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Further treatment of highly concentrated brine with dynamic vapour recompression

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ABSTRACT

Nanofiltration (NF) and Reverse osmosis membranes are widely used for diverse applications for their ability to remove natural organic matters, polyvalent cation (softening), etc. However, concentrate streams arising from these technologies often reaches concentrations up to 60 g/L which makes their disposal a major constraint and usually require additional treatments. In the PWN technologies research facility, in the context of the development of the SIX© Ion exchange process, NF is used to recover NaCl from the brine arising from the regeneration of the resin for further reuse in the process. A pilot scale of the technology aiming at ion separation (monovalent/bivalent) focused on NaCl reuse was implemented recovering 80% of the total SIX brine. Further, NF concentrate minimisation and sodium chloride reclamation is, however, desired to allow a reduction of the disposal fees and chemical uses and therefore largely increase the overall process sustainability. Due to high total dissolved solid concentration of the NF concentrate, between 80 and 100 g/L, it was decided to use the dynamic vapour recompression evaporation technique (DVR). During operation on a pilot scale with a capacity of 250 l/h, the DVR technology has proved itself to be capable to reduce the raw regenerate another 6–10 times reaching meanwhile the solubility limits of NaCl and other salts making their recovery on a solid stream possible. The condensate that resides after DVR treatment is low contaminated and is therefore suitable for re-injection upstream the SIX pre-treatment process approaching that way the term of a zero liquid discharge process.

Keywords: Brine treatment; Evaporation; Dynamic vapour recompression; Controlled precipitation

1. Introduction

Membrane separation technologies, particularly nanofiltration (NF) and reverse osmosis, have found nowadays a wild range of applications within the drinking water production, desalination from sea or brackish water, wastewater or industrial water treatment. All applications have in common to result in a separation between the desired purified permeate and

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the undesired concentrate containing salts and retained compounds. Characteristics of the concentrate largely depend on the membrane application, the influent water quality, the recovery, the pre-treatment methods, chemical addition, etc. When total dissolved solids content in the concentrates reaches 70 g/L to saturation levels, its disposal becomes a major problem.

In the context of the development of the SIX© Ion exchange process, the Dutch water company (PWN) investigates the use on NF membranes for the treatment of brine arising from the regeneration of the resin. This brine is characterised by high sodium and chloride concentration as well as large DOC, nitrate, sulphate, phosphate and bicarbonate contents. After a denitrification (DNF) stage aiming at total removal of nitrate from the brine [1], spiral wound NF is applied to allow the passage of sodium and chloride into the permeate while rejecting DOC and divalent ions, such as calcium and magnesium. This way, the NF convert 80% of the ion exchange brine into a recovered salt solution to be reused in the SIX© process. On the other hand, the concentrate still representing 20% of the total waste flow requires additional treatment in order to minimise volume and further recover sodium chloride.

The dynamic vapour recompression (DVR) is a particularly energy efficient evaporation technique for the treatment of high concentrated brine streams. Based on the mechanical vapour recompression (MVR) process, the vapour is being compressed to a high pressure (temperature) and then being condensed in a plate heat exchanger wherein on the other side of the plates the saline "mother liquid" 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 total dissolved solid (TDS) solutions with a small temperature difference (around 5°C) across the heat exchanger. The evaporation process takes place without boiling phenomena (natural evaporation) in specially designed evaporation units resulting in a very low carry-over of salts in the condensate product.

This paper describes step-by-step orientation studies and the progress made at PWN in the field of saline brine treatment which led to the overall process based on DNF, NF and DVR. Focus is made on the DVR process, as an emerging technology for concentrated brine treatment and on the possibility it offers to further concentrate NF concentrate up to salts crystallisation level in order to recover or separate solids. Investigations made on laboratory and pilot scales aims to give a global solution to highly concentrated and saline brine disposal issue including volume reduction and recovery of NaCl for reuse.

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

Parameter	DNF effluent range	NF concentrate range
Nitrate (mg NO^{-}/L)	0–30	0–30
Chloride (g Cl^{-}/L)	30–50	30–50
Sodium (g Na^{+}/L)	4.0–35	2.5–35
Sulphate (g SO_4^{2-}/L)	3.5–9.0	6.0–20
Calcium (mg Ca^{2+}/L)	15–35	20–100
15–35	20–100	
Tot Phosphate (mg PO_4^{3-}/L)	0.2–12	2.0–17
Bicarbonate (g HCO_3^{-}/L)	2.0−5.0	2.3–6
DOC (mg C/L)	150–300	500–1,200

2. Materials and methods

2.1. Chemical composition of the regenerate

Experiments in this paper are carried out on two types of brine DNF effluent and NF concentrate which compositions are detailed in Table 1. The main difference between the two brines is the sulphate, calcium and DOC ratio to chloride. Impact of this difference on the crystallisation of all salts is to be evaluated by a series of evaporation tests.

2.2. Concentrate volume reduction: experimental set up

The DVR pilot (Fig. 1) is composed of 5 cyclones where a vacuum is applied for the evaporation to take place between 70 and 90°C. After a pre-heating phase, the brine is sprayed into the cyclones through nozzles

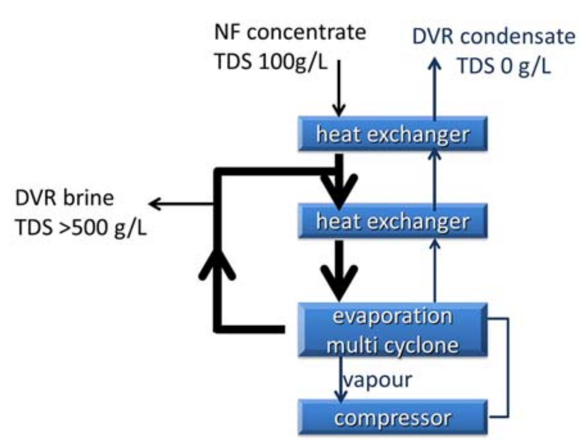

Fig. 1. Process scheme of the DVR pilot.

Table 2
Quality of the DNF effluent, condensate and concentrate of the DVR pilot at a CF of 6

	Chloride (mg/L Cl)	Sodium (mg/L Na)	Bicarbonate (mg/L HCO_3)	Sulphate (mg/L SO_4)	TOC (mg/L C)
DVR feed-DNF effluent	17,000	15,000	5,700	7,200	380
DVR Condensate	2	1.3	15	1	0.9
DVR Concentrate	91,200	86,000	19,000	39,000	1,900

which create a large evaporation area. Over 8 m^3/h of brine is recirculating in each cyclone where the pressure is approximately 0.6 bar (abs). The liquid that has not been evaporated is recirculated into the recirculation stream (40 m^3/h) whereas the vapour is sucked out by the vacuum pump and compressed to the heat exchanger. Compressing the vapour permits to increase its condensation temperature and makes it condensate in one side of the heat exchanger 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.

The DVR pilot was fed by either NF concentrate or DNF effluent, to check the feasibility without concentrating the brine by NF during batch test from 6 to 24 h. The concentratio factor (CF) inside the DVR pilot is controlled by adjusting the concentrate brine flow up to crystallisation levels. The resulting concentrate brine flow from the system is extracted 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.

2.3. Evaporation experiment

This part focuses on separation of the salts contained in the NF concentrate or DNF effluent for recovery purpose. Laboratory-scale evaporation experiments were conducted to determine the behaviour of the NF concentrate and DNF effluent at different crystallisation conditions including the CF at which each particular salt's precipitation occurs, the order of salt's precipitation and the possibility to separate and recover NaCl after precipitation. Evaporation experiments were carried out on a simple distillation set-up, made of glass beakers and electric heaters, in which DNF effluent and NF concentrate were evaporated up to different concentration ratios ranging from 3 to 15. Volumes to evaporate from 1.5 to 7.5 L were calculated according to the concentration ratio leaving a final volume of 0.5L after evaporation. Here after evaporation, solid and liquid phases were separated by vacuum filtration and sent to a certified laboratory (Hetwaterlaboratorium, Haarlem, Netherlands (HWL)) for analysis.

3. Results and discussion

3.1. Brine volume minimisation

Operations on the DVR pilot have shown the possibility of reducing the brine volume for disposal after both NF or DNF. At CF of 6, before any salt crystallisation would occur, the DVR reduces the DNF effluent for disposal of the SIX-pilot 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 is displayed in Table 2.

A calculated energy consumption for full-scale systems is 50–60 kW per m^3 produced condensate at crystallisation level of NaCl (30–40% of NaCl).

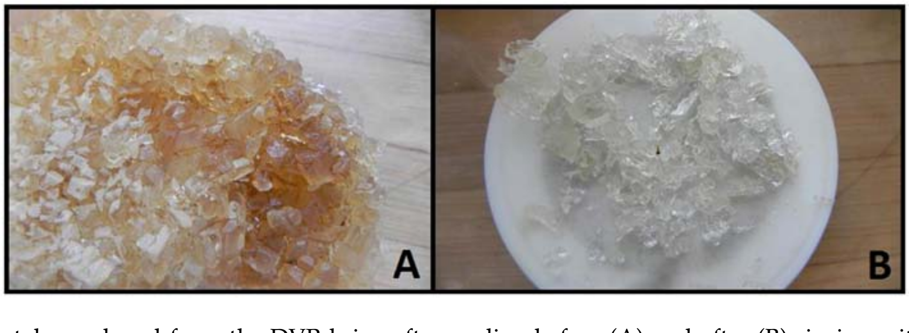

Fig. 2. Raw salt crystals produced from the DVR brine after cooling before (A) and after (B) rinsing with water.

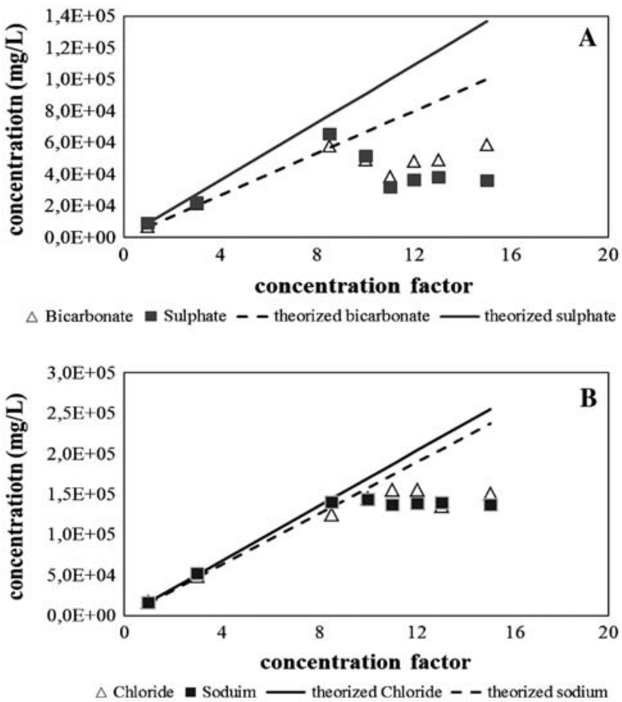

Fig. 3. Concentration of the main compounds (Cl^-, Na^+, HCO_3^- and SO_4^{2-}) of the DNF brine as a function of CF.

3.2. Salts crystallisation

3.2.1. Crystallisation with the DVR

At a CF of 10, crystallisation level was achieved with the DVR pilot. Fig. 2A shows the big crystals obtained from the brine after cooling to room temperature. The brown colour 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 in Fig. 2B.

3.2.2. Sequenced crystallisation

Fig. 3 displays the measured concentrations of the main compounds in the liquid phase of the DNF brine, when further concentrating of the solution by evaporation. These concentrations are compared with theorised values simulating the increase of the concentrations that would occur if those compounds were not precipitated. Concentrations increase proportionally to the concentration factors, until compounds reach their over-saturation points and start precipitating. Total phosphate, calcium, barium and magnesium start precipitating as soon as the brine is being concentrated, but these are negligible amounts. In Fig. 3, it is observed that first anions that precipitate are sulphate and bicarbonate around a CF of 8. At a factor between 9 and 10, sodium starts crystallising, followed by chloride at CF around 11.

Table 3
mass of compounds recovered per litre of DNF brine at various concentration ratios from 10 to 15

	Precipitating compounds (g/L brine)			
Concentration factor	NaCl	$NaSO_4$	$NaCO_3$	DOC
10	0.70	3.49	3.25	0.02
11	4.59	7.80	7.06	0.04
13	6.92	6.92	6.92	0.04
15	12.83	8.39	9.10	0.08

Applying the method on every salt contained in the brine, the following crystallisation order is derived:

$BaSO_4 > BaCO_3 > MgSO_4 > MgCO_3 > CaCO_3 > CaSO_4 > Na_2CO_3 > Na_2SO_4$ and NaCl.

The compositions of the precipitates determined for concentration factors between 10 and 15 are displayed in Table 3.

Main conclusion of this experiment is that the concentration in sequence does not lead to the production of a single pure salt but to a salt mixture which is very difficult if not impossible to separate by controlling the concentration factors. Therefore investigations were orientated on a way to control the salts crystallisation by either temperature or by the addition of $CaCl_2$ to enhance early precipitation of sodium bicarbonate and sodium sulphate.

4. Conclusions

The results, discussed in this article demonstrate that highly concentrated brine disposal problems can be enabled, since we may conclude that:

- When concentrating the brine before crystallisation level (CF <6)

  (a) DVR is a suitable technique for remarkable brine minimisation, i.e. 75–95% volume reduction, depending on use of NF.
  (b) Condensate can be reused upstream as a high quality water to reduce the liquid discharge.
  (c) Residual DVR brine contains mainly NaCl, Na_2CO_3, Na_2SO_4 and DOC.

- When further thickening by DVR, i.e. CF >10

  (a) It leads to a more or less simultaneous precipitation of NaCl, Na_2CO_3 and Na_2SO_4 without fouling/clogging problems of the DVR.

(b) It is not possible to separate NaCl from Na2SO4 and Na2CO3.

- Further waste minimisation can be achieved by increasing CF (>15) resulting in almost complete precipitation of NaCl, Na2CO3 and Na2SO4 which can be seen as the final solid waste fraction. In addition DVR treatment leads to a remarkable reduction of the brine fluid (>95%); the remaining liquid phase that mainly consist of DOC can also be seen as a final waste stream (beneficial application or reuse options are the subject for further investigation). As a consequence, the brine discharge pipe diameter or the amount of transport movements can be reduced significantly which is beneficial for sustainability reasons, in spite of DVR energy consumption which is in turn relative low.

Reference

[1] E. Koreman, W. Hogeboezem, Biological denitrification of high saline ion exchange regenerant proceedings, IWA LET Conference Amsterdam, the Netherlands, 2011.