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Evolution of membrane application for industrial recycling

Greg Turner

Veolia Water Solutions and Technologies, Marlow International, Parkway, Bucks, SL7 1YL Marlow, UK
Tel. +44 1628897286; Fax: +44 1628 897201; email: Greg.Turner@veoliawater.com

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ABSTRACT

Membranes first appeared as a form of pre-treatment for soft drink manufacture in the late 1970's and were very much seen as replacing other forms of physio-chemical treatment, whilst adding a level of disinfection credit because of the porosity of the brackish water reverse osmosis (BWRO) membrane barrier. However, the emphasis through the 1990's and 2000's following industrial applications of the 1980's for reuse of secondary injection water in oil and gas sectors by sulphate removal was to concentrate on recycling and reuse with the economics of water acquisition and disposal becoming more and more expensive. Utilising this sustainability approach, industrial applications of water recycling using the recovery of an effluent with RO processes initiated a culture, which has grown as the economic drivers associated with water supply and disposal, that has made this type of water reuse more and more attractive. Applications in the metal finishing area illustrate some quite exceptional operating conditions for membranes which have proved to be sustainable over many years and in one particular case, rewritten the operating parameters for BWRO. The reuse of a low-grade feed water source, in this case a domestic effluent treated to a secondary level, to derive an 18 megohm quality boiler feed for a power generator utilises the 12× difference in cost in feed water supply as its driver. One of the larger psychological problems of water reuse is subsequent consumption by the population of effluent water recovered without being returned into the environment. However, such closed loop recovery systems are now built for food manufacturers with all of the safeguards required to ensure that a biological system with subsequent membrane separation are meeting the highest level of bacterial and mineral quality. This encompasses the multibarrier approach required to allow for such recovered water being in direct contact with food for human consumption. The major change, however, to industrial utilisation of membrane processes is the association with anaerobic digestion which brings with it biogas and energy conservation as well as reuse of the aqueous portion of the effluent and recovery of sludge, which has been successfully applied in the brewing and distillery industries. This relatively complex process design is now being simplified by the use of an anaerobic membrane bioreactor in the food and drinks sector, which is yielding higher levels of energy recovery as well as very high levels of treated effluent quality for process recycling. All of the above evolutionary applications will be considered with case studies demonstrating their operation over a significant period of time which gives validation to such membrane applications within the industrial environment from not only a process and economic basis but also a sustainable use of natural resources and an improvement in the environmental impact of discharges in industrial processes.

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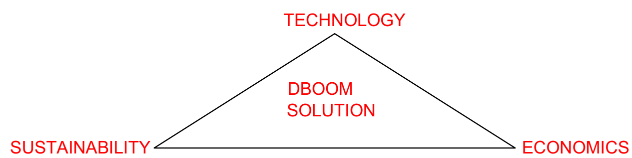
1. Membrane industrial applications–BWRO/SWRO application

The use of membrane processes in industrial applications has been on-going since the mid 1970's but these early applications were for brackish water (B9 membrane) and generally replaced more traditional technologies such as ion exchange as part of a pre-treatment process in the soft drinks and power sector. The benefits to the customer were more associated with ion rejection and micro-organism removal than any environmental impact. With the application of seawater membranes [1] (B10 and TFC), there was a move towards the energy savings, which such technology enjoyed over the traditional thermal processes, but this was seen as a municipal market for potable water rather than having obvious industrial application. It was not until the latter part of the 1980's that seawater reverse osmosis plant (SWRO) saw a very high profile use in the civil engineering sector by providing 3,000 m^3/d of water from the Channel Tunnel Project [2] on the UK side to allow for grouting of the tunnel lining. This was an early application to demonstrate a replacement of a scarce natural resource, drinking water, with that produced by a membrane system.

At a similar time in India, Madras Fertilizers [3] were addressing their acute shortage of process water by employing brackish water reverse osmosis (BWRO) with traditional disinfection and multimedia filtration to use primary domestic waste water as a feed source to produce 12,000 m^3/day of water for the manufacture of fertilisers. The impact was to give a sustainable supply of water for the production plant and release into a very stressed potable supply system drinking water for over 0.25 million population in Tamil Nadu.

2. Industrial application economics

Whereas the above two industrial applications have economic as well as environmental benefit, they are relatively small applications when compared to Orange County Water Factory 21 which has been purifying treated waste water since 1976, but this is based on a need to protect the environment for excessive abstraction. We therefore need to define the industrial recycle, reuse and recovery concept when compared to governmental objectives as the drivers are certainly different. The industrial market sector requires solutions to water and wastewater needs using the Best Available Techniques, but requires good environmental application of economically viable schemes. It is this triangle of requirements which uniquely defines the market sector and differentiates it from the larger municipal market, where scarcity of supply is probably the main driver. The industrial requirement is usually based on a number of contractual models, the most encompassing being design, build, own, operate and maintain (DBOOM).



One of the more mature membrane industrial processes is sulphate reduction (SRP) for secondary recovery from oil wells, mostly on offshore installations. The SRP and SWRO were first commercially applied (a pilot plant having been previously run by Marathon/Dow) on Agip Tiffany [4] (1991 ≈ 16,000m^3/day) and this market is still very buoyant with 30 + plants *in situ*. The recovered product, which is the driver, is additional oil yield from the well and is a perfect fit in the triangle model, where the SR90–400i membrane is targeted to produce < 20 mg/l sulphate from a single-pass system. This gives a high economic return and the reduction in sulphate yields a practical solution to the detrimental effects of barium/strontium sulphate blockage in the well structure when utilising water injection.

A small recycle BWRO(TFC membrane) application (50 m^3/hour) is for a metal finishing plant which is in the Aerospace Industry [5], where a lime precipitation process to remove heavy metal ions is followed by sodium carbonate softening and BWRO. This yields approximately 50–60% of low TDS recyclable water, which is blended with towns' mains and returned to the factory as process water. The return of water cuts down the potable demand, but the unusual operating conditions of the BWRO plant is a cleaning regime every two weeks (biocide/caustic/acid) and the membrane feed pressure of 15–20 bar (initial projection 8–10 bar). This unit has run successfully for 10 years and demonstrates the very different operating conditions which certain industrial applications confer. The process success is based on the cleaning regime that has been developed at site, which has given an average 2-year membrane life.

3. MF/UF pre-treatment

With the advent of MF and UF pre-treatment for BWRO, the reuse of municipal treated effluent as a new source of process water is illustrated by the 100,000 m^3/day Gibson Island, 66,000 m^3/d Bundamba and 66,000 m^3/d Luggage Point plants of the Western Corridor [6] project in S.E. Queensland, Australia, which is taken from six local WWTPs and the product supplied to three power stations. Like many of the projects in Australia, this scheme is presently under preservation as the local water storage is at capacity from abnormal rain fall. This again illustrates the use of wastewater to preserve drinking water, thus adding sustainability to the water cycle by recovery and reuse.

An extension of this reuse concept from domestic WWTP discharge is illustrated at a power station in South Wales [7], UK, where the secondary effluent is dosed with hydrogen peroxide (rather than the chlorine disinfection found in Western Corridor) to avoid chlorinated byproducts and passed through UF(PVDF) tubular membrane to BWRO(TFC) and mixed beds to produce 18-mega ohm boiler feed water. The driver is greater than 10 times feed water cost differential between Potable and secondary effluent source, whilst again making the higher quality water available for distribution and public consumption, and reducing investment in additional potable water infrastructure. The variability of the feed, particularly phosphate levels, requires phosphate sequestrant application. The use of H_2O_2 as a biological safeguard raises difficulties with the use of redox (ORP) control of oxidisation potential prior to the membrane process.

4. Zero liquid discharge (ZLD)/zero discharge desalination (ZDD) for reject stream

One of the problems in large-scale water recovery using BWRO is the disposal of the reject (concentrate) stream, especially in environmentally sensitive areas. This has arisen in food and beverage, power and mining applications, and has traditionally required thermal plant to derive a ZLD by implementing recirculating crystalline evaporation technology. However, the advent of [8] ZDD by utilising electrodialysis metathesis, where sparingly soluble salts ($CaSO_4$) are converted into two highly soluble salts by ion substitution to prevent the divalent salts from precipitating has given a less energetic alternative technology. The 95% + water recovery means very small volumes to the crystallised and can yield a saleable byproduct in certain applications. It is also of great environmental benefit as the concentrate is not discharged to inland ponds or water courses, whilst maximising process water to recycle.

5. Material advance—ceramics

The use of ceramic membranes [9] in industrial applications is targeted at Oil and Gas, Steel and Power where there are oil water wastes, usually containing emulsions. The membranes are 5–50 nm and have the capability of using aggressive cleaners at high temperatures as well as handling the feed streams, which would be injurious to polymeric materials. The systems are capable of TMP up to 4 bar, cross-flow velocity of 2–3 m/s with modules up to 50 m^2 (200 mm diameter, 2000 mm long). The impact on oily water separation is very promising but the economics are difficult to justify in all, but applications with a high rate of return. The MF/UF membrane flux rates vary dependant on the cut-off, 0.5 μm up to 1,000 lmh/bar to 0.01 μm, which typically gives 100 lmh/bar. Materials of construction range from aluminia, silicon carbide, titanium or silica. The recovery of oil from oily water wastes drives the application economics by reducing effluent for disposal and generating a recovered oil stream.

6. UF hollow fibre

The impact of PVDF tubular UF in the waste/effluent recovery sector in food and drink has generated plants to recover copper as its hydroxide from copper whisky stills, to the recovery of protein and animal food supplements from pot ale, a byproduct of the distilled drinks industry. In the latter case, the potential for protein recovery for aquaculture is presently being evaluated in a study at Herriot Watt University in Edinburgh, Scotland. The earlier work on soil improvement by injection of a concentrate from the pot ale has already been seen as beneficial to land improvement and crop yield. The high chemical costs associated with the cleaning of such systems makes the viability very sensitive to byproduct resale price as this can be very volatile. In this case, the membrane concentrate becomes the saleable product.

7. Membrane bioreactor (MBR, AnMBR)

The alternative approach for stillage from the drinks industry is to separate the grains and organic matter, the former going to biomass boiler feed and the latter to anaerobic digestion. This will then yield biogas to supplement to boiler and return energy to the plant. A membrane bioreactor is used to complete the BOD removal with a UF membrane providing a suitable feed to the BWRO plant to recycle water. The sludge from the bioreactors can be used as feed to supplement the boiler combustion. We are now capable of energy and water recovery in such operations which are not only providing excess power to export, but also a reliable sustainable power supply throughout the winter, which the distribution network does not always provide [10]. This process stream using anaerobic digestion has now been refined into a single process unit with the advent over the last year of anaerobic membrane bioreactors which have a higher COD removal, more tolerant feed conditions and use a UF membrane to send permeate for reuse. The biogas yield is enhanced in these units and so it will increase the recovery of energy from the waste/effluent and give a recycled flow of process water for reuse–a truly environmentally friendly membrane technology application [11]. The economics of the application is also sensitive to the non-fossil fuel credits for power generated and the feed in tariffs, which drive the return of such an investment.

8. Closed cycle reuse

The industrial utilisation of the membrane bioreactor has been significant in the food and drinks market sector–which is almost full circle from our starting point of the soft drinks industry using BWRO for feedwater treatment. The COD rich effluent can be aerobically digested with fats, oils and greases being eliminated within the pre-treatment (DAF) plant. The membrane systems have a number of configurations from the hollow fibre modules suspended in the mixed liquor to high velocity side stream, low energy side stream and air assisting configurations being available. The recovered water is generally returned to non-product inclusive use within the food and drinks production unit. However, we now have the acceptance of closed circuit reuse [12] of effluent derived from vegetable washing after biotreatment and UF/NF barriers with subsequent UV (to provide two physical barriers and a disinfection process) for recycle and inclusion in a product for human consumption (salads). This has always been technically possible, but the acceptance by a major food supplier and one of the largest retail chains has finally overcome the psychological prejudice of closed circuit recycle. The environment impact is to reduce water taken from the potable system by 66% in a water-stressed area. The reject from the NF stage is allowed to discharge to soak away, so fully recovering the trade effluent charge as well as removing the potential of the reject stream "washing out" the biology in the small local wastewater treatment plant.

9. Where next

The applications given above show how far the membrane technology has come over the last 35 years, and the benefits it brings to the environment, the reduction in carbon footprint and water impact index. However, the story is still ongoing and the greatest challenge we still have to address is to reduce the energy required in membrane separation. The whole field of material science, chemical dosing and cleaning needs to be optimised to increase membrane life and reduce the chemicals in the discharge from plants. These same challenges have the greatest impact on successful application of membranes as they drive the economics of the processes.

Sludge created must be reapplied to beneficial use and reliability of all processes improved by good operational practices and well-trained personnel. The aim to recover products, reuse water and recycle waste to energy provides an additional economic and environmental benefit for the membrane plant. The future will involve novel design of membrane plants and use of new energy sources. We are still in a developing technology in which process application requires a clear understanding of the industrial needs but is limited by the economics of implementation. This, however, must not be a constraint in developing the environmental benefits which membranes can confer.

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