

Ion exchange brine treatment: closing the loop of NaCl use and reducing disposal towards a zero liquid discharge.

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Abstract

Minimizing the volume of waste streams for disposal and avoiding regulatory and environmental issues while recovering the maximum amount of by products is the main purpose of brine treatment. At PWN (Water Supply Company North Holland), where a full scale ion exchange pretreatment plant for drinking water is being built with a capacity of 4000m³/h, brine treatment options are considered to handle the very saline and NOM rich regenerant solution arising from the process. The two equally important challenges are to reduce volume of waste to be transported to the North Sea and to recover NaCl in a pure form to be reused for regeneration of ion exchange resin. In this regard the implementation of nanofiltration aiming at ion separation (monovalent/bivalent) investigated on a pilot scale has proved a good retention of DOC (87%) and sulphate (85%) while allowing sodium and chloride ions passage of respectively 80% and 100%. The ambition is to recover 80% of the ion exchange regenerant brine under a NaCl solution for reuse while the remaining concentrate would be further concentrated 10 times through Dynamic Vapour Recompression: an energy efficient evaporation technic with as a unique benefit its ability to process very high TDS solutions.

Keywords

Brine treatment, nanofiltration, evaporation, controlled precipitation, NaCl reuse, dynamic vapor recompression

Introduction

The various applications of ion exchange processes in water treatment: softening, deionization or color and DOC removal lead to the production of saline brines that usually varies between 1,5 and 7% of the total amount of water treated [14]. These brines result from the regeneration of the resin by desorption into a solution containing the counter ion (usually Cl-) in excess which make their discharge an issue. Conventional options to dispose brines containing high percentage of salts, dissolved mineral and DOC including discharge to sea or other surface water body, discharge to sewer, deep well injection, land application or evaporation ponds are often restricted because of unavailability, costs of transportation and fees, environmental impact, regulations or public perception. Created in the 70's but developing in the 90's, the zero liquid discharges (ZLD) processes which refer to technologies resulting in the elimination of all liquid wastes, avoiding discharge to surface bodies were thought as a solution for saline brine disposal that would ensure the sustainability of the plant. However, despite major the developments in the technics to achieve either strict ZLD or very high recovery leading the wide choice of equipment based on thermal technologies or membranes processes to choose from according to the brine quality as well as its volume and the expected result; no municipal water treatment plant in the world applies ZLD. The reason for that is the economical viability: thermal evaporation processes are energy intensive and the capital cost of such technologies are high due the high quality material required to handle corrosive brines (stainless steel or titanium). In comparison, membrane processes have lower capital costs and lower energy demand however increased cost in chemicals usage and solid disposal cost may offset a large part of the savings. Therefore despite the cost saving on brine disposal fees and large increase of the overall sustainability, costs associated with ZLD technologies are still prohibitive for water treatments plants.

Solutions to reduce the costs of brine treatment are being heavily investigated at the moment by R&D laboratories around the world. General directions given to it are:

- Alternative treatments to the energy intensive evaporator crystallizer system (RO)
- Pretreatment technologies for main volume reduction at lower capital/ operational costs
- Reuse mean of valuable wastes while reducing solid disposal.
- Alternative power sources such as solar or wind power.

In the case of an ion exchange plant which required large quantities of salt for resin regeneration, NaCl recovery from the brine is particularly beneficial. In fact, closing the loop of salt usage in the ion exchange besides cutting off chemical and disposal expenditures and environmental impacts would largely increase the plant sustainability by reducing indirect energy demands linked to salt production and transportation.

At PWN Water Supply Company North Holland a full scale ion exchange process, the so called SIX© process [6;7], is under construction for raw surface water pre-treatment to remove dissolved organic carbon (DOC) and nitrate prior to ceramic membrane filtration and advanced oxidation with UV/H₂O₂. The SIX process offers a complete regeneration of the resin by desorption in highly concentrated NaCl solution for further reuse which lead to the production of a spent regenerant solution or brine which characteristics are high sodium and chloride content combined with, due to desorption, DOC, nitrate, sulphate, phosphate and bicarbonate. In this context, investigation over brine treatment option were overtaken: starting with the application of a spiral wound nanofiltration to permit ion separation and sodium chloride reuse; it allows passage of monovalent ions as sodium and chloride while retaining DOC and divalent ions. Ideal set up for nanofiltration would be a recovery of 80%, to allow a major salt reuse and waste stream volume reduction however the challenges of such high recovery are on long term operation with the high risk of organic fouling. As nitrate (monovalent ion) was passing through the membrane, an additional biological denitrification steps was added upstream the NF to prevent the permeate pollution prior to reuse as a sodium chloride solution during ion exchange resin regeneration. Biological denitrification in an extremely saline environment has already been proven as a successful technology for complete nitrate removal at the PWN pilot plant in Andijk [11]. And as a final step the DVR is aiming at further NF concentrate volume reduction towards a ZLD system with NaCl recovery. The DVR is an energy efficient evaporation technique for treatment of highly concentrated brine streams, based on the mechanical vapour recompression process. The vapour is being compressed to a higher pressure (temperature) and then being condensed in a plate heat exchanger wherein on the other side of the plates the feed brine picks up the energy to reuse it again for evaporation. Unique benefits from the DVR over the MVR are its ability to process very high TDS solutions with a small temperature difference (around 5°C) across the heat exchanger. Further research on crystallization aiming at salt separation was undertaken in this context in order to recover the 20% remaining sodium chloride in the NF concentrate as well getting closer to a closed loop of salt usage.

This paper describes step by step orientation studies and the progress made at PWN in the field of ion exchange brine treatment which led to the overall process based on denitrification, nanofiltration and dynamic vapor recompression. Investigations made on laboratory and pilot scales aims to give a global solution to saline brine disposal issue including volume reduction, recovery of NaCl for reuse and separation of valuables compounds as humic acids. Focus will be made on the nanofiltration pilot's performances enhanced with air water cleaning for brine treatment and NaCl separation and on the DVR process, as an emerging technology and on the possibility it offers to concentrate the brine up to salts crystallization level in order to recover or separate organics from solid salts. However the denitrification results, already published (Koreman, 2011), will not be repeated in this presentation.

Material & Methods

NF pilot

NF pilot consists of two parallel units independently operated to achieve comparative studies. Particular feature of each units are:

- 4 inches NF270-4040 spiral wound membrane element,
- a recirculation loop (controllable flow from 1 to 4 m³/h)
- air injection system into the pressure vessel

Operation are controlled by set up permeate flow of 50L/h and concentrate 12,5L/h (recovery 80%). Every 30 min a forward flush is performed with either a mixture of air and feed water or only feed water for 30 seconds.

DVR pilot

Downstream the NF, the DVR further concentrate the brine another 10 times by evaporation at an approximate pressure of 0,6 bar (absolute) and temperatures between 70 and 90°C. In each of the 5 cyclones over 8m³/h of NF concentrate is recirculating while the vapour is sucked out and compressed to the heat exchanger where it condenses transferring its energy back to the liquid phase on the other side. A second small heat exchanger is used to pre heat the feed flow (250 L/h) while further cooling down the exiting condensate.

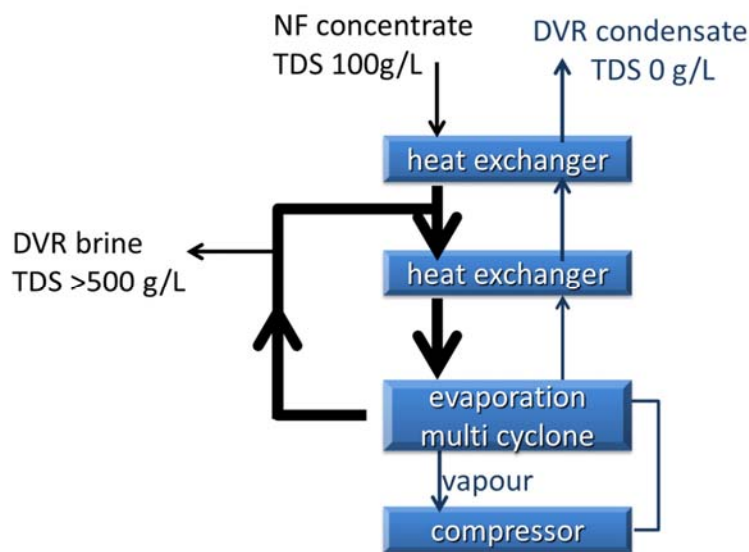


Figure 1: Process scheme of the DVR pilot.

The DVR pilot is operated in batch tests from 6 to 24 hours. The concentration factor inside the DVR pilot is controlled by adjusting the concentrate brine flow up to crystallisation levels. The resulting concentrate brine flow from the system can then be cooled down to start the formation of solids. When these solids are separated through a physical separation process the remaining brine is fed back to the system as influent.

Results

Nanofiltration:

Permeate quality

Nanofiltration has shown good separation property and a stable permeate quality despite the high variation in the brine concentrations due to variation of the raw water quality (IJssel Lake), ion exchange performance and applied regeneration procedure. Influent and effluent quality ranges are presented in table 1 as well as the average retention over the membrane per compound.

Table 1: Average chemical composition of the regenerate in Andijk SIX pilot.

Parameter	DNF effluent range	NF permeate range	NF concentrate range	% retention over the membrane
Chloride (g Cl ⁻ /L)	7 – 28	6 – 35	10 – 35	0
Sodium (g Na ⁺ /L)	5 – 35	4.0 – 25	4.5 – 35	20
Sulphate (g SO ₄ ²⁻ /L)	6.5 - 11	0.2 – 3.5	6.0 – 20	85
Bicarbonate (g HCO ₃ ⁻ /L)	5- 8.5	2 – 8	2.3 – 8	15
DOC (mg C/L)	200 – 500	6.0 – 90	500 – 1200	87

Regeneration of the resin by desorption into the saline solution is followed by a rinsing step with fresh water aiming at limiting the chloride level increase in the drinking water which causes a dilution of the IEX concentrate. In addition the water treatment during which DOC, nitrate and sulphate are being exchanged onto the resin surface against chloride ions necessarily consumes chloride, the loss due to Cl exchange was calculated on pilot scale to be 20 to 25gCl/L of regenerant solution. As a result of what a strict recovery of NaCl isn't possible by simple mass balance and a concentration step is needed after NF treatment for the permeate to reach a NaCl content of 90g/L to be reused as a regenerant solution. Therefore, two options: implementing a reverse osmosis downstream the NF on the permeate flow or dissolution of additional NaCl crystals. Possible risk of bicarbonate and sulphate accumulation in the NF permeate is still to be assessed. Nevertheless these results indicate a promising, robust solution to recover large part of the NaCl and reduce brine discharge in the ion exchange plan.

Fouling control

In all its application, the use of membrane is restrained by fouling occurrence; in this particular case at high DOC concentration the process incurs a serious risk of fouling of the feed spacer due to biofouling or particulate fouling which result in pressure drop increase over the membrane, operational problem and higher feed pressure. Common practice in membrane plant operation is the use of chemical cleanings referred as cleaning in place (CIP) to reverse the effect of fouling, inactivate the biomass and restore the membrane permeability. However studies showed that inactivation is not fully efficient without physical removal of the biomass which can be achieved by creating friction with turbulent flow and air bubbles addition. Therefore in order to both delay fouling occurrence and improve biomass and particles removal between two CIPs, the application of air during forward flush and high recirculation flow during operation, were assessed on pilot scale. Figure 2 shows the effect on feed pressure of air injection during the regular forwards flush with feed water: one unit, street 1, is being flushed with AWC the all-time while the other, street 2 is being flushed with feed water only for 11 days before air is re-established during flushes.

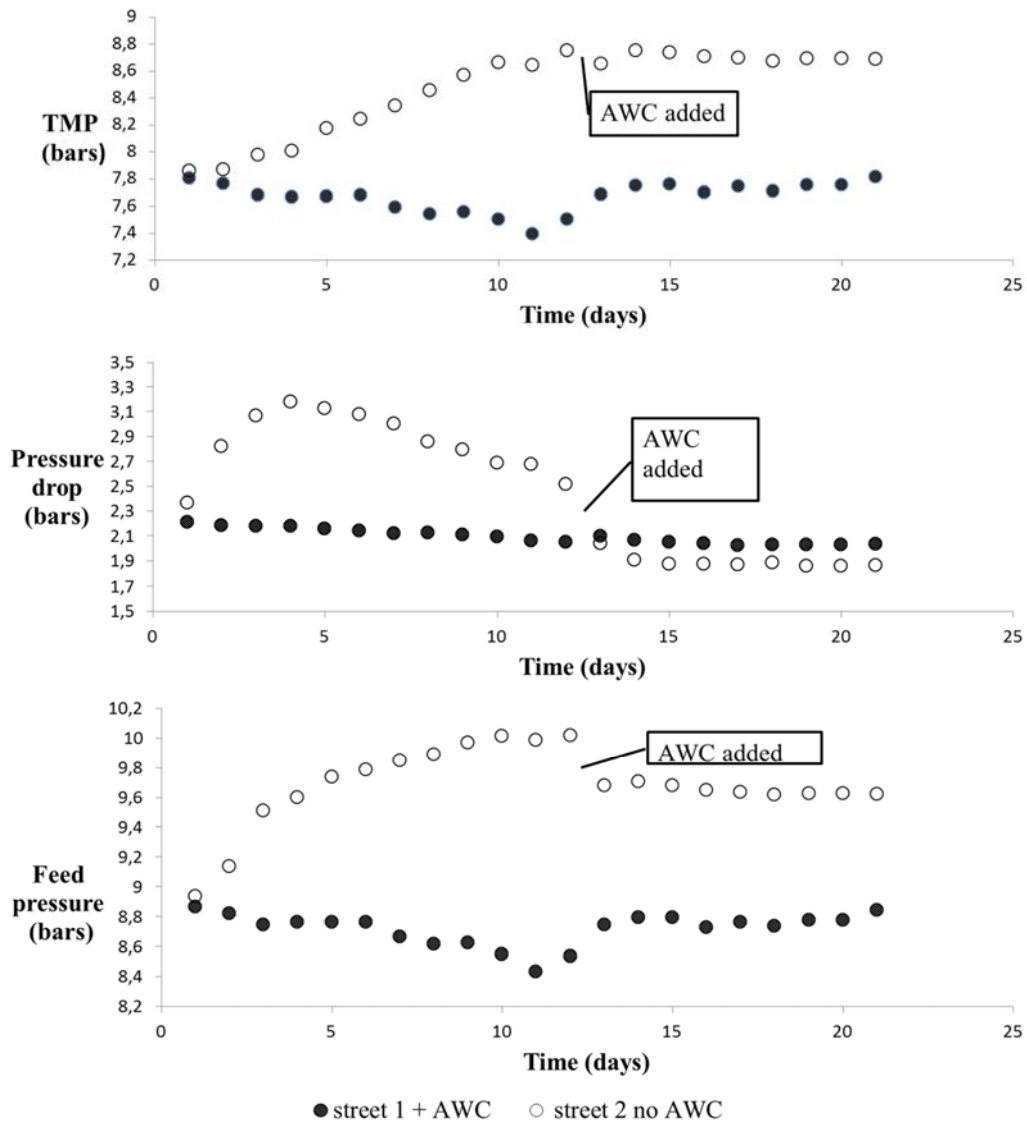


Figure 2: Feed pressure to the NF pilot with and without AWC

Results obtained after 11 days of testing are significant; AWC has a actual positive impact on operations by keeping the feed pressure to a stable level around 8,6 bars whereas street 2 without air injection shows rise in feed pressure indicating a fouling event. Pressure drops across the membrane display the same trends: AWC maintains the pressure drop at a stable level around 2,1 bars whereas without air it rises up to 3,5 bars. These results are in accordance with similar experiments from E.Cornelissen et al [2; 3; 4], performed using sodium acetate enriched solutions to test biofouling removal with AWC. After AWC in re-established on street 2, the effect of fouling show to be partly reversible, in fact pressure drop is restored to 2 bars (same as street 1) indicating that AWC is capable on reversing spacer fouling however, TMP does not reach its reference level, probably due to particle blocked into the membrane pores on which AWC has no effect

Long term operation:

Details of operations over 100 days with the nanofiltration unit with AWC are shown in figure 3. For the first 20 days the flux was maintained at 5,6 LMH then increased to 6,2 LMH. Instabilities appear at the beginning of the operation due to the new element put in place but the pilot quickly reaches a steady state. Feed pressure fluctuates under the effect of the varying brine ion exchange concentrations however the overall trend shows a slow increases over time due to organic deposition despite AWC application. Therefore on day 50, a cleaning in place is performed which successfully reestablish the feed pressure from 9,5 bars to 8,5 bars.

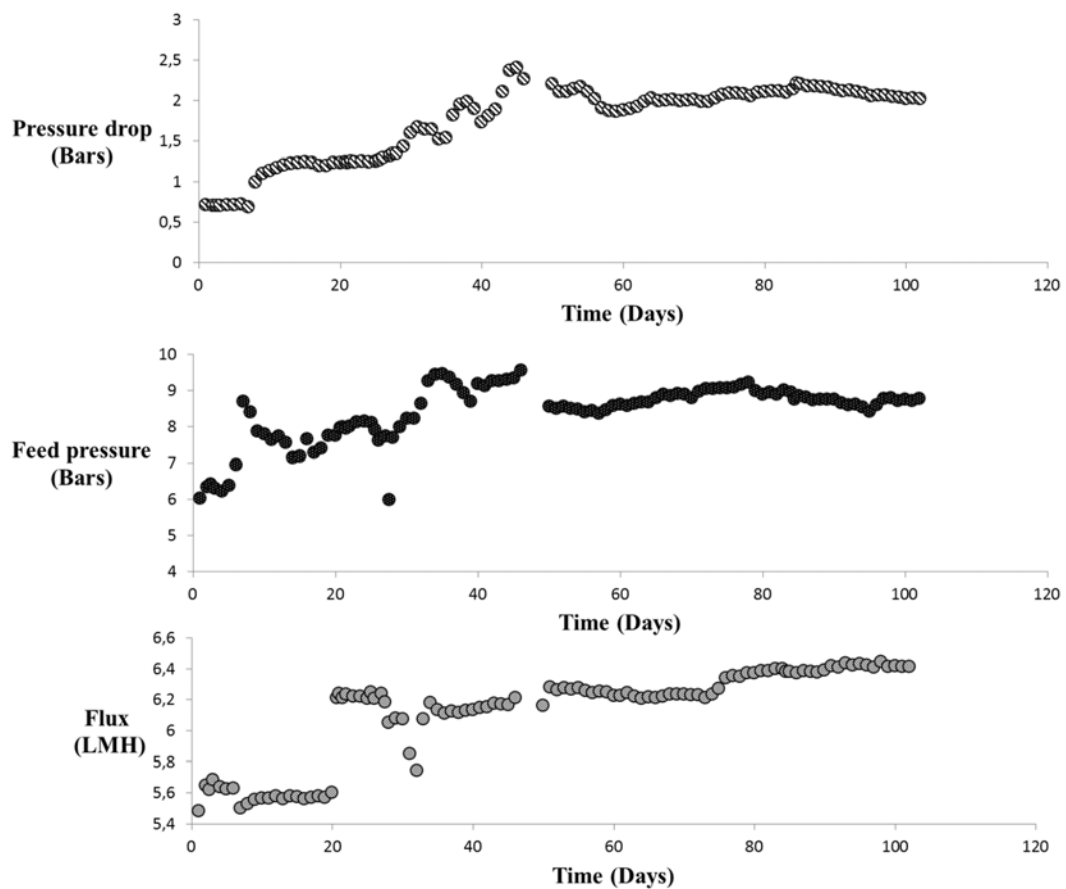


Figure 3: Operation on nanofiltration pilot enhanced with AWC

DVR

Brine volume and salt crystallization on pilot scale

Regular operations of the DVR are performed at a concentration factor of 6, before any salt crystallization would occur. At this concentration factor, the pilot reduces the NF concentrate from 275 L/h to 45 L/h and offers 230 L/h of water recovery that can be re-injected upstream the SIX. Quality of the concentrate and condensate obtained at this ratio are displayed in table 2. The DVR pilot during its operation has proved its ability to treat various qualities of brines without any sign of fouling/ scaling making it a very robust process.

Table 2: Quality of the DNF effluent, condensate and concentrate of the DVR pilot at a concentration factor of 6.

	Chloride	Sodium	Bicarbonate	Sulphate	TOC
	mg/L Cl	mg/L Na	mg/L HCO ₃	mg/L SO ₄	mg/L C
DVR feed -DNF effluent	17000	15000	5700	7200	380
DVR Condensate	2	1.3	15	1	0.9
DVR Concentrate	91200	86000	19000	39000	1900

In addition operation of the pilot at concentration factor around 10 showed the possibility to reach the salt solubility limit and produce the big crystals displayed on figure 4. The brown color (figure 4A) is most likely due to some DOC residuals not involved in the crystal formation, since it can be easily rinsed leaving a clear precipitate as displayed on Figure 4 B.

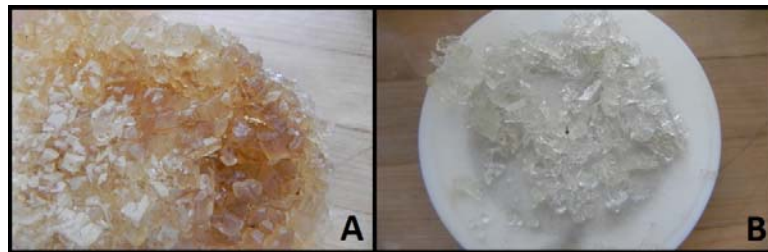


Figure 4: Raw Salt crystals produced from the DVR brine after cooling before (A) and after (B) rinsing with water.

A calculated energy consumption to concentrate the brine up to 30% NaCl (crystallization limit) is estimated to be around 50 kWh per m³ of condensate produced

Separation of NaCl

Experimental precipitation work of a laboratory scale showed that a sequenced thickening of the NF concentrate leads to a more or less simultaneous precipitation of NaCl, Na₂SO₄ and Na₂CO₃. However this heterogeneous (co)precipitate is not suitable reuse purpose and therefore the experiments were directed toward salts separation. [13]

Several tests conducted in the past to selectively precipitate sulphate and (bi)carbonate ions into low soluble salts prior to nanofiltration by addition of Ba(OH)₂ to form BaSO₄ and BaCO₃ or CaCl₂ to form CaCO₄ and CaCO₃ have shown very relative success. Though the literature depict barium hydroxide as very suitable for sulphate removal in the mine effluent water to concentrations lower than 200mg/L [8;9]; experiences showed that in the NOM rich ion exchange brine, the sulphate precipitation is significantly disrupted by organics which are obstructing the crystals surface and prevent their growth. Results in table 3 show the compositions of the liquid phase before and after precipitation with 0,16 moles of either CaCl₂ or Ba(OH)₂ in two different media: an artificial water with similar salts concentration as the NF brine but no organic matter and the actual NF brine. Precipitation occurred in a jar tester after 4 hours of mixing at room temperature. Molar percentage removal due to precipitation have been calculated and from the results, it can be concluded that in artificial media, barium has a better overall sulphate and bicarbonate removal with a lower residual concentration but in a presence of organics both calcium and barium capacities to precipitate sulphate drop respectively from 74% removal to 2% and from 52% removal to 10%. In addition the large quantities of salts required to precipitate both sulphate and carbonate make the process not attractive even when barium salts can be partially regenerated [1;9]

Table 3: Results from precipitation with CaCl₂ and Ba(OH)₂ in a artificial water and in the NF concentrate brine

	Artificial brine					NF concentrate				
	Initial	after addition of 18g/L (0,16mol/L) CaCl ₂		after addition of 27g/L (0,16 mol/L) Ba(OH) ₂		Initial	after addition of 18g/L (0,16mol/L) CaCl ₂		after addition of 27g/L (0,16 mol/L) Ba(OH) ₂	
	Liquid phase composition (mg/l)	Liquid phase composition (mg/l)	molar percentage removal	Liquid phase composition (mg/l)	molar percentage removal	Liquid phase composition (mg/l)	Liquid phase composition (mg/l)	molar percentage removal	Liquid phase composition (mg/l)	molar percentage removal
SO ₄	18.500	4.761	74%	8.815	52%	20.250	19.845	2%	18.170	10%
NA	30.700	30.850	0%	30.740	0%	24.030	25.300	0%	23.420	3%
CL	41.000	41.812	0%	41.520	0%	17.572	21.454	0%	17.494	0%
HCO ₃	5.654	6.686	0%	147	97%	8.712	6.245	28%	0	100%
CA	-	399	-	-	-	-	33	-	-	-
BA	-	-	-	1	-	-	-	-	3.850	-

Conclusions:

The results, discussed in this article demonstrate that beneficial treatment of ion exchange brine is possible and highly concentrated brine disposal problems can be enabled, since we may conclude that:

- Nanofiltration is suitable for highly concentrated brine treatment with NaCl recovery and constitutes the essential part of it as it allows 80% recovery of sodium chloride and first volume reduction to bring the process towards a ZLD at low energy demand.
- NF technology uses for highly concentrated brine treatment has shown to be only possible in by applying the combination of high recirculation flow and AWC. This was successful at regulating pressure drop increase along the element. It allows stable operations of the membrane and delays the need for chemical cleaning while CIPs are successful at reestablishing stable operation after a fouling event and reducing TMP across the membrane.
- Reducing to zero the need of sodium chloride in an ion exchange plant is utopic as a non negligible part of the Cl⁻ ions (about 30%) are lost when exchanged against pollutants during the treatment.
- DVR a promising technology for its robustness and relatively low energy consumption, it is capable of further volume reduction regardless the brine composition. It has the particularity to treat brines at very high TDS content.
- While separation of NaCl contained in the NF concentrate through crystallization has not been successful, DVR finds its beneficial use in crystallizing the remaining salts to isolate the organic matters.
- Further investigations on the possible uses of organic matters should be undertaken and their commercial value should be estimated.
- When separation of all valuable compounds (NaCl, water and DOC) is possible, the cost saving associated their reused and/or sale provides additional resources to make ZLD treatment more affordable offering additional solution for inland municipal water treatment plants to handle their saline brines.

References:

[1] Bologo, V. Maree, JP. Carlsson, F. (2012) Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water. *Water SA* Vol 38 No 1, 23-28

- [2] Cornelissen, ER. Rebour, L. van der Kooij, D. Wessels, LP. (2007) Optimization of air/ water cleaning (AWC) in spiral wound elements. Proceedings IMSTEC 2007> Sydney.
- [3] Cornelissen, ER. Vrouwenvelder, JS. Heijman, SGJ. Viallefont, XD. van der Kooij, D Wessels, LP. (2006). Air/ water cleaning for biofouling control in spiral wound membrane elements. Proceedings EuroMed 2006> Montpellier.
- [4] Cornelissen, ER. Vrouwenvelder, JS. Heijman, SGJ. Viallefont, XD. van der Kooij, D Wessels, LP. (2007). Periodic air/ water cleaning control of biofouling in spiral wound membrane elements, *Journal of Membrane Science*. Vol 287. 94- 101
- [5] CRC Handbook of Chemistry and Physics (2003), 84th Edition, David R. Lide, CRC Press LLC, USA
- [6] Galjaard, G. Kamp, P. and Koreman, E. (2009), SIX: a new resin treatment technology for drinking water. Proceedings SIWW 2009> Singapore.
- [7] Galjaard, G. Martijn, B. Koreman, E. Kamp, P. and Bogosh M.. (2011), Six-Ceramac new pre-treatment techniques for surface water treatment. Proceedings SIWW 2011> Singapore.
- [8] Geldenhuys, A.J. Maree, JP. De Beer, M. Hlabela, P. (2003). An integrated limestone/ lime process for partial sulphate removal. *Journal of the South African Institute of Mining and Metallurgy*. Vol 103. Issue 6. 345- 354.
- [9] Hlabela, P. Maree, J. Bruninsma, D. (2007) Barium carbonate process for sulphate and metal removal from mine water, *Mine Water Environment*, Vol 26, Issue 1, 14- 22
- [10] Kabsch-Korbutowicz, M. ,Wisniewski, J.,Lakomska, S.,Urbanowska, A. (2011), Application of UF, NF and ED in natural organic matter removal from ion-exchange spent regenerant brine, *Desalination*, Vol 280, Issue 1-3, 428-431
- [11] Koreman, E. and Hogeboezem W. (2011), Biological Denitrification of High Saline Ion Exchange Regenerant Proceedings. IWA LET Conference Amsterdam, the Netherlands. Congress Talk paper, Amsterdam, the Netherlands .
- [12] Salehi, F.,Razavi, S.M.A. ,Elahi, M., (2011), Purifying anion exchange resin regeneration effluent using polyamide nanofiltration membrane, *Desalination*, Vol278, Issue 1-3, 31-35
- [13] Vaudevire, E. Koreman, E. Galjaard, G. Trommel, R. Visser, M (2012) Further treatment of ion exchange brine with Dynamic vapour recompression, *Water Practice and Technology*, Vol 7, Issue 4
- [14] Wachinski, AM. (2006) Ion exchange treatment for water, AWWA, Denver CO (USA), p109
- [15] Wadley, S.,Brouckaert, C.J.,Baddock, L.A.D.,Buckley, (1995), C.A. Modelling of nanofiltration applied to the recovery of salt from waste brine at a sugar decolourisation plant, *Journal of Membrane Science*, Vol 102, Issue 1-3, 163-175