NEW ADVANCES AND FUTURE NEEDS IN THERMAL-MEMBRANE HYBRIDS FOR WATER DESALINATION

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Abstract

The hybrid desalting concept is the combination of two or more processes in order to provide better environmental solutions, lower energy consumption and a lower water cost product than either alone can provide. For purpose of this paper hybrid in desalination will deal with combination of distillation and membrane processes with power generation. It will outline new advances and future needs in thermal-membrane hybrids for water desalination.

The hybrid system received significant attention recently as a result of several major awards of projects based on hybrid concepts. The largest seawater desalination and power project in the world Ras Az Zawr awarded by SWCC in Saudi Arabia with capacity 1,039,000m³/day and 2400 MW Combined Cycle Gas Turbine is based on 70% Multistage Flash Distillation (MSF) and 30% Reverse Osmosis. Similar the largest seawater hybrid using Multi-Effect Distillation (MED) is Fujairah 2 inaugurated in May 2011 with net capacity of MED equal 455,000m³/d (100MIGD) and RO of 136,000 m³/d (30MIGD) and 2000 MW of power. All of past hybrid projects where based on simple parallel approach producing distillate and permeate and blending the products together.

The future projects of hybrid will consider the integrated approach taking advantage of warm coolant seawater outflow from thermal desalination and power plants as source of feed to membrane processes of Nanofiltration (NF) and RO. Using higher temperature feed to membrane will providing better fluxes, higher overall recovery, minimizing the size of intake and outfall and of course reducing overall cost and environmental impact. Future development of High Temperature RO and NF membranes will significantly improve the capacity, efficiency and recovery of thermal MED, MSF processes as well as membrane fluxes and recovery.

The ability to use effectively the available water sources is emerging as a top priority for all types of power plants. The current trend is to retrofit operating desalination and power plants that currently use once-through cooling with wet or hybrid wet-dry cooling towers, which requires novel solutions for providing desalinated high quality water and disposal of blowdown for both the coastal and inland power plants.

Hybrids of NF-RO-MED or NF-RO-MVC could provide unique desalination solutions to utilization of solar energy, Gas Well Water Supply and Wastewater Disposal, Treatment, and Recycle Technology for shale gas “Frac” water, Coal seam gas (CSG) water, petroleum waters and Zero Liquid Discharge.

The paper outlines research and development needs for making Hybrid the most effective technology.
I. INTRODUCTION

Early suggestions for hybrid desalination were based upon elimination of the requirement for a second pass to the RO process so that the higher-salinity RO product could be combined with the better quality product from an MSF plant. This is the simplest application of hybrid desalination. Since then, other concepts have been proposed for hybrid desalination. Today, although RO can produce potable TDS in one pass, blending allows a simple solution where national standards require low levels of boron.

Dual purpose power-desalination plants make use of thermal energy extracted or exhausted from power plants in the form of low pressure steam to provide heat input to thermal desalination plants for multistage flash (MSF) or multi-effect (MED) distillation processes. The electrical energy can be also effectively used in electrically-driven desalination processes like Reverse Osmosis (RO) and Vapor Compression Distillation (VCD).

1.1 General Background

1.1.1 Energy Conservation Using Hybrid Systems

In view of the dramatic concern with global climate conditions and a rise in fuel prices in excess of US$ 80 per barrel, hybrid (RO + distillation) systems offers significant savings in fuel costs in comparison with the distillation-only option. This is well demonstrated by the presentation provided by Dr. Corrado Sommariva in his course on Thermal Desalination Processes and Economics.

In the base case for a 100 MIGD (455,000 m³/day) MSF desalination and 400 MW of electric power generation plant, the fuel consumption is 191 tons/hr and the annual cost requirement will exceed 735 million US$. By comparison, a hybrid 100 MIGD (455,000 m³/day) desalination plant based on 60% thermal and 40% RO will operate at reduced fuel consumption of only 115 tons/hr and a cost of 443 million US$ per year. This hybrid system reduces the carbon dioxide footprint by 40%, and the annual fuel cost difference is almost 300 million per year, which will pay back for the total Capex of desalination in less than three years. Of course, in the base case, we produce more power, and to some extent, this compensates for the additional cost – but this assumes that we need the power.

In many countries, particularly in the Middle East, peak power demand occurs in summer and then drops dramatically to 30-40%. In contrast, the demand for desalinated water is almost constant throughout the year. This creates a situation where over 50% of power generation is idled. This inequality of demand between electricity and water can be corrected by diverting the excess of available electricity to water production.

Water can be stored, while electricity storage is not practical.

In this case, excess electricity can be diverted to water production incorporating electrically-driven Seawater Reverse Osmosis (SWRO) and/or Vapor Compression with the low-pressure steam-driven technology of MSF or MED, making its advantages to design an integrated Hybrid Plants. One method of making use of idle power capacity is the use of electrically driven RO or VCD plants in combination with Desalination Aquifer Storage Recovery (DASR) both for averaging the desalination capacity, for strategic and economic fresh ground water storage or improving quality of the basin.
1.1.2 Hybrid – the New Alternative

In the simple hybrid MSF/RO desalination power process, a seawater RO plant is combined with either a new or existing dual purpose MSF/power plant, resulting in the following advantages:

- A common, considerably smaller seawater intake can be used.
- Product waters from the RO and MSF plants are blended to obtain suitable product water quality.
- Product waters from the RO and MSF plants are blended, therefore allowing higher temperature of distillate.
- A single pass RO process can be used.
- Blending distillation with membrane products reduces strict requirements on Boron removal by RO.
- The useful RO membrane life can be extended.
- Excess power production from the desalting complex can be reduced significantly, or the power-to-water ratio can be significantly reduced.

1.1.3 Examples of Existing Hybrids

**Jeddah Hybrid**
The first straightforward hybrid plant scheme has been adopted in Jeddah I and II to blend higher TDS RO permeate with distillate from existing MSF plants, and is described in detail by Awerbuch and by many other papers.

The results of conceptual and design work led to construction of the simple hybrid project at Jeddah 1, phase I and II plants. The Jeddah 1 RO plant is 30 MGD (113,600 m³/day) combining Phase I, which has been operated since 1989, and Phase II, which has been operated since March 1994. The plant is owned by Saline Water Conversion Corporation (SWCC), design by Bechtel, and constructed by Mitsubishi Heavy Industries, Ltd. The plant, which utilized Toyobo Hollosep double element type hollow fiber RO modules, demonstrated that the life of the membrane was extended to over 10 years. In addition to 30 MGD RO permeate, the Jeddah complex produces 80 MGD distillate from Jeddah II, III and IV and 924 MW of electricity. Jeddah I RO plant successfully adopted an Intermittent Chlorine Injection method (ICI) in order to prevent membrane degradation by oxidation reaction and biofouling.

**Yanbu – Medina Hybrid**
The objective of minimizing the power-to-water ratio led to the construction of the integrated Medina and Yanbu Phase II in the Kingdom of Saudi Arabia, with 130,000 m³/day (33.8 MGD) in Medina and Yanbu. The plant is able to produce power at 164 MW electricity and 288,000 m³/day (76 MGD) of desalinated water. Two 82 MW back pressure steam turbines (BTG) provide steam to four 36,000 m³/day (9.5 MGD) MSF distillation units and the electricity to 15 RO units of 8,500 m³/day (2.25 MGD), each. Although the plant was not designed as an integrated Hybrid, it provided a very good example of significant reduction of the power to water ratio (PWR).

**Fujairah 1 Hybrid**
The original Fujairah 1 plant, due to hybridization, generated only 500 MW net electricity for export to the grid, and 674 MW gross for water production capacity amounting to 455,000 m³/day (100 MIGD). Otherwise, a similar MSF-only plant in Shuiwaihat required 1,500 MW for the same 455,000 m³/day (100 MIGD) capacity. The Fujairah desalination plant is split into 284,000 m³/day (62.5 MIGD) from...
the thermal part with MSF 5 units each of 12.5 MIGD and 170,000 m³/day (37.5 MIGD) from the RO membrane process.

Doosan Heavy Industry and Construction Company was the Engineering-Procurement and Construction (EPC) contractor. The main contract was awarded in June 2001. Doosan selected Degrémont as a subcontractor to receive the basic design and major equipment supply of the SWRO Plant. The 100 MIGD (455,000 m³/day) water production started on June 31, 2003 with a total construction, commissioning and startup time of less than two years. Effective September 2006 the plant was purchased by new owner Emirates Sembcorp Water & Power Co. (ESC) and in 2009 followed plant power extension with Gas Turbine of 219 MW. ESC is currently bidding further expansion in capacity with 30 MIGD RO plant.

The ESC is 60% own by Union Power Holding Company a Unit and 40% owned by Sembcorp Gulf Holding Company a unit of Singapore Sembcorp Industries Ltd. Recently the Union Power Holding Company ownership changed and 10% shares is owned by ADWEA and 90% of its shares by TAQA which is a unit of ADWEA.

**Fujairah 2**
The largest and the latest MED hybrid projects in the world were won by Japan's Marubeni Corp with International Power /Suez. An IWPP was formed with the Abu Dhabi Water and Electricity Authority in the 20-year project, which will oversee the entire power and water output from the Fujairah F2 IWPP in the UAE.

Fujairah Asia Power Company owns the plant, with Marubeni and International Power/Suez holding 20% equity interests. Both companies will, however, oversee operations with a 50-50 management stake.

The Greenfield development completed in May 2011, produce 2000 MW of power and 130 MIGD of water. The have five high-efficiency Alstom GT26 gas turbines in combined cycle mode and 12 SIDEM 8.3 net MIGD Multi Effect Distillation desalination units with a 30 MIGD Reverse Osmosis desalination plant. Engineering, procurement, construction and commissioning of 12 desalination units of 38,640 m³/day (8.5 MIGD) each and 30 MIGD reverse osmosis plant, together with: Potabilization plant, CO2 plant, limewater injection system, sea water pumps, 4 x 90,000 m³ storage tanks and other ancillary equipment

The plant will utilize the latest combined cycle power technology and simple hybrid water desalination technology, which combines a multiple effect distillation system and reverse osmosis system to maximize efficiency and minimize gas consumption and emission of CO₂.

**II. INTEGRATED HYBRID**
The fully integrated MSF/RO desalination power process, which is particularly suitable for new seawater desalting complexes, takes additional advantage of integration features, such as:

- The feedwater temperature to the RO plant is optimized and controlled by using cooling water from the heat-reject section of the MSF/MED or power plant condenser.
The low-pressure steam from the MSF/MED plant is used to de-aerate or use de-aerated brine as a feedwater to the RO plant to minimize corrosion and reduce residual chlorine. Some components of seawater pretreatment process can be integrated. One post-treatment system is used for the product water from both plants. The brine discharged-reject from the RO plant is combined with the brine recycle in the MSF, or is used as a feed to MED. The hybridization of Nanofiltration as softening membrane process for feed of distillation plants MSF and MED could lead to significant improvement in productivity of desalination plants.

**Integrated hybrid**

- Blending distillate and membrane permeate will reduce requirements on Boron removal by RO.
- The RO and NF membrane life can be extended. (12 years)

In general, the hybrid idea allows part of the distillation plant’s heated coolant reject to be de-aerated, using low-pressure steam from the distillation plant (to reduce corrosion and residual chlorine), and used as the feed to the SWRO plant. The higher temperature of the feed improves membrane performance (flux, at constant pressure, increases by 1.5–3% for each degree C). This is particularly important during the winter, when seawater temperatures can drop to as low as 15°C. The MSF or MED plant’s distillate, at less than 20 ppm TDS, is blended with the SWRO plant’s product, making it possible to meet potable water standards for maximum TDS and chloride concentrations with higher SWRO plant product salinity. This, in turn, means that the SWRO plants can be operated at higher conversion ratios, thereby reducing consumption of energy and chemicals and extending membrane useful life.

In one variant of the “classic scheme,” the SWRO plant’s reject brine becomes the feed to the MSF or MED plant particularly if the seawater is softened by Nanofiltration membrane, utilizing its high pressure, with a special turbocharger, to boost the MSF plant’s recirculation pump. The conversion ratio of the hybrid NF/SWRO+ MSF/MED plant is significantly increased. The ongoing work on Nanofiltration membrane softening technology, combined with distillation and hybrid options of NF-MSF-RO or NF-MED-RO, offers new potential for improving hybrid systems.
Integrated hybrid environmental benefits

- Cool RO Reject and Feed to be used as a cooling source for heat reject section of distillation plants.
- The blend of reject stream from RO with warm seawater and blowdown from distillation or power plants reduces heavy density plume of RO outfall.
- Blend of RO permeate reduces temperature of distillate.
- A common, smaller seawater intake & outfall.

Let Proprietary
Patented and Patents Pending

The use of distillation plant coolant reject as feed to a SWRO plant within selected hybrid plant schemes reduces both seawater supply and brine and coolant rejection requirements vis-à-vis non-hybrid, separate and independent (“stand-alone”) thermal and SWRO plants.

Where seawater supply and pretreatment and brine rejection costs are high (long intake and reject lines, large pumping power requirements, high seawater turbidity, etc.), they add an important cost element to the energy vs. capital cost trade-off equation for deriving the optimal distillation Performance Ratio (PR) the plant efficiency.

For all membranes, water permeability (i.e., permeate production) declines with operating time, while product salinity and chloride concentration increase. The drop in production can, with time, be compensated by installing extra membrane rack space and installing additional membranes as required.

The increase in product salinity cannot be compensated for except with large scale membrane replacement. In the case of hybrid systems (RO + distillation), a single pass RO system can be specified while maintaining a long membrane life. This is made possible by blending the RO product water with the high purity distilled water produced by the thermal desalination unit.

2.1 Membrane Performance as a Function of Seawater Temperature

The use of all or some of the preheated cooling water discharge from a thermal desalination plant as feed to a SWRO plant enables elevating and controlling the SWRO plant’s operating temperature at its optimal or any other higher desired value. Feed water temperature affects the two main performance characteristics of a membrane: flux and salt rejection. Higher feed water temperatures increase not only flux but also salt passage. For all membranes, water production is a function of temperature, at constant feed pressure. Production will go up with temperature increasing by 1.5% to 3% per degree Celsius for nearly all membranes, thereby
enabling reduction of the number of RO membrane modules required for a given permeate capacity. This is, of course, contingent on feed water of sufficient quality so that membrane fouling rate will not increase during operation at higher flux.

The results imply that the energy consumption of RO can be reduced using a simple integration of MSF/RO hybrid arrangement in which the RO plant is fed the preheated seawater rejected from the MSF heat rejection section.

It is quite obvious that higher recovery can be obtained with lower salinity feed, which has clear process implications when we consider Nanofiltration in front of RO system or the use of blending seawater feed with lower salinity water (concentrate of brackish RO, for example) to lower the feed salinity to RO system.

Higher membrane permeability at elevated temperature may also result in a higher recovery rate. However, higher feed water temperature and recovery rate are associated with an increase of osmotic pressure. The permeate TDS systematically increases as the feed temperature and recovery rate are increased. Fortunately, this salinity increase can be easily compensated in hybrid systems (RO + thermal desalination unit) where the ratio of distilled water to membrane permeate can be controlled to achieved required product TDS.

The increase of recovery rate at constant feed pressure at increased temperature in a RO hybrid system leads to reduction of specific power consumption.

Some critics of higher temperature of operation of RO and NF membranes suggest higher rate of fouling due to increased biological activities. If this is the case, an effective method of biological control would have to be developed for high temperature operation. The increase of seawater temperature, which is happening inside the condenser or rejects section of the distillation plant, is being achieved in a matter of seconds. The assumption is that this rapid rate of temperature increases results in a thermal shock, possibly reducing biological activity in seawater feed to the membrane unit.

Another issue of concern is the compaction of membrane material (permeability decline) during long term operation at high feed pressure and elevated temperature. We plan to test both of these issues for newly developed HT NF/RO and pretreatment Media

In Nanofiltration systems, the increase in temperature of seawater feed results in higher rate of water permeability increase more than is expected in RO unit. In Nanofiltration membranes, the concentration polarization increase with temperature is lower than in RO membranes due to significantly higher salt transport through NF membranes.

In hybrid systems, the use of Nanofiltration membranes operating at higher temperatures in combination with RO and MSF/MED provides additional opportunities to reduce desalination costs due to available heat from the power plant condenser or reject section of distillation plants. Specifically by using feed comprising variable proportions of softened seawater and water containing a higher concentration of hardness ions than the softened stream, concentration of hardness is sufficiently reduced, thereby allowing a beneficial increase in the Top Brine Temperature (TBT) of the distillation desalination process. Higher operating temperatures provide an increase in productivity, recovery and performance at
lower energy and chemical consumption. As a result, the cost of desalinated water production, including operation and maintenance, could be significantly reduced.

Hybrid plants have the potential to increase the average annual membrane permeate flow through increased flux rate and reduce the required membrane surface in the SWRO plants.

2.1.1 High Temperature seawater feed

LET for a long time is dedicated to develop use of High Temperature (HT) membrane applications in Integrated Hybrid solutions of membrane and thermal processes. The original target was Sharjah Electricity and Water Authority (SEWA) where LET-Besix built MSF-NF high temperature Integrated Upgrading system with our own patented processes and achieved an increased capacity of existing distillation plant by over 42% using Dow NF membranes.

HT membrane have to respond to raising seawater temperature and potential benefit from high fluxes and recovery from cooling seawater discharge streams of power and thermal desalination plants. Also the hybridization of thermal/membrane plants can significantly benefit from pilot developments using the feed to RO/NF from exit of MSF and MED plants.

More and more projects will adopt particularly in GCC, the hybrid idea of taking outlet from thermal and power plants to reduce intake costs and environmental issues problems, increase capacity and recovery with NF and benefit from steady state and higher flux for both NF and RO if we can solve the compaction of polysulfone support and other issues described below.

The temperature of seawater intake in DEWA is consistently rising by about 2°C per year and last summer exceeded 44°C, the challenge is even more important with more projects adopting outlet heated seawater from power, MSF and MED as a source of feed to Reverse Osmosis plants. The HT membrane elements could provide direct long term replacement for operation of Reverse Osmosis plants using higher temperature seawater as feed. Several examples of adopting LET solution to hybridization by using outlet seawater from discharge culvert of power-MSF plant is demonstrated in the specification for 30 MIGD Al Zour South in Kuwait a project recently awarded (03/2011) to Veolia Water and Fouad Alghanim to comply with the requirements to take the warmer seawater.

Similar specification for 30 MIGD at Fujairah 1 RO expansion by SembCorp provide the requirements for taking outlet seawater from MSF reject section to blend with limited supply of seawater. The provision of piping to supply the warm seawater was already built in the existing MSF plant.

I believe similar approach will happened on future hybrid projects specified in the GCC or future expansion with RO of existing thermal and hybrid projects. In the past bidders seriously consider the

Once the HT RO/NF/UF membranes are developed there are many applications of the technology to hot petroleum formation waters, chloro-alkali industry, food industry, geothermal resources, brackish well waters, cooling tower application, pollution control flue gas desulfurization (FGD) and mineral recovery which, we are also currently investigating.
2.1.3 R&D needs of High Temperature membrane for future hybrids

Below is a technical description of challenges to achieve HT membrane. It is well known that in normal range the productivity fluxes of membrane are improved with increased temperature. At elevated temperatures of greater than 35°C and pressures greater than 70 bars, with conventional elements some irreversible changes to the RO element will occur. These changes are attributed to several factors: effect of ionic strength on the active polyamide layer, partial collapse of the polysulfone layer and intrusion of the membrane into the permeate water carrier. Additionally components of elements like glues, seals and connectors have to be able to resist high temperature and pressure.

The challenge is to make Spiral wound, thin film composite RO elements using multiple water permeable polymers such as polyamide films and polysulfone support layers resistant and recoverable at this HT and pressure conditions. Ideally, membrane elements should be stable under the above-mentioned conditions and no irreversible negative performance changes should occur.

As to RO HT membrane parameters it should be able to operate efficiently in full range of 55°C in summer to 15°C in winter, in pressure range of 40-75 bars. The RO pilot program should incorporated HT a UF/ Mix Media and HT NF system.

Here is the current understanding of HT on existing elements previously investigated by Dow:

Polysulfone Compaction
This is the classic interpretation for pressure-induced water flux loss in thin film composite membranes. The microporous polysulfone layer has an open cell pore structure that can become deformed, density, or in some regions fully collapse, under elevated pressure and temperature operation. This results in a significant increase in the resistance for water transport through this layer. The polysulfone layer provides no intrinsic salt rejection capability for the membrane so clearly the most important issue to be solved.

Polyamide Barrier Layer Compaction:
The classic view of thin film composite membrane behavior is that the barrier layer does not undergo pressure compaction due to its cross-linked density. Indeed, in most commercially practiced operation, the polyamide layer permeability is remarkably stable. Nonetheless, it is well known that the permeability of this layer can be strongly and reversibly affected under the influence of varying ionic strength, or by chemically induced swelling, or by thermally induced "tightening". These changes result in simultaneous changes in the transport properties of water and solutes, an effect most often stronger for the solutes. As a result, under constant pressure test conditions, when such a change causes the water flux to go up, the salt rejection will go down. In increase of flux with temperature is clearly beneficial and reduction in salt rejection is not so critical in condition of GCC where most of the RO permeate is blended with distillate from thermal processes.

Intrusion
The membrane composite may be pushed into the permeate carrier. This is a function of operating temperature and pressure, as well as spacer geometry and strength of the composite membrane. The effect of membrane intrusion may lead to increased permeate side pressure drop, which will cause a permeability reduction. It may also cause cracking of the polyamide layer, which results in rejection losses.
2.2 Hybrid R&D needs for membrane Rejection and Recovery

The blending of SWRO and thermal plants’ products makes it possible to use the low-salinity (less than 20 ppm TDS) distillation plant product to compensate for higher salinity SWRO plant product. However, if the plants are designed to operate at the high conversion ratios used today in most modern SWRO plants (45–50%), it is projected that product salinity will exceed 500 ppm TDS after about four years of operation, as a result of membrane performance degradation.

Recovery ratio (conversion) is one of the key RO design parameters. It determines the size of the feedwater handling system (e.g., intake-outfall, pretreatment, high pressure pumping) for a given plant size. Higher recoveries decrease the cost of the feedwater handling system and the required electrical and chemical consumption, while increasing the initial and replacement costs of the membrane system.

Some of the reasons why higher recovery ratios have not been used in the past are related to the performance characteristics of the membranes and the product water quality specifications. Higher recovery ratio increases required feed pressure due to increase of the average osmotic pressure in the RO system. Also, due to the salt rejection property of available membranes, product water specifications (typically 500 ppm TDS and/or 250 ppm chloride) could not be easily met at higher recovery ratios. In a hybrid system, higher recovery ratios of RO unit can be incorporated into the plant design. A high flux lower rejection, high recovery membranes are needed to be developed for an optimal design of hybrid system.

2.3 Chlorination-dechlorination challenges and developments in hybrid systems

LET idea of taking outlet from MED or MSF to feed RO was challenge by the practice that RO systems requires intermittent chlorination whereas thermal processes use continuous chlorination. The recent research after detail analysis on several plants demonstrated that the residual chlorine after continuous chlorination of MSF intake is 0.25 ppm and downstream the heat reject section is 0.09 ppm. So downstream of the MSF or MED plant warm seawater should not be an issue from chlorination point of view and would allow intermediate chlorination for the RO feed.

The more general challenge is the question why membrane system by far more sensitive to fouling can operate successfully on intermediate chlorination and thermal processes require continuous. It needs to be demonstrated that thermal desalination and hybrids can successfully operate with intermediate dosing reducing clearly cost and environmental impact.

The Most aromatic composite membranes require dechlorination of the feedwater as they are very sensitive to even very small concentrations of residual chlorine and/or bromine. If feed water to an RO system is being chlorinated, then the addition of large quantities of sodium bisulphite is required to reduce free chlorine in the feed water. In hybrid system an alternative, free chlorine removal can also be accomplished by use of a vacuum de-aerator commonly used in thermal process, significantly reducing quantities of sodium bisulphite.

De-aeration of the feed water also reduces corrosion significantly. In the case of hybrid systems, low pressure steam suitable to operate the deaerator is readily available from the MSF plant at low cost. De-aeration can reduce the specification for high pressure piping from SMO - 254, to lower grades and more economical SS 316L.
2.4 Hybrid Variations

As the concepts and applications of hybridization are accepted between distillation processes and RO, we believe that membrane manufacturers will develop a new generation of membranes. This new generation of membranes is characterized by a very high specific flux – about double the flux of the current generation – with a small reduction in salt rejection. Developed for brackish water desalting, high flux membranes have demonstrated the ability to significantly reduce the cost of desalting and will be ideal for hybrid plants that include distillation units.

Hybrid System Using Multi-Effect Distillation

Multi-effect distillation (MED) is, in our opinion, the most important large-scale evaporative process offering significant potential for water cost reduction. The major potential advantage of the MED process is the ability to produce a significantly higher Gain Output Ratio (GOR) in excess of 16 pounds of the product per pound of steam, where MSF limits GOR to 11.

Example of the very advanced MED plant is SDIC 4000 MW Tianjin Electric Generation Plant in China where IDE installed in 2010 four units of 25,000 m³/day each with GOR varying from 13-16 depending on available steam pressure. The MED units has 14 effects, with 1.3 kWh/m³ electric power consumption and recovery of 50% with brine blowdown from MED is send to evaporation ponds production of edible salt. IDE won the second phase for identical 100,000 m³/day plant.

The size of MED units is growing rapidly. In Sharjah, SEWA operated for the last several years the Sidem MED units of 36,400 m³/day (8 MIGD). A 12 units of 8.5 MIGD started operation at Fujairah 2 is constructed by Sidem at 130 MIGD MED-RO hybrid plant. The largest single unit MED under construction is a Yanbu MED unit awarded recently by SWCC to Doosan with capacity of 15 MIGD a 68,190 m³/d capacity unit is under construction in SEWA Layyah Station, and the design and demonstration module already exist for a 45,500 m³/day (10-MIGD) unit.

MED recently received a lot of attention, as a result of numerous commercial successes of MED for Hidd Bahrain, Marafiq in the Kingdom of Saudi Arabia and in Qatar the Ras Laffàn C constructed by Sidem for Mitsui Bahrain consortium, the 286,000 m³/d seawater desalination plant uses multi-effect distillation/thermal vapour compression of 10 desalination units at 28,640 m³/d each was officially opened on 31 May 2011.

2.5 Future improvements in Hybrid systems using Nanofiltration

The future calls for increasing the top operating temperature TBT of MED, finding new ways to improve heat transfer performance to reduce the heat exchange area, searching for an increase in heat transfer performance by tube enhancement, and using a very thin wall in tubular materials. The critical challenge is to adopt Nanofiltration as means to dramatically increase output and increase the efficiency of MED plants.

2.5.1 Hybrid Using Nanofiltration - Membrane Softening

Membrane softening technology adapted to hybrid with distillation processes could lead to a significant increase in the productivity of existing and future distillation plants as well as resulting in better process
economics. As a result, the selectivity of NF membranes for monovalent and bivalent anions is significantly different as compared to RO membranes. Specially designed NF membranes have the capability of high rejection for divalent ions (Ca, Mg and SO₄), while allowing relatively high passage of monovalent ions (Cl, Na and K).

Today, pioneering work on Nanofiltration membrane NF softening technology as applied to desalination processes and specifically to seawater desalination is under active development by two groups: Leading Edge Technologies Ltd (LET) and the Saline Water Conversion Corporation (SWCC) of Saudi Arabia.

The great potential of Nanofiltration membrane softening technology was brought to focus by a recent award by Sharjah Electricity and Water Authority (SEWA) to LET and Besix Consortium for the first commercial LET Nanofiltration System to increase the capacity of an existing MSF plant from nominal 22,7000 m³/day to 32,800 m³/day (5 MIGD to 7.2 MIGD). This 40%+ increase in capacity of MSF unit was a result of a two-year demonstration and simulation program developed jointly with SEWA.

While certain features of the plant need to be adjusted to further increase and maximize the plant output, in response to higher operating temperatures and increased product volumes, no major technical issues were encountered that could prevent the application of the LET technology.

The additional capacity is achieved without building a new intake structure or new power plant in a very limited space that would not allow construction of a new desalination plant. The system involves construction of a NF plant to provide partial membrane softening of feed to MSF as well as modifications to existing MSF plant to be capable to achieve the increased capacity.

NF membrane softening technology could significantly improve operation and reduce the cost of the MED process, by eliminating the risk of scaling and fouling. NF technology will permit an increase in the top temperature resulting in a significant increase in output and the performance ratio.

Figure: LET NF system for upgrading MSF and MED capacity
Of course, the LET Integrated Modification approach of using NF could be also effectively introduced to MED technology. The Figure above gives an example of NF softened feed being introduced to high temperature effects of MED, by blending with normal seawater feed. At the same time, the additional NF-softened feed could be introduced to the brine recycle stream at high temperature stages. If it is required, the NF membrane softened feed could be preheated to feed water Heat Exchangers.

There are many potential variants for NF hybridization with NF-MSF-RO as well as NF-MED-RO. One option is for seawater to be preheated in MSF or MED reject section, and then softened by Nanofiltration membrane, followed by SWRO. The reject brine of SWRO has significantly reduced level of scaling ions sulfate, calcium and magnesium and therefore, the reject brine can be the feed for the distillation plant.

2.5.2 Hybrid Systems Using MSF-MED

In distillation processes, there is no interaction between MSF and MED energy process streams. Substantial efficiency improvements could be obtained if process streams between MSF and MED were exchanged in order to take advantage of the different operating temperature conditions of each plant.

In particular, due to the low MED operating temperature (61-67° C), this process could be thermally driven by process streams properly sourced by an adjacent MSF plant.

Figure: Integrated hybrid MSF-MED using distillate
A number of novel technology options have been studied, and their possible implementation in a real scale plant should be available soon.

The objective of the MSF-MED hybrid is to increase energy efficiency, increase distillate production and minimize operational costs. Of course such a MSF-MED combination can be further improved by hybridizing with Nanofiltration and Reverse Osmosis.

2.6 Resource Conservation and Environmental Impacts of Various Hybrid Configurations

Resource conservation and environmental impact are aspects that have to be considered when designing hybrid systems. The reduced primary (fuel) energy consumption when coupling reverse osmosis with thermal processes in a hybrid configuration conserves from 30% up to 40% against reference plants (boiler for heat and condensing turbine power plant for electricity). CO₂ emissions from a gas-fired combined cycle plant with a corresponding SWRO share are, likewise, substantially lower than for a conventional cycle. Showing a substantial reduction is dissipation of heat from a hybrid plant to the sea as compared with the conventional heat cycle/SWRO configuration. In recent years, the consideration of carbon dioxide footprint will have a significant impact in justifying hybrid plants in the Gulf.

2.7 Rehabilitation and Upgrading of Existing Plants

Many of the existing distillation plants are approaching the design life of 25 years, and the owners have to consider life extension with additional upgrading in the capacity and efficiency of the desalination plants. There are new technologies using Nanofiltration softening membranes of seawater and integrated upgrading of distillation plants, which as result of hybridization, permit distillation plants to raise top operating temperature and increase the design production from existing plants by over 40%. Such rehabilitation and upgrading minimizes the environmental impact and produces more critically needed water without building new intake – outfall structures and new power plants.
2.8 Hybrid Technology for Gas Well Water Supply, Treatment, and Fracture Recycle Technology

The huge Marcellus black shale deposit, which underlies most of northern Appalachia, is estimated to contain 168+ trillion cubic feet of natural gas. Due to the depth and compact nature of this formation, horizontal drilling with follow-up fracture of the formation using a mixture of high pressure water and sand (or ceramic) is required to obtain economic gas production.

From 2 to 10 million gallons of fracture, “frac”, water, mixed with various additives, is required to completion fracture each horizontal deep well. Once used, this now contaminated water must be removed from the well and is commonly referred to as “flowback” water. Obtaining the needed water to makeup frac water, with subsequent disposal of the flowback water, presents significant problems for gas production firms. In many areas, the amount of clean water needed for formulation of frac water is just not available, while disposal of the contaminated flowback water is a very a significant problem.

Once a gas well is in production, additional water is generated entrained in the gas flow, this is commonly referred to as “production” water and also presents a substantial disposal problem to the gas production firm. Production water can be treated much as flowback water and reused as frac water, or pretreated for removal of specific hazardous constituents, such as barium, and discharged to a publicly owned treatment works (POTW) for additional treatment and subsequent discharge.

Frac Water Chemistry: Frac water is formulated by dosing a clean, low scale forming potential water with the following chemical products. Friction Reducer, Wetting Agent: generally a nonionic surfactant which reduces the surface tension of the water, Biocides: several materials are used as biocides in frac water formulations to control growth of microorganisms and Scale Inhibitor generally either a polyacrylate or a phosphonate.

2.8.1 Flowback Treatment and Recycle:

The major problem with use of flowback, or production, water for makeup of frac water is the very high content of scale forming constituents present. The high levels of barium, calcium, iron, magnesium, manganese, and strontium common in flowback water will readily form precipitates, scale, which would rapidly block the fractures in gas bearing formations required for economic gas production. Removal of these constituents to much lower levels is thus required for recycle of flowback water, or use of production water, as frac water.

Recycle Process: The existing recycle processes depend on a unique sequential precipitation treatment process that try to remove the majority of these problem constituents to levels suitable for recycle via chemical precipitation which results in the removed constituents being disposed of as a solid cake. The solid cake from our process is disposed of as all toxic materials.
Evaporation: the second disposal method, involves evaporation of the wastewater, producing effectively distilled water, which can be used in various applications or discharged to either surface waters.
Due to the problems presented by scale formation on heat transfer surfaces during evaporation and the positive economics of selling recovered salt for use as a deicing product, removal of the toxic barium, as well as all other scale formers, from the wastewater prior to evaporation is required.
2.8.2 Hybrid of Nanofiltration NF with Mechanical Vapor Compression (MVC) or a MED

Future demonstration of LET Patented Technology of Hybrid NF-MVC or NF-MED would allowed to recover significant amount of distillate and at the same time concentrate the flowback or production brine without risk of scaling in the evaporators.

The ability of a treatment program to prevent mineral scale formation from hardness salts (sulfate, barium, calcium and magnesium), silica often defines the maximum cycles of concentration for a given make-up of water.

In order to reduce total dissolved solids (TDS) in the return water involve is possible use of reverse osmosis, electrodialysis reversal or forward osmosis but all the membrane processes have clear limitation due to osmotic pressure limiting recovery to about 7% TDS.

The LET is utilizing the Nanofiltration NF softening membrane in combination with Vapor Compression or MED. It will prove promising solution with respect to maximum recovery of highly saline brines, leading to zero liquid discharge of blowdown and use of the brine minerals for an environmental control.

• Maximize recovery of the “flowback” and Production water to produce distillate for blending frac water and other potable use and concentrate the blow down to the level of 15-20% TDS using combination of Nanofiltration Membrane to soften the feed to Vapor Compression (NF VC) or NF MED for large plants. This would allow a significant increase in CT cycles of concentration without the use of chemical side stream softening.
The LET technology aims to allow efficient distillate production of highly saline waters with ability to increase recovery of thermal distillation unit MVC and MED, increase the output and optimize the performance of thermal desalination units. The development and implementation of the technology would allow the thermal units to be safely operated at an increased recovery and Top Brine Temperature (TBT) thus allowing to substantially increasing the potable water production.

The water is softened by Nanofiltration technology. The plant would incorporate the following features:

1. A blending system with an alternative to preheat feed water to keep the feed water temperature in the right range to improve fluxes and operation. The blending facilities of NF softened water with raw feed. After blending, the water is pumped to the MVC unit. The temperature control of the raw water allows steady state operation of the membrane.
2. The water needs to be properly pre-treated to avoid pre-mature membrane fouling and clogging. Therefore, the water is first pre-treated by means of sand filtration depending on quality would follow by UF. The SDI requirement is below (SDI < 5). Prior to NF membrane the treatment incorporates the injection of SBS to remove free-chlorine, the shock dosing of biocide to control bacteriological growth and the continuous, on-line dosing of Antiscalant.

3. Water then passes a two stage Nanofiltration membrane system. The system is of the two stage design and incorporates Dow Filmtec Nanofiltration XUS229323 elements which are under continuous joint development of Dow and LET.

4. In order to pass the water through the membranes, medium pressure pumps are used. The main-booster pump is to pressurize the feed water prior to injection in the membrane system. System pressure: 20 to 32 bars

5. After leaving the membranes, the softened water is discharged to an intermediate storage tank. From this tank, the water is pumped at a controlled flow to MVC or MED to blend with raw water at design percentage of blending.

6. The typical power requirements for two stage NF system are from .80 to1.5 kwh/m3 depending on salinity and recovery.

The computational analysis for NF is based on Dow Filmtec NF membranes XUS-229323 which LET used in LET INTEGRATED UPGRAADING PROJECT at Sharjah. Based on the ROSA projection we will run Genesys MM3VC projections for scale chemistry and selection of antiscalants. The two stage design allows to obtain a high recovery rate (recovery = ratio between useful softened water output and total feed water flow to the membrane system). The recovery rate of this system is approximately at 73% and if possible with Genesys inhibitor up to 80 %. The total salinity of the concentrate from NF-MVC system reached in the brine from MVC levels of 15.6 to 22% TDS. With such results the quest for zero discharge with NF-VC technology is possible.

To further improve the MED thermal desalination with hybrid technologies we foresee plants optimized and integrated with a set of technologies including:

- The addition of a nanofiltration (NF) unit to pre-treat a portion of the feed. With pre-treated feed, the TBT of the MED unit can be safely raised to higher temperatures to achieve increased output and efficiency. NF controls and removes critical hard scale formation by calcium sulfate and reduces magnesium ions and alkalinity. This allows dramatic improvement of desalination operations with reduction in environmental impact.

- There is a potential for adding HT NF in order to soften feed for High temperature effects and increase number of additional effects to achieve the higher performance ratio.

**III HYBRIDIZATION FUTURE NEEDS AND CONCLUSION**

The paper outline the potential and the needs for further improvements in membrane and thermal distillation processes in order to take full advantage of Hybrid potential. The key is development of Nanofiltration and Reverse Osmosis membrane specifically designs for Hybrid purposes. It includes loose membrane with high flux, high recovery elements. We need to develop High Temperature NF and RO elements to take advantage of the warm seawater available from power plant and thermal desalination heat reject section. We need to further test and demonstrate higher TBT in MED plants hybridized with NF to achieve significant improvements in efficiency capacity and recovery. There are requirements for demonstration of new ideas for NF-MED or NF-MVC for application to frac waters,
petroleum application leading to ZLD. The ideas of tri-hybrid of NF-RO-MED also need further development and demonstration.

The current application of Hybrid already shown significant advantages of Hybrids, but it is our strong believe that future developments of combining thermal and membrane desalination processes and technologies within a single plant in hybrid plant schemes can reduce desalinated water costs, in dual-purpose stations; add flexibility and better match the demand to the combined water and power production; and, most importantly, minimize the environmental impact of power desalination plants.