NANOFILTRATION AS MEANS OF ACHIEVING HIGHER TBT OF ³ 120^{o}C IN MSF *

Mohammad AK. Al-Sofi, Ata M. Hassan, Ghulam M. Mustafa, Abdul Ghani I. Dalvi and Mohammad N. M. Kither

Research and Development Center, P. O. Box # 8328, Al-Jubail 31951, Kingdom of Saudi Arabia

ABSTRACT

The Saline Water Conversion Corporation, Research and Development Center (SWCC-RDC) carried out exploratory research study to evaluate the adaptability of brackish water softening NANOFILTRATION technique as a permeation pretreatment of feed to Sea Water Reverse Osmosis (SWRO) and as make up to MSF. This exploratory work was designated as part I of an applied research project that was carried out from March 1997 to May 1998. Based on initial remarkable results SWCC placed in a patent application on the process during 1997.

This paper reports on this pretreatment approach and its application to thermal desalination by MSF process. In this paper the work carried out in part I of this project is reported where makeup to a 20 kilo liter per day MSF pilot plant distiller was either fresh Nanofiltration Permeate (NFP) or SWRO reject (while SWRO was fed with NFP). This paper also addresses the plan of elevating MSF Top Brine Temperature (TBT) to as high as 160^{o}C since operation at TBT of 120^{o}C with very little or no scale control treatment gave excellent results.

Keywords: Pretreatment, Permeation, Nanofiltration, Reverse Osmosis, MSF distillation, TBT, Hardness and Total Alkalinity.

---

[1] Paper presented in Conference for Membranes in Drinking and Industrial Water Production, September 1998, Amsterdam.

INTRODUCTION

For the first time, a 20 kilo liter per day pilot Multi Stage Flash (MSF) distiller was operated at a Top Brine Temperature (TBT) of 120 ^{o}C for a total of 1400 hours while being fed with NFP as make-up [1&2], see Figure 1 & Table 1. Figure 1 is self explanatory (refer to [3]) and Table 1 represents research and application stepwise development plan. Even without scale control chemical dosing [4&5] during above test runs there was no observed scaling of the unit. It is worth to note that the MSF test unit was operating very smoothly during a five week run from 19/10 to 25/11/1997. During the last week of November, inspection of brine heater and stage one were performed. Samples of scale (small quantities could only be obtained) and corrosion products were taken for chemical analyses. During the months from February to May 1998 few runs were conducted to check the scheme of NF-SWRO$_{reject}$-MSF operation (SWCC NF4).

The limitation of 20 kilo liter per day MSF pilot plant distiller and its steam supply source boiler were thoroughly reviewed. Based on which, it was established that with this set-up the boiler could furnish adequate supply of steam at the required temperature and pressure (T&P) to a brine heater operated at 160^{o}C.

RESULTS AND DISCUSSION

Suitability of NFP as makeup to MSF without chemical dosing was established in laboratory. Threshold experiments were carried out with seawater, brine and NFP without scale control additives(SCA). To carryout the threshold experiment[6], three samples (of 0.5 liter each) were taken into reaction vessel and heated to 95^{o}C with constant stirring. Controlled vacuum was applied to the reaction vessel so that each sample flashed gently. Saturation condition was created by addition of one molar sodium carbonate solution to each sample. Small portions from each sample were then withdrawn on a set time intervals. Total alkalinity of each portion was determined after filtration. Figure 2 is a plot of threshold effect where total alkalinity is plotted against time and it shows that loss of total alkalinity (LTA) is highest in brine and lowest in NFP in the absence of SCA. The order of LTA is as follows:

Brine >> Sea water >> NFP

Lower LTA value means lower scale formation potential. Data indicate that the scale formation potential of NFP is negligible and very much lower than brine. This fact was confirmed by running the pilot plant without SCA while makeup was NFP.

Throughout five weeks of operation (19/10 -25/11/97), the terminal temperature difference (ΔT_{bh} that is equal to brine heater shell minus top brine temperature) was in the range of 0.7 to 1.7^{o}C. In the last week (of these five week tests) the MSF pilot unit was run with no antifoaming chemical injection. Moreover, the decarbonator was taken out of service in the last day of this run, while it was kept in service up to 24/11/1997 as a precautionary measure so that the restart of acid injection would instantaneously be effective should the need arise (if there is to be a sudden unexpected rise in ΔT_{bh} beyond a preset limit of 2^{o}C). Table 2 gives results of one of the tests of this group (which are identified in Table 1 as SWCC NF3). Due to limitation in NFP availability the MSF was run by introducing make-up as a blend of one-third NF product plus one-third distillate product and one-third brine blow down. These equal proportions were based on NF process yield and MSF product to blow down ratio. It is worth stressing that one-third fresh NFP plus two third artificially reconstituted (of quite representative constituents) stock was used as make-up to the MSF pilot distiller for 5 weeks at a TBT of 120$_{o}$C without any scale control chemical dosing.

Unit inspection (in November) indicated that most of the passes of brine heater tubes were showing shining metal surface.except the last two, where some thin deposits were present. As would be expected, the stage one tubes where totally clean. Chemical analysis of scale collected from brine heater showed that its sulfate content is around 0.1%, compared to 27% sulfate of the total hardness ions (SO_4^{--} + Mg^{++} + Ca^{++} + HCO_3^{-}) in the NF product used as make-up to the MSF pilot plant. It is also worth stating that hardness ionic content of this make-up was as low as 234 compared to 5417 ppm in seawater, i.e., the hardness reduction is in the ratio of 0.043 to 1. Furthermore, the sulfate reduction by the NF membrane is up to 98% which explains the sparingly present (and the extremely low sulfate content of the collected sample of) scale. In order to establish a safe upper limit recovery ratio, five equal samples of NFP were subjected to partial evaporation in the laboratory. Analytical results are shown in Table 3. This table shows that even a 10% residual brine when cooled down remained clear and that a 6% residual became turbid after cooling to room temperature.

The above laboratory checks would imply that under laboratory conditions percent recovery from NFP can be as high as 90%. Based on this a test was performed to establish safe make-up to distillate production ratio. The unit was restarted, keeping in mind the above findings, on December 2, 1997, at a TBT of 120^{o}C (ΔT_{bh} was measured to be around 2^{o}C i.e., at the end of this test), and brine recycle flow rate of 6.50 m^3/hr for an average distillate yield of 0.96 m^3/hr with only 1.20 m^3/hr of fresh NFP as make-up (compared to normal value of around 2.5 m^3/hr) with no artificial blending whereby achieving 80% product recovery (while maintaining over 10% safety margin - comparing recovery with Table 3).

Table 4 gives results of this test run. Upon completion of this run, the MSF pilot unit was switched to normal mode of operation with seawater as make-up. Amazingly, after restoration of normal make-up flow rate back to 2.1 m^3/hr, the 2^{o}C ΔT_{bh} reduced to a level even lower than its value at the start of the (almost) 5 weeks of operation with low flow rate of NFP as make-up to MSF, i.e., less than 0.7^{o}C. At that point in time (over 5 weeks earlier) ΔT_{bh} was 0.7^{o}C compared to a range of 0.4 to 0.6^{o}C after switching and dosing polyphosphonate as an antiscalant at a low dose rate of 0.8 ppm and a TBT of 90$_{o}$C. This clearly supports previous inspection observation of limited scaling due to extremely low sulfate content. Moreover, it indicates the softness of scale and the ease of its removal which could be attributed to reduced salinity.

Table 5 gives results of runs conducted in 1998 (Feb. to May) while Reverse Osmosis Reject (ROR) brine was fed as make-up to the MSF at a TBT of 120^{o}C. It can be seen in this table that bicarbonate levels of all streams are low and comparable to those in Table 4. Bicarbonate levels in various streams are yet by far lower than their levels in the corresponding streams during normal SCA sea water operation of MSF at TBTs lower than (or even upto) 120^{o}C. On the other hand, acid injection in these runs were limited to the requirements of NF-SWRO and with no further injection in the MSF make-up stream. Acid injection was thus reduced drastically. It was brought down to 18% (or less) of the normal acid required in MSF operation at a TBT of 120$_{o}$C when using natural seawater compared to NF-ROR as make-up.

Nanofiltration is found to be an attractive approach for relaxing the MSF process traditional TBT limit of 121^{o}C. As commonly known, this limit has so far been imposed by the inverse solubility of calcium sulfate which drops appreciably above the said temperature at the elevated concentration of recycle brine which is at 1.1-1.6 times the concentration of salts in natural seawater. The limit within this (1.1-1.6) range is controlled by calcium sulfate concentration in natural seawater. This in turn is governed by total dissolved solids (TDS) content of the seawater, hence proportionally increased sulfate ion concentration. NFP as make-up could, therefore, provide a way into higher TBT operation in MSF due to the rejection of many scale forming ions specially (near total of 98%) sulfate by such membrane process pretreatment. This has led to seriously considering trial runs at TBTs of higher than 121 $_{o}$C.

However, it was established that the available MSF unit and more importantly its brine heater could not be operated at such elevated T&P. Nevertheless, utilization of existing MSF distiller (with the exception of its brine heater) are found to be possible provided that the system is upgraded. In order to operate the existing distiller with no change in its terminal conditions, it was mandatory to design an expansion by adding (two to four) high T&P stages plus even higher T&P brine heater and a high pressure recycle brine booster pump.

In designing this expansion, it was essential to consider future development of adequate quality of cleaning balls for such elevated TBT of up to 160^{o}C. It was also essential to survey materials' performance. Literature survey indicated that UNS S44660 is highly resistant to localized pitting and crevice corrosion in aggressive chloride solutions, such as seawater. In view, of the above this alloy is considered to be at the top of a selection list as a single alloy for almost the entire expansion of the existing MSF distiller, (be it), high temperature and pressure pipes and linings (and/or solid alloy) for vessel(s), water boxes, gates, orifices and tube sheets also for heat transfer tubes, partition walls, channels, baffles, nozzles, and the mesh of demister pads. Moreover, this alloy was primarily chosen because it was developed specifically to resist corrosive nature of seawater. Reference can now be made to the proposed expansion process flow diagram to be integrated with the existing unit as shown in Figure 3 with the most suitable alloy which was found to be UNS S44660.

CONCLUSION

SWCC-RDC have come up with a true break-through in operating MSF with low to no scale control chemical treatment other than NANOFILTRATION of make-up. Moreover, MSF operation utilizing SWRO reject again with very limited scale control chemical treatment became feasible i.e., hybrid concept. These achievements were possible at a TBT of 120^{o}C in either case.

FUTURE WORK

Based on the above, MSF process expansion to allow for operation at a TBT of upto 160^{o}C while makeup is NFP or SWRO reject (ROR) is in the final design stage.

REFERENCES

1. Hassan, A. M., Al-Sofi M. AK., Al-Amoudi A., Jamaluddin A. T. M., Mohammad N. K., Mustafa G. M. and Al-Tisan I. (1997) A new approach to membrane and thermal seawater desalination using nanofiltration membranes", In the proceedings of 8th IDA Desalination International Conference, Madrid, Spain.

2. Hassan, A. M., Al-Sofi, M. AK., Al-Amoudi A., Jamaluddin A. T. M., Mohammad N. K., Mustafa G. M. and Al-Tisan I. (1998) Desalination & Water Reuse, **8**, 53-59.

3. Al-Sofi, M. AK., El-Sayed E. F., Imam M., Mustafa G. M., Hamada T., Tanaka Y., Haseba S. and Goto T. (1995) Heat transfer measurements as a criterion for performance evaluation of scale inhibitor in MSF plants, In the proceedings of 7th IDA Desalination International Conference, Abu Dhabi, UAE

4. Shams El Din, A. M. and Mohammed R.A. (1994) Desalination, **99**, 73-111.

5. Al-Sofi, M. AK., Khalaf S. and Al-Omran A. (1989) Desalination, **73**, 313-325.

6. Al- Sofi, M. AK., Al- Sulami S. A., Hamada T. and Tanaka Y. (1995). In the Proceedings of 2nd. Gulf Water Conference, Bahrain

Table 1. Nanofiltration Plan of various desalination processes testing identifications

Plant Testing Level	Process Scheme NF	NF-SWRO	NF-MSF	NF-SWRO-MSF	NF-MEB	NF-VC	NF-ME-VC
Pilot size modules	SWCC NF1	SWCC NF2	SWCC NF3	SWCC NF4	SWCC NF5	SWCC NF6	SWCC NF7
Actual module sizes	SWCC NF1A	SWCC NF2A	SWCC NF3A	SWCC NF4A	SWCC NF5A	SWCC NF6A	SWCC NF7A
Balanced actual module sizes*	SWCC NF1B	SWCC NF2B	SWCC NF3B	SWCC NF4B	SWCC NF5B	SWCC NF6B	SWCC NF7B
Commercial application	SWCC NF1C	SWCC NF2C	SWCC NF3C	SWCC NF4C	SWCC NF5C	SWCC NF6C	SWCC NF7C

*Optimization and Integration of Hybrid Concept, Especially in SWCC NF 4B.

Table 2. Chemical Analysis of Various Streams During Tests Carried in Nov 97

Testing Level	Unit	Seawater	Nano-Filtrate	Brine Recycle	Brine Heater Outlet	Brine Blowdown
pH	-	8.24	7.89	8.41	8.34	8.38
Conductivity	µS/cm	55400	33600	85600	86200	97000
M. Alk. as $CaCO_3$	mg/lit.	130	30	52	49	58
Total Dissolved Solids	do	46640	22560	66540	66920	77180
Calcium	do	521	52	164	168	192
Magnesium	do	1453	89	258	255	321
Sulphate	do	3500	65	216	216	243
Chloride	do	23013	13700	-	-	-
Sodium	do	12860	8877*			

*By Calcuation

Table 3. Laboratory Partial Evaporation Results Using NF Product

Parameters	Units	Experiment Number 1	2	3	4	5
Initial Volume of the Sample [(1)]	ml	250	250	250	250	250
Final Volume After Evaporation	ml	136	80	40	25	15
Percent Residual Brine	%	54.4	32	16	10	6
Turbidity at Room Temp.	FTU	0	0	0	0	80[(2)]

(1) Nano Permeate of TDS 24000mg/l (approx.)

(2) The solution was clear at boiling temperature, but the dissolved salts precipitated out when cooled to room temperature and also the precipitate settles very quickly

Table 4. Chemical Analysis of Streams During Tests Carried in Dec 1997 using NF Product

Parameters	Units	Make-up	Brine Recycle	Brine Blowdown
Total Dissolved Solids at 150°C	mg/l	22060	91762	105700
Bi-Carbonate	do	32	104	121
Sulphate	do	63	258	302
Calcium.	do	54	228	265
Magnesium	do	91	307	443

Table 5. Chemical Analysis of Streams During Tests Carried in April 1998 Using ROR*

Testing Level	Unit	Make-up	Brine Recycle	Brine Heater Outlet	Brine Blowdown
pH	-	7.88	8.56	8.29	8.63
Conductivity	µS/cm	44900	87900	88100	100300
M. Alk. as $CaCO_3$	mg/lit.	47	75	65	84
Dissolved Oxygen	do	< 0.01	-	-	-
Total Dissolved Solids at 105°C	do	32840	75080	74800	85440
Total Hardness as $CaCO_3$	do	1650	3600	3700	4250
Bi-Carbonate	do	57	73	75	77
Calcium	do	120	273	281	329
Magnesium	do	328	710	730	834
Sulphate	do	560	1224	1242	1440

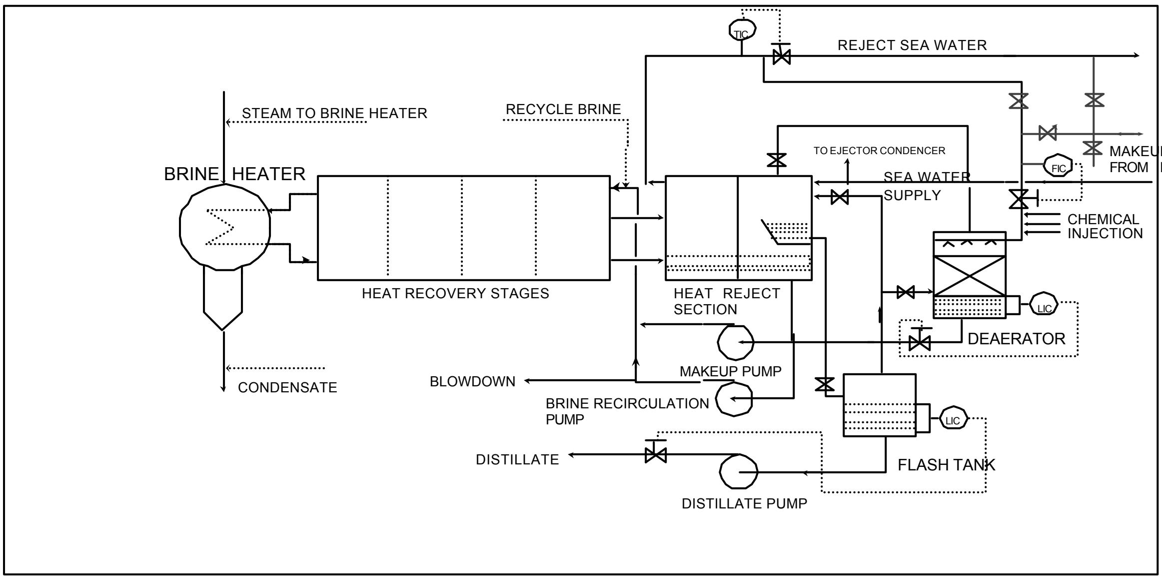

Figure 1. Existing Pilot Plant MSF Distiller

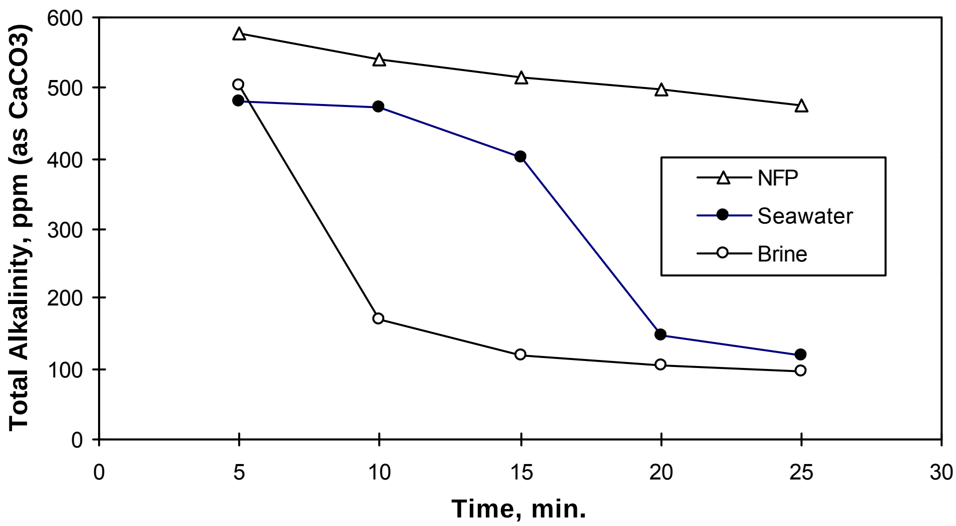

Figure 2. Scaling potential

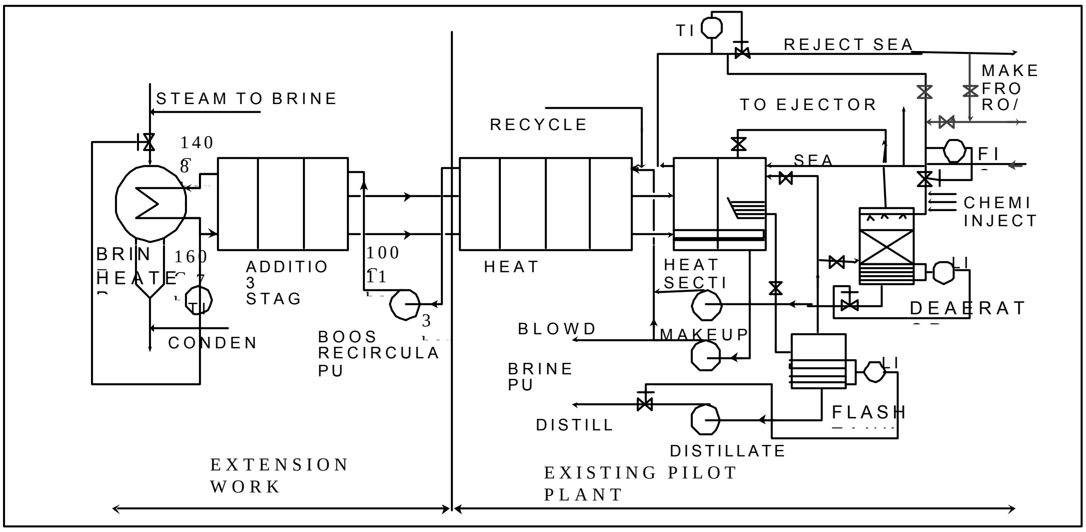

Figure 3. Pilot Plant MSF Distiller with Proposed Extension