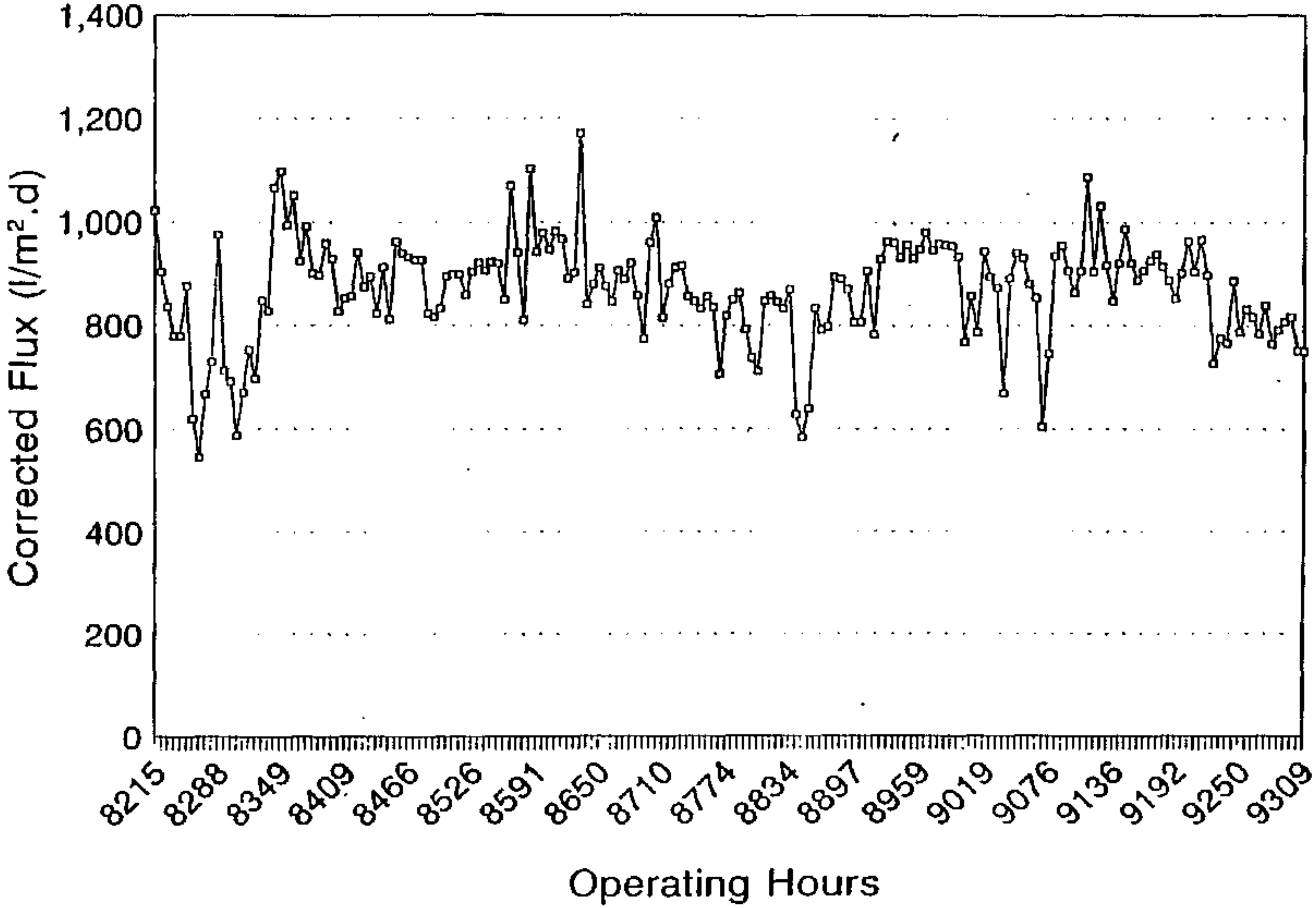


Figure 2 : Variation in Membrane Salt Rejection

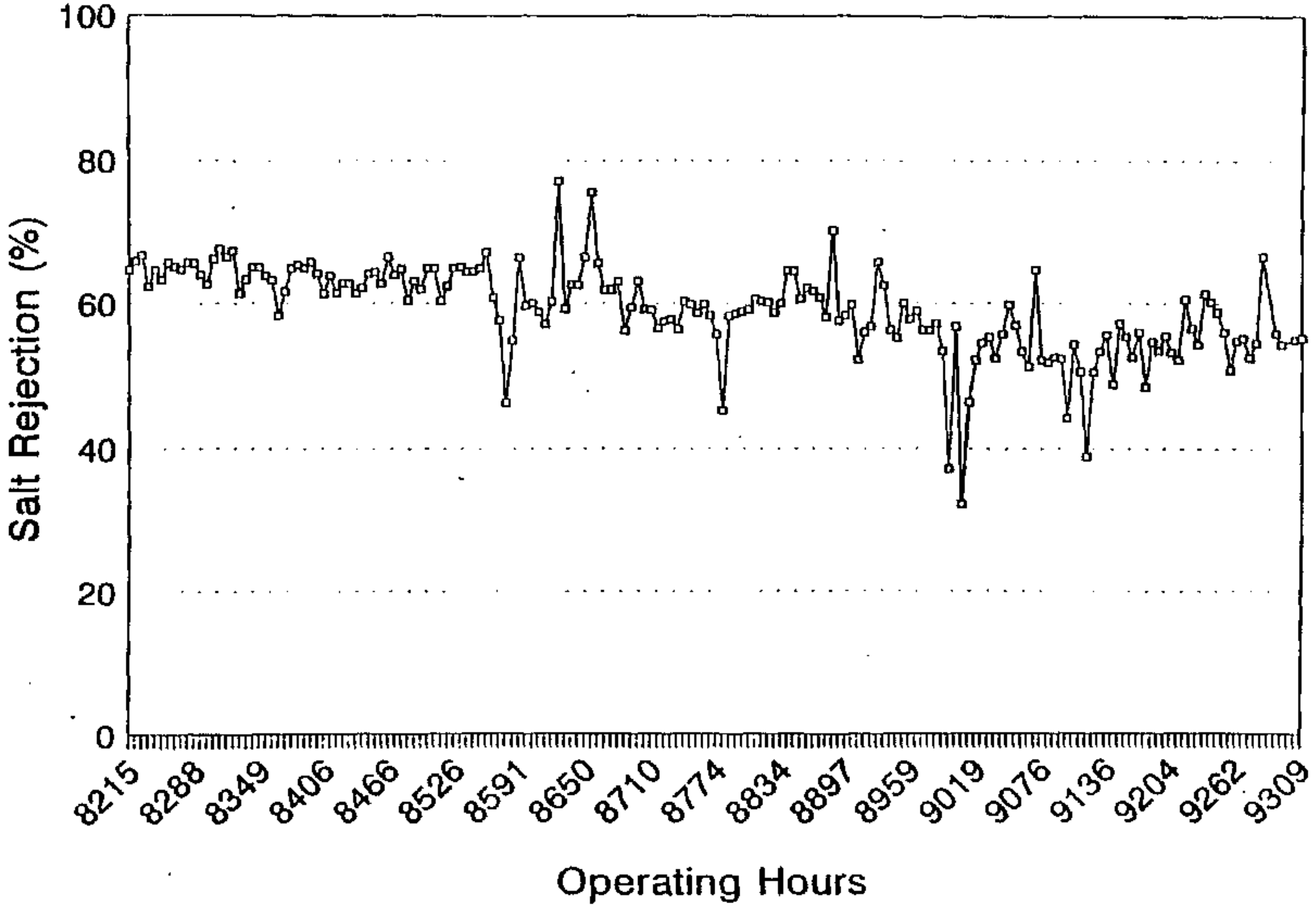


Figure 3 : Selected Module Salt Rejection

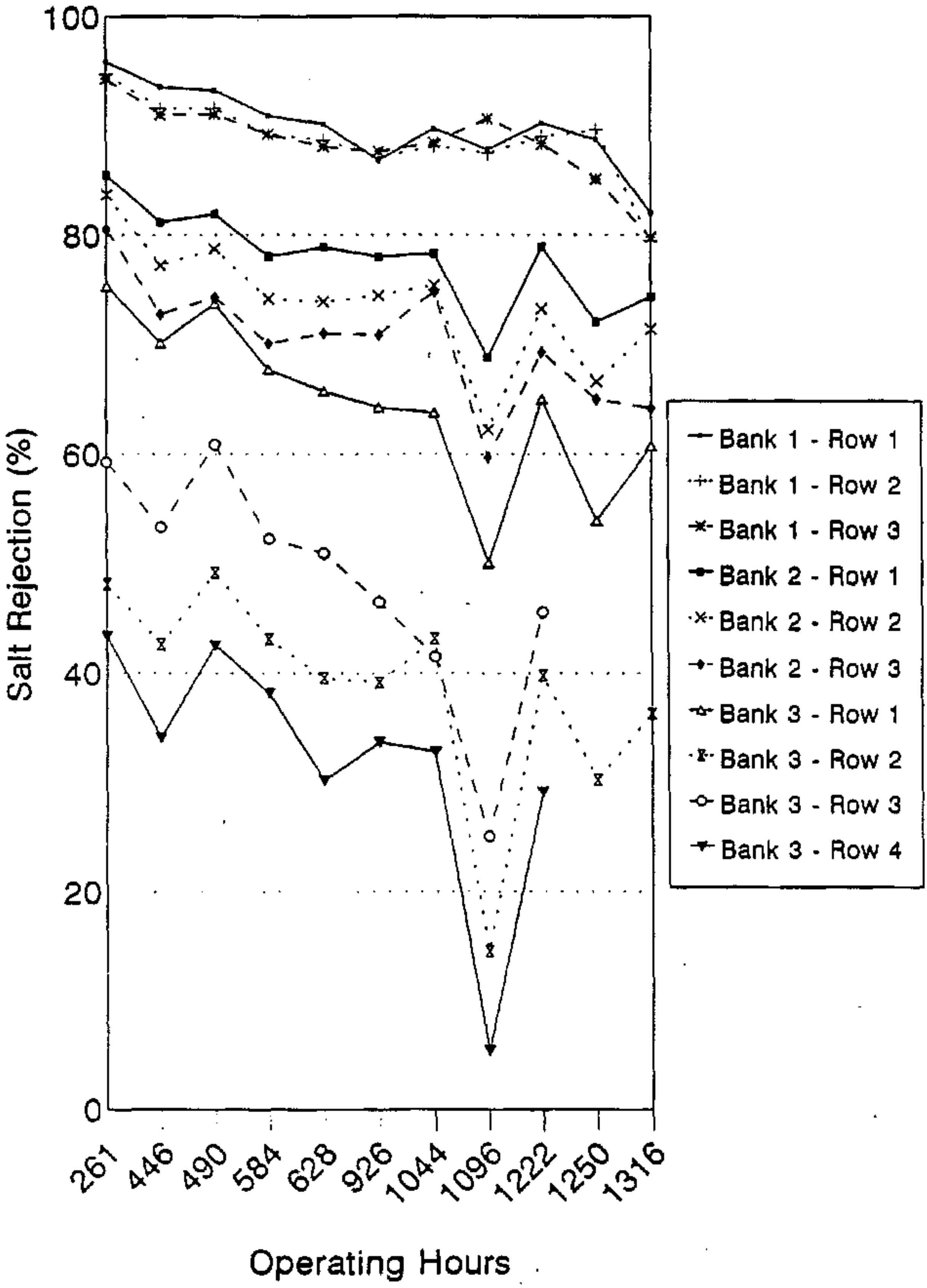


Figure 4 presents the variation in membrane flux (corrected to 4 000 kPa and 25 °C) for each of the same membrane modules. Here there was a tendency towards increasing flux with operating time, with the degree of flux increase being more pronounced in the third module bank.

Looking at the first module bank in isolation shows that it contained the modules with the best salt rejection (80 - 90 %) and the steadiest flux (500 - 600 $l/m^2.d$). These modules could be considered to be equivalent to those in the old MLT plant. In other words, if these modules were the only ones in the plant the perception could be that the membrane performance was reasonably good (considering they have over 3 000 hours of operation). However, the performance of the membranes appeared to change in significant steps from good in the first bank, to poor in the second bank, to very poor in the third bank. The only variable that was different in the three module banks was the quality of the feed water. It became more and more concentrated as it passed through successive rows of modules.

Although there was a general downward trend in module performance from the first row to the last, the results show that the deterioration occurred faster towards the back end of the module stack. What is important is that the results also indicate that, given sufficient time, the modules in the first and second banks would also deteriorate similarly. It can be seen from Figure 3 that, at the end of the 1 300-hour period, the salt rejection of modules in the first bank had dropped to values similar to those in the second bank at the start of this period.

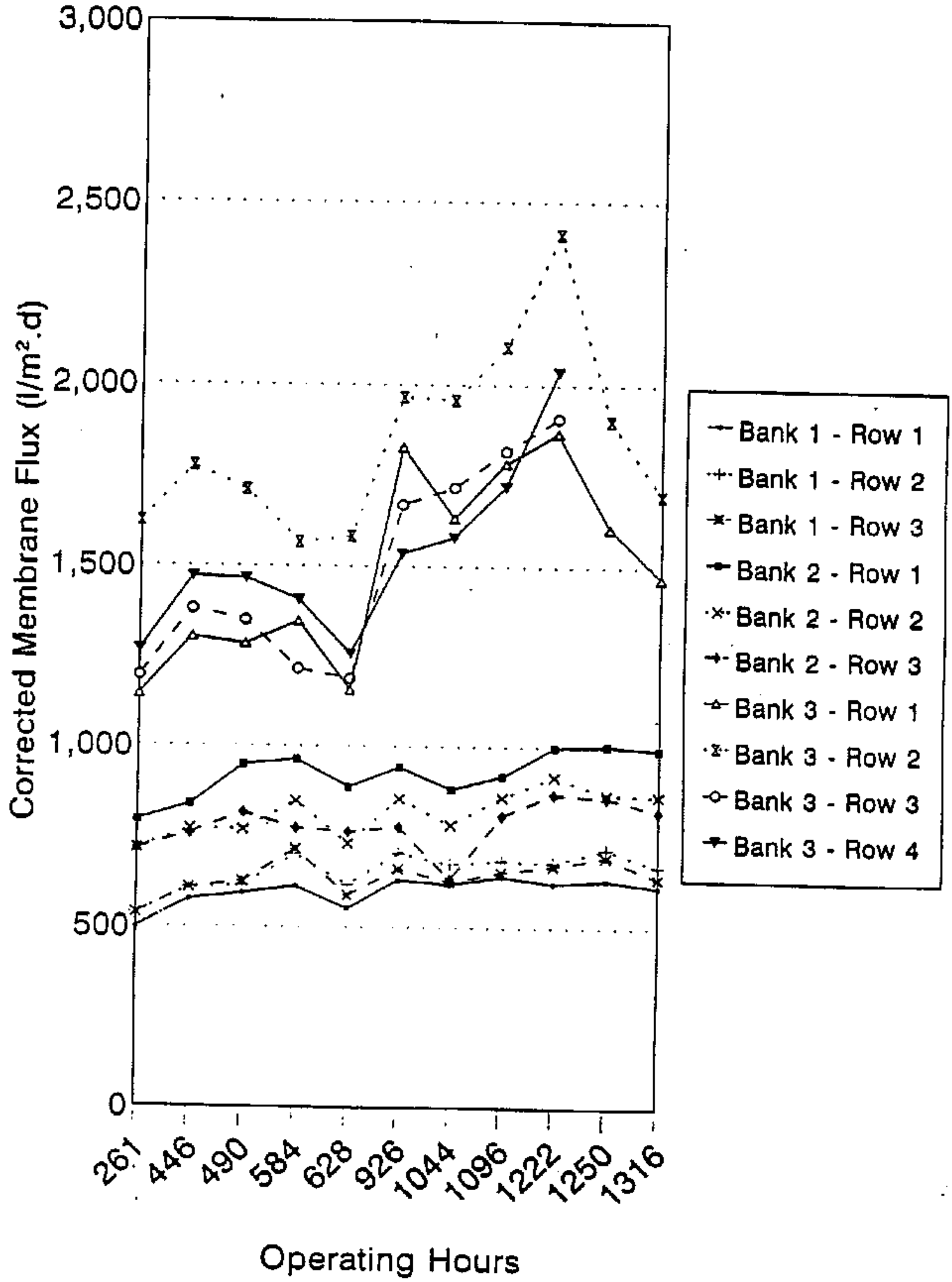
The drop in membrane salt rejection and the simultaneous increase in membrane flux indicated that the structure of the membrane was being affected. It appeared that the membranes had become more porous, allowing larger volumes of permeate to pass through them (increased flow) and a larger degree of salt leakage (decreased salt rejection). However, the present membranes have not ruptured and still retain all the suspended seed material.

5. DISCUSSION

All the work conducted by COMRO on seeded reverse osmosis systems to date (since 1984) has shown that the concept of seeding to prevent scale formation in RO processes is technically viable. The problem areas throughout this period have in general been the pumps and the poor membrane performance in terms of expected membrane life.

The pumping problems have not yet been overcome. To some extent this has been because of the relatively small capacities of the test plants. With the small flow rates involved, it has been difficult to select commercially available pumps that are optimally sized for the required duties. However, with a great deal of perseverance the operating personnel have managed to keep the pumps, and therefore the plants, operational. The pumping problems are not insurmountable; however, the interest shown by pump manufacturers in the pilot studies has been minimal. If and when a larger-scale plant is constructed, the interest shown by these manufacturers is expected to be much greater, and this should help to solve the pumping problems.

Figure 4 : Selected Module Flux



The poor membrane performance is another issue altogether. The membranes are the essence of the process, and degradation of the membranes in a short period of time (six months) would not be acceptable.

It is recalled here that the overall objective of this study was to investigate precipitation reactions occurring in the seed reactor of a SPARRO system, in an attempt to identify the mechanism causing membrane deterioration and hence identify practicable methods that could be used to overcome it.

5.1 Experimental Results in Kinetic Study

The results obtained from the limited number of experiments conducted in the kinetic study appear to be consistent with what would conceptually be expected when mixing a highly saturated solution with an unsaturated one. They indicate that, although precipitation could still occur after such mixing, it would be at a slow rate. Therefore, the likelihood that "contaminants" would be trapped within the growing crystal matrix seems low because of the slow rate at which the crystals would grow.

If operating the SPARRO plant in the MLT mode were to reduce the concentration of "contaminants" in the mine water significantly and thereby reduce membrane degradation, it could be expected that, once in the MLT mode, the membrane performance within the plant would stabilise.

The results obtained for the overall performance of the plant - as well as the performance of the individual membrane modules over a 1 300-hour period - show the opposite. Membrane degradation has continued in the MLT mode. Unfortunately, there was no time to switch the operation back to the SPARRO mode so that a direct and conclusive comparison could be made. Nevertheless, it is clear that the membrane performance did not stabilise or improve.

5.2 Performance of Tubular Membrane Modules

Interestingly, some comparative information on operation of the plant in the SPARRO mode was available from operating records of early 1992, before the present study commenced. The performance of the plant in early 1992 is fully described in Appendix B. Briefly, the plant was operated then because its product water was required for the Water Reclamation Test Plant (see Section 3.1.4 above). Operation was in the SPARRO mode. During January and February 1992, the performances of individual rows of modules were surveyed. Overall plant performance was stable; however (as for the present study), membrane performance worsened progressively from Bank 1 to Bank 3 of the tapered module stack, with increasing flux and decreasing salt rejection. That is, membrane degradation, similar to that observed when operating in MLT mode in the present study, occurred nine months earlier when operating in the SPARRO mode.

Table 5 provides a summarised record of all tests carried out on the SPARRO plant since its commissioning in July 1989. In all, there were four tests.

Test No.	Period	Reference
1	July - Dec. 1989	Appendix A
2	Jan. - Aug. 1990	Appendix A
3	Jan. - Feb. 1992	Appendix B
4	Oct. 1992 - Feb./Mar.1993	Present study

Table 5 summarises the key events in each of these tests, together with the average pass conversion and overall water recovery. The key inlet conditions are also listed. From examination of this table, the following may be noted.

5.2.1 Comparison of tests of 1990 and early 1992

In these two tests (Tests 2 and 3), the feed water was chlorinated, and the only significant difference in operating conditions was the lower pass conversion of Test 3 (30 per cent vs 35 per cent). In both tests, the plant operated in the SPARRO mode. Yet membrane performance deteriorated in fundamentally different ways. In Test 2 (1990), salt rejection was stable, but fouling (indicated by flux decreasing over time) was experienced twice. In Test 3, no fouling was experienced, and plant performance was stable over time. Salt rejection decreased, and flux increased, progressively from Bank 1 to Bank 3 of the module stack.

If, as postulated, the fouling experienced by the SPARRO plant in 1990 had been due to its essential difference in configuration from the MLT plant (the feed of raw mine water directly into the modules, instead of into the reactor where "contaminants" were removed in some way) fouling should also have occurred in Test 3. It did not, and thus this postulate must still be regarded as unproven.

5.2.2 Comparison of tests of early 1992 and present study

Test 3 (early 1992) used chlorinated water in the SPARRO mode. Test 4 (the present study) used unchlorinated water and operated in the MLT mode. Yet similar membrane degradation, progressively worsening from Bank 1 to Bank 3 of the tapered module stack, occurred. The symptoms of degradation, increasing flux and decreasing salt rejection, indicate membrane hydrolysis or structural damage.

In both tests, the significant point is that degradation worsened between successive banks. Of course, the feed to the modules becomes more concentrated in TDS from Banks 1 to 3. Furthermore, this TDS appears to be the only variable which changes significantly between banks. Therefore, both tests suggest that some combination of phenomena associated with increasing TDS in module feed was causing the membrane degradation observed.***

If the membranes had indeed been structurally damaged, such damage could have been caused by chemical attack, mechanical erosion by the flowing slurry, or a combination of these and other phenomena. One such other contributory phenomenon could have been radioactivity in the mine water.

*** The more pronounced degradation in Test 4 may be due to the pass conversion being 45 per cent, which was considerably higher than for Test 3 (30 per cent).

Table 5: Summarised Record of All Tests Carried Out on SPARRO Plant

				INLET CONDITIONS				
TESTS AND PERIOD THEREOF	SUMMARY OF EVENTS	AVERAGE PASS CONVERSION (%)	OVERALL WATER RECOVERY (%)	MODULE INLET PRESSURE (kPag)	SEED CONC. IN FEED WATER (mg/l)	FEED WATER CHLORINATED?	FEED WATER TEMP. (°C)	FEED WATER pH
Test 1: July to Dec. 1989	Mode of operation: SPARRO; all 88 modules in all 4 banks. Modules were not all new; some had previously been used by ISCOR. Total operating hours: 2 615 Flux and salt rejection continually worsened during operation. Start / End Corrected flux ($l/m^2.d$): 950 / 1 850 Salt rejection (%): 70 / 29 Modifications made to raw mine water pre-treatment plant: Nov. 1989: chlorination stage added Dec. 1989: removal of trace (end) metals (Fe, Mn) discontinued	?	?	?	?	NO until November 1989 YES (Nov. & December 1989)	?	~6
Test 2: January to August 1990	Mode of operation: SPARRO; all 88 modules in 4 banks completely renewed. After 500 hours, 4th bank of 10 modules was decommissioned due to high flux, low rejection. Damage was attributed to excessive $CaSO_4$ supersaturation in 4th bank. Afterwards, plant was operated with 78 modules in 3 banks for a total of ~3 300hours. Hours / Flux / Rejection 0 / 550 / 91% ~1 600 / <300 / same Fouling was indicated. Membranes were washed with Biotex and citric acid. Hours / Flux 1 600+ / 400 ~2 000 / <300	50 (4 banks) 35 (3 banks)	95	4 000	22 000	YES	27 (design)	~6

Table 5: (cont.) Summarised Record of All Tests Carried Out on SPARRO Plant

TESTS AND PERIOD THEREOF	SUMMARY OF EVENTS	AVERAGE PASS CONVERSION (%)	OVERALL WATER RECOVERY (%)	INLET CONDITIONS: MODULE INLET PRESSURE (kPag)	SEED CONC. IN FEED WATER (mg/1)	FEED WATER CHLORINATED?	FEED WATER TEMP. (°C)	FEED WATER pH
Test 2: January to August 1990 (cont.)	Flux then increased suddenly to 400 1/m².d after seed conc. fell to <10 000 mg/l. Rejection fell to ~85%. Membranes were renovated : no further flux increase. Rejection was restored to >90%. Thereafter, flux again declined to <300 1/m².d.	35 (3 banks)	95	4 000	22 000	YES	27 (design)	~6
Test 3: December 1991 to April 1992	Mode of operation: SPARRO; 78 modules, 3 banks. All these 78 modules were replaced. Some in 2nd bank came from old MLT plant; the rest were brand-new. Total operating hours: 1 120. Over this period, performance was stable; overall rejection was ~82%. However, module surveys showed: Bank 1 Bank 2 Bank 3 Flux increasing Rej. maintained decrease	~30	?	2 200 2 500	?	YES	?	?
Test 4: October 1992 to Feb./ March 1993	Mode of operation: MLT MODE! Only 64 modules in 3 banks were in operation. Total operating hours: 1 300. Overall performance was fairly stable: high overall flux, slowly decreasing at rejection. Individual module surveys showed: Bank 1 Bank 2 Bank 3 Flux increasing Rej. decreasing After ~2 900 hours; last 2 rows in 3rd bank decommissioned, salt rejection too low.	~45	98 - 99	~3 000 Slightly greater during last 400 hours	~20 000 at first during last 400 hours, ~10 000	NO	27	~6

5.3 Possible Influence of Radioactivity on Membrane Degradation

Recent chemical analyses of liquid samples taken from the SPARRO plant indicate that there are significant concentrations of uranium (U^{238}) in the recycled slurry and brine reject. In these samples, the U^{238} concentration in the feed to the modules and brine reject from the modules was 588 μg/l and 920 μg/l respectively. A sample of product water analysed showed a relatively low concentration of U^{238} (30 μg/l), indicating that this radionuclide is rejected effectively by the membranes, even when their performance is poor.

A sample of the seed taken from the reactor showed no sign of radioactivity or any detectable concentration of U^{238}. This indicates that the radionuclides are concentrated within the SPARRO process and can only be effectively removed from the system during purging of the concentrated brine solutions, such as from the cyclone underflow and overflow.

It is reported in the literature that cellulose acetate (CA) is susceptible to degradation by radioactivity[4]. It is stated that the type of degradation expected could be either significant loss of acetate groups or chain scission, leading to the point where failure of the membrane takes place. Tests were reportedly carried out at high dosages of radioactivity, and it was shown that as a result the membranes ruptured.

It is well known that in RO systems the effect of concentration polarisation can increase the concentration of ionic species close to the membrane surface, typically by three to five times. This implies that the concentration of radionuclides in contact with membranes treating mine water may be large enough to detrimentally affect the integrity of the membrane.

Due to the concentrating effect of the radioactivity within the membrane stack, the membranes at the front of the stack would take longer to receive a given dose of radioactivity. It thus stands to reason that, if radioactivity is a cause of the membrane deterioration being experienced in the study on the SPARRO plant, then the performance of the membranes would deteriorate progressively from the inlet side of the stack to the outlet. This is precisely what the results have shown. The high values of flux indicate membrane hydrolysis to which radiation could be contributing. Of course, the concentrating effect through the membrane stack also applies to other soluble and insoluble (seed) components, which indicates that several phenomena could be contributing to the membrane degradation observed.

In order to prove or disprove the influence of radioactivity, considerably more analyses (for radioactive components of the solutions in the plant) would be required. Furthermore, a detailed hydraulic analysis would have to be undertaken to determine the degree of concentration polarisation experienced in a system such as this, particularly in view of the complicating factor of the presence of a slurry of $CaSO_4$ crystals. In addition, a method of accurately assessing the radioactive dosage received by the membranes would need to be developed. It is conceivable that a correlation between membrane performance and radioactive dosage received could be found.

The gold mining industry has undertaken a large survey of the extent of radioactivity in mine service water being circulated underground in mines. The results indicate the definite need for establishing an efficient method by which the radionuclides can be removed from this water to minimise the potential health risk to workers when drinking chilled service water underground. The above-mentioned water samples taken from the SPARRO plant indicated, in brief, that even when the overall salt rejection of the membrane modules declined to a poor 60 per cent, they were still able to reject U^{238} by up to 98 %. This encouraging finding suggests that, firstly, the membranes may have a far longer acceptable operating life in terms of radionuclide removal compared with TDS removal, and secondly that it may be possible to use more porous nanofiltration membranes for the removal of radioactivity. These could still be operated in the SPARRO mode, but at lower pressures and therefore at lower operating costs.

6. CONCLUSIONS

Based 1 300 hours of plant operation, the following conclusions were drawn.

6.1 Kinetic Study

Even with the limited extent of the test work, the results obtained indicated the following.

(i) Due to the limits of the accuracy with which the laboratory was able to analyse aqueous samples, it was only possible to make qualitative assessments of what was occurring to the macro constituents of the reaction mixture.

(ii) The influence of the time required for the highly concentrated brine reject stream to flow from the modules to the reactor is likely to be significant in the overall precipitation process.

(iii) The effect of mixing raw mine water and brine reject in the MLT mode of operation was that the supersaturation concentration with respect to $CaSO_4$ was reduced significantly. Therefore the rate of any precipitation reactions was reduced commensurately. The likelihood that any "contaminants" in the raw mine water would be trapped within the matrix of the growing crystals and be removed from solution is accordingly considered to be remote.

While the initial motivation for this work was justified, the two experiments that were conducted have shown the limitations of this approach, and have indicated that the possible removal of "contaminants" from the raw mine water feed by operating in an MLT mode is unlikely to be significant.

Therefore, continuing with this kinetic study to complete the work proposed therein is considered to be unwarranted.

6.2 Performance of Tubular Membrane Modules

6.2.1 Overall plant performance

The SPARRO plant has operated in the MLT mode for approximately 1 300 hours. Monitoring of the overall membrane performance in terms of salt rejection and flux has taken place.

Generally the performance of the plant was steady (apart from the mechanical problems with the pumps and the need to replace plungers and packing material quite frequently). However, gradual deterioration in membrane performance continued.

This supports the indications from the results of the kinetic study that changing the plant to operate in the MLT mode would be unlikely to improve the performance of the membranes.

6.2.2 Individual module performance

Monitoring of 30 selected modules in the membrane stack while operating in the MLT mode showed a distinct decrease in salt rejection and increase in membrane flux throughout the period. The modules in the first bank showed the best performance, those in the second bank were worse and those in the third bank were worse still.

Similar degradation occurred in a previous test, carried out in early 1992 in the SPARRO mode. Both these tests therefore suggested that a combination of phenomena associated with the increasing TDS in the feed to successive banks of modules was damaging the membranes.

In this previous test of early 1992, no fouling occurred; yet operating conditions were not markedly different from the earlier test of 1990, where fouling did occur. This does not lend support to the postulate that the fouling of 1990 was inherently due to operation in the SPARRO mode instead of the MLT mode. This postulate must still be regarded as unproven.

In view of the results obtained while operating in the MLT mode, it is believed that a comparison of the performance of the same selected membrane modules while operating in the SPARRO mode for a similar length of time would be conclusive. It would prove or disprove the above-mentioned postulate, and reveal useful design data.

Measurements of the concentration of one of several radionuclides in the feed solution and concentrated brine reject suggest that exposure of the membrane to radioactivity may be contributing in a significant way to the observed degradation in membrane performance. This should be investigated further.

6.3 Appropriate Designs for SPARRO Seed Reactors

One of the objectives of this work was to define appropriate design considerations for a SPARRO seed reactor, in order to maximise the life of tubular reverse osmosis membranes.

Accomplishment of this objective relies upon the successful determination of the cause of membrane deterioration in the process. The results obtained in this study suggest that the postulate that, in the MLT mode of operation, reactions in the desupersaturation reactor with the incoming raw feed water could in some way prevent membrane deterioration is unlikely to be correct. Consequently, it would be premature to make a conclusive statement regarding design of seed reactors for maximum membrane life, and the objective remains unaccomplished.

6.4 General

The results obtained during this study and the findings of previously unreported data from the SPARRO plant operation during 1991/1992, in which no membrane fouling was observed, indicate that there are no clear advantages (from a membrane performance point of view) to operating a seeded slurry RO system in the MLT mode as opposed to the SPARRO mode.

7. ADDITIONAL INVESTIGATIONS FOR CONSIDERATION

Based upon the findings presented in this report, it is clear that the issue of poor membrane performance and degradation that has been observed in the SPARRO process remains unresolved. To-date, all investigations have been primarily process-oriented relating to issues such as pumping methods, seed concentrations, feed velocities, layout of the membrane stack, design of the seed reactor, etc; while the performance of the membranes has been largely of a general and observed nature.

It now appears that the research has reached the point where detailed investigations of the membranes are required in order to address the problem of poor membrane performance and degradation.

As mentioned in the report, one possible cause of the observed membrane degradation is the presence of radioactive isotopes (radionuclides) in the mine water being treated. The concentrating effect which occurs within the membranes as a result of reverse osmosis means that the membranes at the front end of the stack are exposed to a lower concentration of possible contaminants than those at the end of the stack. This effect coupled with the well known phenomenon of concentration polarization could concentrate radionuclides present in the bulk solution by a further three to five times at the membrane surface, increasing the possible exposure levels to radiation that the membrane could receive.

The motivating factors for additional investigations are as follows: firstly, the mining industry may face a potentially serious problem due to the presence of radionuclides in their mine service waters. A method to efficiently remove these contaminants from chilled service water, which may be consumed by miners, is now an important issue in the industry. Secondly, the SPARRO process has demonstrated that, even with membranes which have poor salt rejection properties, excellent rejection of radionuclides can be achieved.

The implication to the mining industry of membrane degradation caused by the presence of radionuclides could make treatment of these waters by processes using synthetic media (electrodialysis, reverse osmosis, ion exchange) very difficult and costly.

The proposed work has one major objective in mind: to develop a conclusive statement with regard to the effects of the presence of radioactive isotopes in the feed water on membrane degradation and performance characteristics of locally-produced cellulose acetate membrane modules.

7.1 Method

The proposed research does not relate to process issues, but centres around the influence of radionuclides on the performance of membranes. In previous work there have been a considerable number of variables that could influence the performance of the membrane. Therefore in this study it is proposed to reduce that number considerably and concentrate on the issue of radionuclides.

This would be achieved by utilizing the existing infrastructure at the ERPM site and by operating a pilot plant on mine water containing different concentrations of radionuclides.

The aims of the proposed research would therefore be achieved by:

7.1.1. Recommissioning the Sparro plant

i) Re-calibration of the flow, temperature and pressure measuring instrumentation on the pilot plant which has not been carried out since 1989-1990. This is critical to monitoring membrane performance.

ii) Modifying the plant to be able to operate at reduced flow rates so that the size of the membrane stack can be reduced from the present 75 modules to about 35.

iii) Re-training of the existing operating staff and training of new operators who would replace some of the old staff.

iv) Recommissioning of the plant.

7.1.2. Operating the Pilot Plant

i) Replacing the existing modules in the pilot plant with "new" refurbished modules from Membratek/Debex and operating the plant on mine water at various concentrations of radionuclides.

ii) Regular monitoring of the overall plant salt rejection, membrane flux, and radionuclide content of product water and brine.

iii) Similar regular monitoring of selected membrane modules within each row of the membrane stack to establish a pattern of membrane performance within the plant. The position of membrane modules in the stack has been shown to influence its performance and rate of degradation.

iv) Removing and analysing membrane modules from each module bank both before and after the operating period for:
- evidence of erosion
- evidence of scaling
- acetate concentration (evidence of hydrolysis)
- evidence of bacteriological growths
- presence of radionuclides

v) Operating the plant for an anticipated period of about 500 hours at the different radionuclide concentrations in the feed water. This operating period is based on previous work carried out in 1990 in which degradation of the tail-end modules occurred within this period. A total operating time of 1 500 hours is envisaged.

7.2 MOTIVATION FOR CONTINUED RESEARCH

The practicalities of the application of the SPARRO process need to be realistically assessed. There is no doubt that this technology is expensive from a capital point of view. Its operating costs are also high, a major portion of which are allocated to the cost of membrane replacement (greater than 50 per cent based on a 2 year membrane life). With the present uncertainties surrounding the cause(s) of membrane degradation it would be unwise to make a definitive statement with regard to expected membrane life at this point. Consequently, under the present circumstances, it would not be possible to recommend the use of this process at any scale larger than pilot scale or semi-tech scale. Nevertheless, the scope for the application of this process remains great and is increasing as the mining industry becomes more pressurised to improve the quality of mine service water re-circulated and being re-used within the mines, and to manage environmental pollution resulting from it's wastes.

Realistically therefore, there would appear to be two choices available with respect to further research. The first is to discontinue the research and to accept that there are technical issues that have been unresolved and that it is unlikely that the process would ever be applied. This means that all the development costs spent since 1986 on seeded RO systems would not have produced a definitive statement on this technology.

The second option is to focus research effort at clearly identifying the reasons for, and causes of, membrane degradation in order to obtain a definitive understanding of the problem. When the cause of degradation has been identified then possible solutions can be sought in order to make the process more economically viable.

One possible cause of the observed membrane degradation is the presence of radioactive isotopes (radionuclides) in the mine water being treated. The concentrating effect which occurs within the membranes as a result of reverse osmosis means that the membranes at the front end of the stack are exposed to a lower concentration of possible contaminants than those at the end of the stack. This effect coupled with the well known phenomenon of concentration polarization could concentrate radionuclides present in the bulk solution by a further three to five times at the membrane surface, increasing the possible exposure levels to radiation that the membrane could receive.

Should exposure to radionuclides be found to be a major contributing factor to membrane degradation then this would have far-reaching consequences for treatment of mining effluents in general, and therefore for the mining industry as a whole. This is because not only would the SPARRO process be affected but any desalination process making use of synthetic media (EDR, RO, TRO, ion exchange etc)could be affected due to the concentration of the radioactivity within these processes. Ali and Clay (1979) showed that ionization from radioactive isotopes caused chain scission of cellulose acetate resulting in large increases in flux and eventual membrane failure.

In addition to this the industry faces a potentially serious problem with the presence of radionuclides in their mine service waters. A method of efficiently removing these contaminants from the mine water to be re-used in the working areas and concentrating them into a small volume that can be disposed of in a controlled way is becoming an important issue in the industry. The SPARRO process has demonstrated that, even with membranes which are considered poor in terms of salt rejection, U^{238} can be rejected at approximately 96 % while operating the plant in excess of 98 % product recovery.

Based on the above, it is suggested that further research work should be undertaken as soon as possible to identify the causes of membrane degradation and to confirm, in particular, whether or not the presence of radionuclides in the feed water to membrane processes, using locally produced cellulose acetate membranes, has a negative impact on membrane performance.

8. REFERENCES

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APPENDIX A
REVIEW OF PREVIOUS WORK IN 1989 AND 1990

During 1989 and 1990, two pilot water-desalinating plants, employing the seeded reverse osmosis technique, were operated at the COMRO test site at the Hercules Shaft, East Rand Proprietary Mines (ERPM) Ltd. Both were operated simultaneously on the same pretreated mine water pumped from underground. The first plant was termed the MLT (Membrane Lifetime Test) plant, and the other the SPARRO plant. Their design and construction have been fully detailed by Pulles et al[1] and Busby et al[2]. The comparative performance during 1989 and 1990, also fully described in these two references, is briefly reviewed here.

A.1 Comparative Performance in 1989

Table A-1 summarises the record of the first comparative tests carried out in 1989. Membrane performance deteriorated unacceptably in both plants; salt rejection decreased, whilst flux increased.

In the MLT plant, though, almost all this deterioration in membrane performance occurred suddenly, in two large steps just after two long plant shutdowns. ****In contrast, membrane performance in the SPARRO plant deteriorated continuously during operation.

Four membranes from the MLT plant were examined microscopically, revealing the following:

- considerable surface deformation by impinging seed crystals;
- evidence that the membranes had been chemically modified;
- evidence of surface deposits (silicates and a lesser amount of sulphates) on two membranes.

Unfortunately, no similar examinations of membranes from the SPARRO plant were carried out.

On the basis of these microscopic examinations, it was concluded that the poor membrane performance was due to hydrolysis, most likely due to microbiological attack (the feed water had plate counts of up to 250 per 100 ml.[1]).

Accordingly, a chlorination stage, dosing sodium hypochlorite to give a total chlorine level of between 1 and 3 mg/l, was added to the mine water pretreatment plant in November 1989.

**** This was suspected to be due to algal fouling and inadequate preservation techniques during these shutdowns.

A.2 Comparative Performance in 1990

At the beginning of 1990, 10 out of the 20 modules in the MLT plant were renewed (most others had been replaced four or fewer months before). All 88 modules were completely renewed in the SPARRO plant.

Table A-2 summarises the record of the tests in 1990. The MLT plant behaved in an orthodox way, settling down to stable performance close to design expectations. However, the SPARRO plant again performed unacceptably, but in an entirely different way to that of 1989.

Table A-1: Summarised Record of Simultaneous Tests on MLT and SPARRO Plants in 1989

Tests and Period Thereof	Raw Mine Water Pre-Treatment Plant	0,17 l/s MLT PLANT	0,85 l/s SPARRO PLANT
Test 1: March to Dec. 1989	February 1989 Plant incorporated a stage to remove trace metals (Fe.Mn).	March 1989 Plant was started with all 20 modules new. March - November 1989 0-~1 300 hours (incl. a long shutdown of about 500 hours): av. corrected flux: ~600 $l/m^2.d$; salt rejection: ~95%. ~1 300 - ~1 750 hours: 2nd long shutdown. ~1 750 - ~4 350 hours: av. corr. flux: 750-800 $l/m^2.d$; salt rejection: ~85 Thus flux increased, and salt rejection decreased, suddenly after 2nd long shutdown. ~4 350 - ~4 800 hours: 3rd long shutdown. ~4 800 - ~7 000 hours: av. corr. flux: ~970 $l/m^2.d$; salt rejection: ~65% Again, flux increased, and salt rejection decreased, suddenly after 3rd long shutdown. These sudden deteriorations in membrane performance were suspected to be due to algal fouling and inadequate preservation techniques during shutdowns. Four membranes were removed and microscopically examined. They showed considerable surface deformation, and appeared to have been chemically modified. Surface deposits (silicates and sulphates) were found on two.	July 1989 Plant was started. All 88 modules were not new; some had been used previously by ISCOR. July - November 1989 0-~2 000 hours: av. corrected flux increased from an initial 950 $l/m^2.d$ and gradually stabilised at ~1 300 $l/m^2.d$; salt rejection decreased from an initial ~70% and gradually stabilised at ~40%. ~2 000 - ~2 600 hours: av. corr. flux increased further, salt rejection decreased further. In sum, flux increased, and salt rejection decreased, continuously during operation.
	November 1989 A chlorination stage was added. December 1989 (end) Removal of trace metals (Fe,Mn) was discontinued.	It was concluded that the poor membrane performance was due to hydrolysis, most likely resulting from microbiological attack.	

Table A-2: Summarised Record of Simultaneous Tests on MLT and SPARRO Plants in 1990

Tests and Period Thereof	Raw Mine Water Pre-Treatment Plant	0,17 l/s MLT PLANT	0,85 l/s SPARRO PLANT
Test 2: January to August 1990	Turbidity of pretreated water increased to between 1 and 10 NTU.	January 1990 Ten worst modules were replaced. (Most others had been replaced four or fewer months before.) January - August 1990 Plant behaviour was satisfactory. Flux stabilised at ~550 l/m².d. Salt rejection remained at >90%.	January 1990 All 88 modules were replaced. January - August 1990 0-~500 hours: av. corrected flux increased from 800 to >1 000 l/m².d. Damage was found to be occurring in the 4th bank of 10 modules. Microscopic inspection of these showed perforation and crystal growth in the membranes. This damage was attributed to excessive $CaSo_4$ supersaturation in this 4th and last module bank. The 4th bank was decommissioned. Average pass conversion was thus reduced from >50% to 35%. Flux then declined to ~550 l/m².d. Rejection increased to 91%. ~500-2 100 hours: Then, flux declined steadily to <300 l/m².d. Membranes were washed with Biotex and citric acid to remove organic and inorganic foulants. Flux climbed to 400 l/m².d. ~2 100 - ~2 500 hours: Then, after a "process accident" where seed concentration in the feed water fell below 10 000 mg/l, flux increased to 400 l/m².d. Salt rejection decreased to 85%. Membranes were then renovated with PVME and tannic acid. Rejection was restored to >90%. Thereafter, flux again decreased to about 350 l/m².d.

A.2.1 **Performance of SPARRO plant**

During the first 500 hours of operation, severe structural damage to membranes (revealed by microscopic examination) occurred in the fourth bank of modules in the SPARRO plant. The symptoms were a rapid increase in flux and decrease in salt rejection. The cause of the damage could have been chemical attack, mechanical erosion by the flowing slurry, or a combination of both.

This fourth bank of modules was then removed from service. The average pass conversion thus decreased from over 50 per cent to 35 per cent. Thereafter, a completely different problem was experienced: salt rejection was maintained, but flux decreased to unacceptably low levels. This indicated fouling of the membranes. Flux increased after a chemical washing to remove foulants, but then dropped again. It remained at the unacceptably low value of about 350 $l/m^2.d$ except for a brief period of time just after the membranes were renovated.

Unfortunately, no membranes were microscopically examined to find the cause of this decrease in flux. Possible causes were:

- membrane compaction: if this had been the dominant cause, the above-mentioned chemical washing to remove foulants would have had no effect, as membrane compaction is irreversible. The opinion of the membrane manufacturers was that compaction should not have been excessive under the operating pressures employed[1]. This cause was therefore discounted;

- membrane fouling: this could have been due to:

    * organic macromolecules: the water was never analysed for these, but they were unlikely in the presence of abrasive calcium sulphate slurry passing through the membranes;
    * biological deposits: these were discounted because the water was being chlorinated, and salt rejection was stable, indicating no significant hydrolysis. Additionally, these were also unlikely in the presence of abrasive slurry;
    * inorganic scale formation: calcium sulphate scale could have formed, but this was deemed unlikely (preferential precipitation onto the seed crystals should have occurred). The likelihood of scale consisting of iron or manganese compounds was discounted;
    * suspended solids or colloids: this was deemed possible. In the SPARRO plant, the raw mine water (RMW) is fed directly to the modules, and hence it was thought that (in contrast to the MLT plant) the suspended solids in the RMW could not be encapsulated in growing calcium sulphate crystals in a desupersaturating solution. Hence these suspended solids might have been deposited on the membrane surfaces. (As seen in Table 2, the turbidity of the mine water delivered by the pretreatment plant increased to between 1 and 10 NTU in 1990.)

A.2.2 Poor performance of SPARRO plant due to essential difference from MLT plant?

In summary, both the MLT and the SPARRO plants were operated simultaneously on the same pretreated, chlorinated RMW in 1990. Yet the MLT plant performed satisfactorily and the SPARRO plant unacceptably poorly.

The essential difference in configuration between the MLT and SPARRO plants was the point of feed of the pre-treated RMW. This was into the reactor in the MLT plant, but into the modules (having mixed just beforehand with the desupersaturated slurry) in the SPARRO plant. It was postulated[1,2] that this essential difference contributed significantly to the fouling problems experienced in the SPARRO plant. As mentioned in the main text, the Water Research Commission therefore funded the present project to determine the reaction kinetics in the desupersaturation reactors used.

One important observation must be made here. It indeed seems obvious that something different between the two plants was causing the poor performance of the SPARRO plant. However, the point of entry of the pretreated RMW was not the only major difference between the two plants. The major differences are tabulated in Table A-3 below.

Table A-3

Major Differences between MLT and SPARRO Plants Operated in 1989 and 1990

	MLT PLANT	SPARRO PLANT
PHYSICAL DIFFERENCES		
Pretreated raw mine water fed to:	Reactor vessel	Membranes
Residence time (hours) in reactor vessel	4	1
Configuration of membrane modules	non-tapered: 5 successive banks of 4 modules each	tapered (fewer modules in successive banks): sub-bank 1: 3 successive banks of 10 modules; sub-bank 2:3 successive banks of 8 modules; sub-bank 3: 4 successive banks of 6 modules; sub-bank 4: 2 successive banks of 5 modules
Operating Differences		
Design product water flow rate (l/s)	0,17	0,85
Feed pressure (kPag)	3 000	4 000
Pass conversion (% of feed to modules which permeates to form product)	20%	50% (with four module banks; 1989 and 1st 500 operating hours of 1990) 35% (with three module banks; remainder of 1990)

Thus, other differences, which should not be dismissed as unimportant without careful evaluation, were:

- the module banks in the SPARRO plant were tapered, but non-tapered in the MLT plant;
- average pass conversion in the SPARRO plant was 35 per cent (1,75 times that of the MLT plant) or greater;
- inlet pressure in the SPARRO plant was 4 000 kPa, whereas in the MLT plant it was 3 000 kPa.

APPENDIX B

PERFORMANCE OF SPARRO PLANT IN EARLY 1992

As mentioned in Section 3.1.4 above, another Water Research Commission funded project, the Water Reclamation Test Plant, was in progress at the COMRO test site during 1991 and the first part of 1992. During one of its phases, this project required product water from the SPARRO plant, which was accordingly in operation from October 1991 through to March 1992.

As noted in Section A.2.1 of Appendix A, the fourth bank of modules had been removed from service in 1990. The tapered module stack thus consisted of 78 modules in three banks. In October 1991, at the beginning of the above period of operation, all these 78 modules were replaced as follows:

Bank 1: all new;
Bank 2: all in Row 1 and one in Row 2 with modules from old MLT plant; the rest all new;
Bank 3: all new.

As previously, the plant was operated in its design mode, the SPARRO mode, during this period. The chlorination stage in the raw mine water pretreatment plant was operational, achieving total chlorine levels of between 1,0 and 2,5 mg/l.

Between December 1991 and February 1992, plant performance was stable. Four surveys of performance of individual module rows were carried out during this period; the results are presented in Figures B-1 and B-2. Figure B-1 depicts average salt rejection of selected module rows. For Bank 1, that of Row 1 is shown; those of its other two rows (not shown) were virtually identical. For Bank 2, the salt rejection of Row 1 is likewise shown; again, those of its other two rows are not shown, but were virtually identical. For Bank 3, the salt rejections of all four rows are shown.

As seen, the salt rejection of Bank 2, averaging 90 per cent, was noticeably lower than that of Bank 1, which averaged 96 per cent. The average rejection of Bank 3, 76 per cent, was unsatisfactory and considerably lower than that of Bank 2. It must further be noted that Banks 1 and 2 maintained their salt rejections throughout the operating period; that of Bank 3 gradually decreased.

Figure B-2 depicts average fluxes of the same selected module rows. These fluxes have not been corrected to 4 000 kPa and 25 °C, so valid comparisons are confined to those between different rows for selected values of operating hours. Here, it is seen that the flux of Bank 2 was noticeably higher than that of Bank 1. In turn, the flux of Bank 3 was considerably higher than that of Bank 2.

Figure B-1: January-February 1992:
Average Salt Rejection of Module Rows

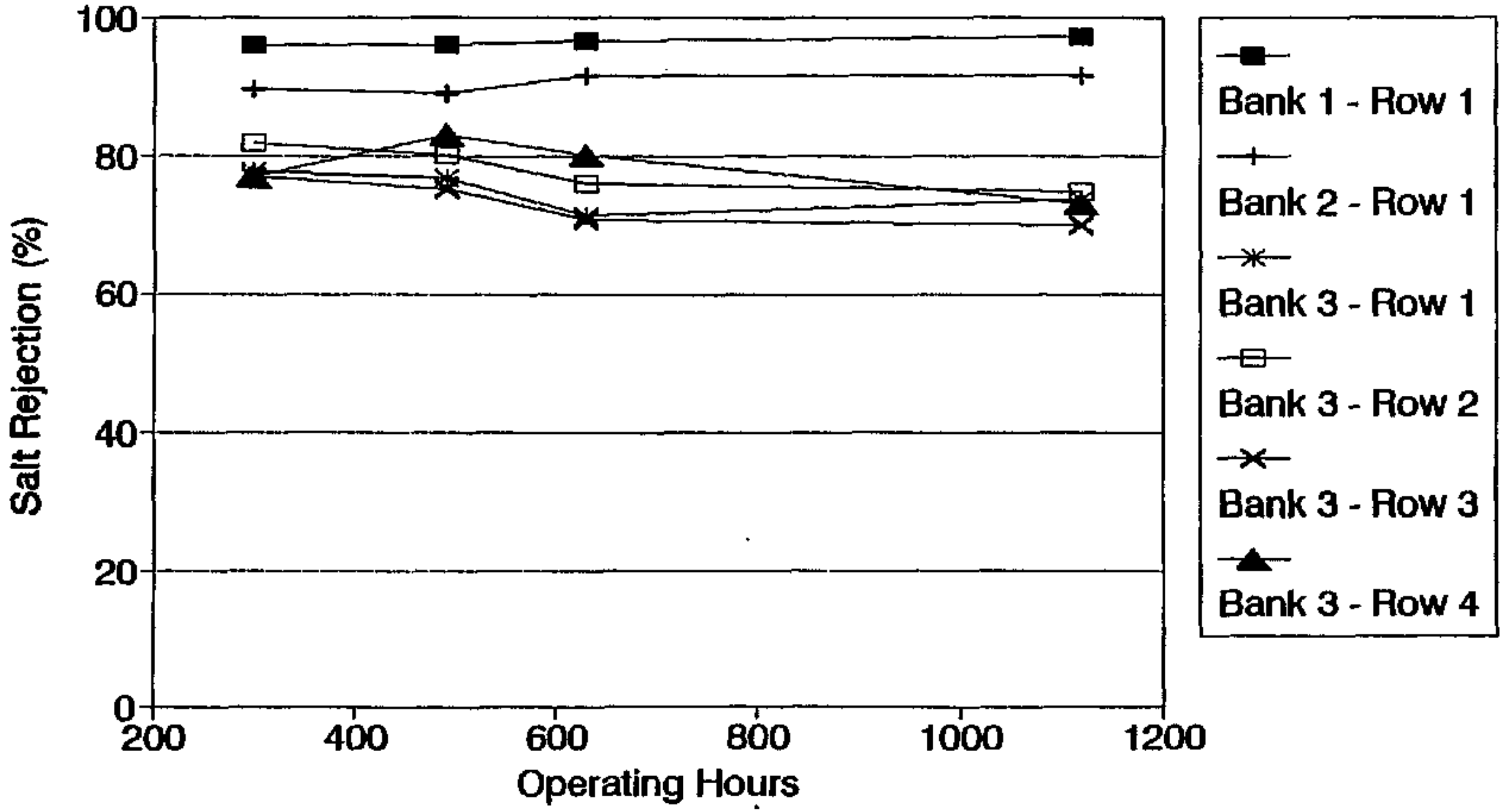
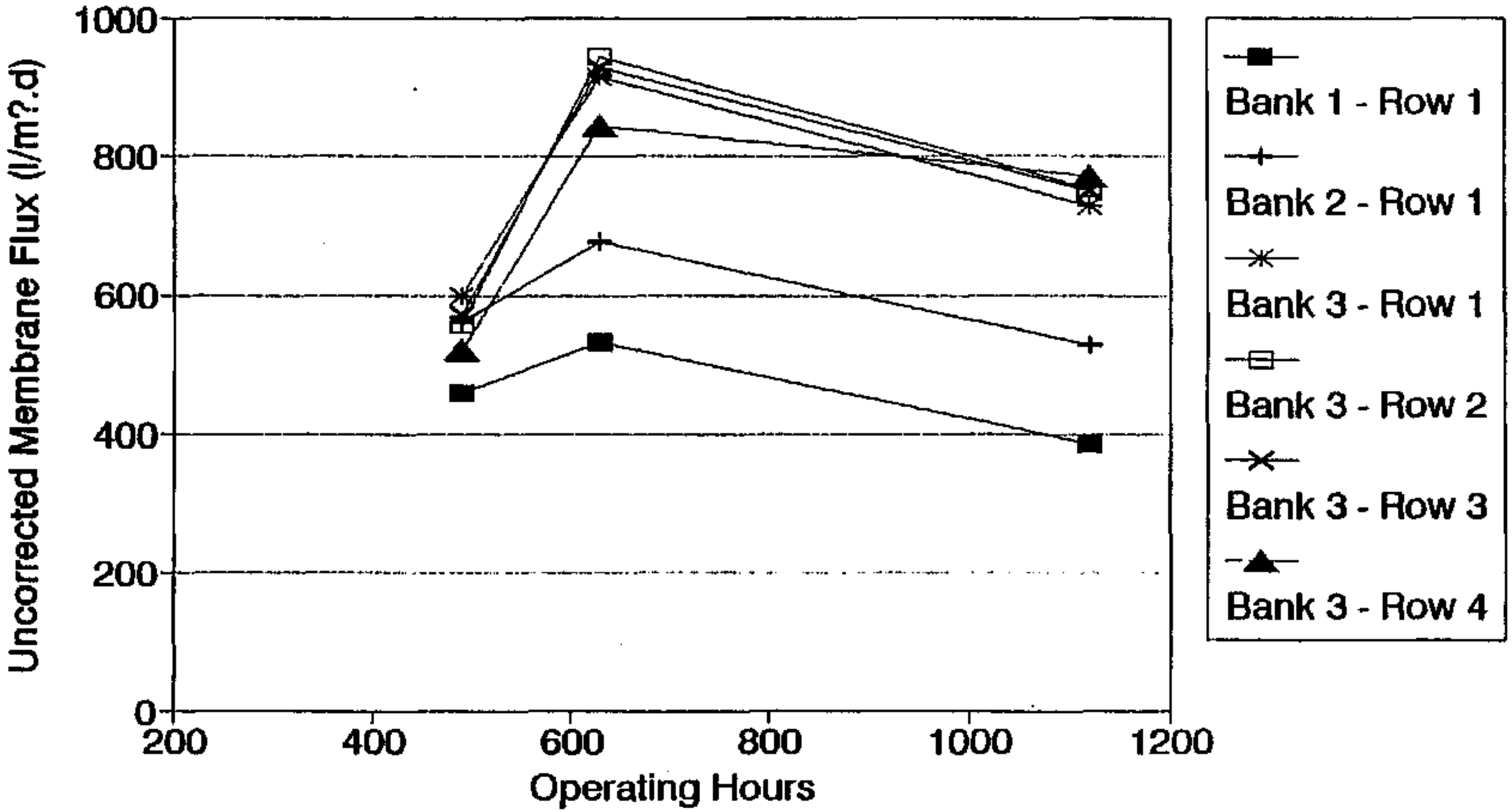


Figure B-2: January-February 1992:
Average Fluxes (uncorr.) of Module Rows



Overall salt rejection for the plant averaged 82 per cent. Average pass conversion was 30 per cent, with inlet pressure at Bank 1 varying between 2 200 and 2 500 kPa.

In summary, therefore, although plant performance over the period was stable, membrane performance was progressively worse in the three banks of the tapered module stack. Salt rejection decreased and flux increased, with the highest such worsening taking place between Bank 2 and Bank 3. The feed to the modules, of course, became more concentrated in TDS from Banks 1 to 3, and this TDS appeared to be the only variable which changed significantly between banks. The surveys of performance of module rows thus suggested that some phenomenon associated with increasing TDS in module feed was causing the membrane deterioration observed.

The symptoms of increasing flux and decreasing salt rejection suggested either structural damage to or hydrolysis of membranes. It is noteworthy that, in the 1990 tests (as described in Appendix A), membrane performance was fundamentally different, fouling being experienced. Yet, in both cases, the tapered module stack consisted of the same three banks, fed with pretreated, chlorinated raw mine water. Furthermore, average pass conversion was approximately the same.

The SPARRO plant was shut down in April 1992. It was restarted in mid-1992, when work on the Water Reclamation Test Plant had virtually been completed.

APPENDIX C

KINETIC STUDY: PROPOSED PROCEDURE FOR EXPERIMENTS TO DETERMINE THE DEGREE OF VARIANCE TO BE EXPECTED IN TEST WORK

(i) Decide on the solution mixing ratio, seed concentration and mixing speed to be used.

(ii) Determine the solids concentration in the brine reject stream of the plant.

(iii) From the required solution mixing ratio and the brine seed concentration, calculate the mass of seed in the combined mixture. Determine the mass of spare seed that would have to be added to provide the required seed concentration in terms of the experiment.

(iv) To calculate the effect on pH, mix correct proportions of brine reject and raw mine water in a four litre container and determine the pH. Adjust the pH to within the correct range for the experiment and calculate the volume of acid/alkali that would have to be added to the 500 litre reactor to provide the correct pH range.

(v) Take a sample of the raw mine water for chemical analysis.

(vi) Take a 500 ml sample of the brine stream and mix it immediately with 500 ml of deionized water in an attempt to stop any precipitation reactions that may be occurring. Filter the sample and keep the filtrate (recording its volume) and the filter cake for later chemical analysis.

(vii) Fill the 500 litre pilot reactor with the calculated amount of raw mine water. Start the mixer and check that it is running at the correct speed for the experiment.

(viii) Begin the addition of the calculated volume of brine reject to the reactor and start the timer. Add the calculated volume of acid/alkali and mass of additional seed to the reactor to produce the desired pH and seed concentration for the experiment. Note the elapsed time after the correct volume of brine has been added and the temperature of the mixture.

(ix) After five minutes of elapsed time take the first 500 ml sample from the reactor. Immediately transfer this sample to a 1,5 litre beaker and mix it with 500 ml of deionized water in an attempt to stop any precipitation reactions that may be occurring. Filter the resultant solution and keep the filtrate (recording its volume) and the filter cake for later chemical analysis.

(x) After 17 minutes and 45 minutes of elapsed time take the second and third 500 ml samples, respectively, from the reactor. Treat these samples as outlined in (ix) above.

(xi) Drain the reactor and flush it out, in preparation for the next experiment.