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Recovery of water from saturated solutions by membrane processes

Payel Sarkar*, S. Prabhakar, Sushil Tiwari, D. Goswami, P.K. Tewari

Desalination Division, Bhabha Atomic Research Centre, Mumbai 400085, India
Tel.: +2225594729; fax: +2225505151; Email: payelb@barc.gov.in

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ABSTRACT

Recovery of water from spent aqueous streams is well known through the use of reverse osmosis (RO) but the extent of recovery is limited primarily by the scaling potential of dissolved species and the osmotic pressure of the concentrate stream. Mining industries, particularly the ones which use sulphuric acid leaching, discharge large quantities of effluents containing dissolved solutes with significant amounts of calcium and sulphate. Chemical method for the removal of sulphate is economically prohibitive to meet the discharge norm. The effluents therefore are often diluted and discharged or sent to dry areas for solar evaporation. Application of RO for the recovery of water is restricted by the scaling of sparingly soluble calcium sulphate. The use of commercial antiscalants does not help as they do not reduce the quantity of sulphates in the discharge stream. Experiments were carried out using nanofiltration (NF) membrane process with commercially available membrane element primarily to remove sulphates with minimal scaling problems. Furthers based on commercial software the performance of RO was assessed to estimate the extent of water recovery for reuse. The studies have indicated that it is possible to recover significant quantity of water for reuse. The sulphates in the concentrate stream can be converted to a solid form in a lime column. The stream depleted of sulphate can be recycled through NF. The paper presents the salient features of our bench scale studies, a precursor for field trials indicating the technical feasibility of achieving 'zero-liquid discharge (ZLD)' through membrane processes.

Keywords: Saturated calcium sulphate; Water recovery; Nano-filtration (NF); Membrane processes; Zero liquid discharge (ZLD); Mining effluents

1. Introduction

With limited availability of water resources, it is necessary to adopt appropriate methodologies to reduce water consumption, minimise pollution to water bodies and recover water for reuse. Membrane processes have been found to be quite attractive as they are predominantly physicochemical in nature, requiring less chemicals and foot print area compared to conventional operations. The availability of membranes with wide range of pore-sizes, surface charges and chemical matrices, provides the opportunity to synthesise process sequences to achieve the objectives of improving water use efficiency, value recovery and cost reduction. Large quantities of effluents are generated in mining and ore processing operations particularly where acid leaching is practiced. Awadalla and Kumar [1] have made a review on the opportunities of the membrane technologies for the treatment of the mining and mineral processing streams. Reverse osmosis (RO) is extensively practised for the recovery of water from effluents [2] but its application is limited by the scaling

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*Corresponding author

potential of the dissolved species and the osmotic pressure of the concentrate. As the acid effluents are normally discharged after neutralisation with lime [3] it is considered appropriate to investigate the utility of the membrane processes for this stream to recover water and the possibility of approaching towards zero liquid discharge (ZLD). With the significant presence of calcium and sulphate in the discharge stream, the application of RO process does not lead to economic recovery of water. The method of utilising the addition of barium salts to precipitate sulphate is economically prohibitive. Lime treatment also does not help in removing sulphates below dischargeable limits. The use of antiscalants as in seawater desalination plants [4] do not allow the gainful processing of the reject stream of RO/NF. Glater and Schwartz [5] in her studies on the behaviour of sparingly soluble species has indicated that the scaling potential in RO and nanofiltration (NF) is controlled by a number of factors including kinetics of nucleation, hydrodynamics of the system and the presence of impurities. As the problem of discharges becoming acute and the need to conserve water imminent, it is felt appropriate to revisit the membrane processes to evolve a method to recover water for recycling and approach towards ZLD. Accordingly, bench scale experiments were carried out initially with saturated solutions of calcium sulphate and later with simulated effluents (uranium mill effluents) containing calcium sulphate to assess the membrane behaviour under different operating parameters with a view to evolve a scheme for field trials and subsequent implementation.

2. Theoretical background

In order to achieve higher recovery, it is necessary to minimize scaling. In RO, all the dissolved solutes are rejected better compared to NF. Consequently, the boundary layer solution of RO would exhibit higher degree of super saturation which would favor scaling and restrict the percent recovery of water. The osmotic pressure of the boundary layer also would be higher requiring higher operating pressure. In NF where the mono-valent passage is significant, the boundary layer would contain less solute leading to lower ionic strength and less osmotic pressure under comparable recovery conditions. The existence of residual charge on NF membranes delay the onset of scaling on NF membrane surface compared to RO.

The objective of this study demands prevention or at least minimisation of scaling due to calcium sulphate on the membrane surface enabling higher recovery than permitted by the solubility product considerations. Even though three types of scales are possible namely $CaSO_4 \cdot 2H_2O$ (gypsum), $CaSO_4 \cdot 1/2\ H_2O$ (hemi-hydrate) and $CaSO_4$ (anhydrate) in solutions containing calcium and sulphate species, gypsum ($CaSO_4 \cdot 2H_2O$) is predominant at ambient temperatures [5]. As NF process is carried out at ambient temperatures all the discussions pertain only to gypsum scaling. The scaling depends on the ionic product of calcium sulphate in the given chemical environment [7], kinetics of nucleation and hydrodynamics of the process [6]. It is well known that RO membranes preferentially allow water to permeate through, while NF membranes allow monovalents to permeate to some extent, depending on the membrane. Due to preferential permeation of water, the concentration of the dissolved species in the boundary layer increases leading to the formation of scales (due to precipitation). Antiscalants are extensively used in desalination processes but reports indicate that they may favour fouling of membranes at higher recoveries and is not suggested for gypsum whenever the saturation index is likely to exceed 2.38 [8].

Uchymiak et al. [9] have studied the kinetics of calcium sulphate dihydrate scaling in detail with reference to RO membranes. Various studies [7,10] on scaling mechanism of calcium sulphate di-hydrate indicate the formation of mineral scales through three steps: initially the sparingly soluble species becomes *supersaturated* leading to the formation of *crystal nuclei* and thence to crystal leading to *scale* formation [11]. Sangho Lee and Chung-Hak Lee [12], and Che-Jen-Lin et al. [13,14] have extensively studied the scaling aspects of calcium sulphate species with reference to NF membranes. The flux decline in NF was considered to follow four stages namely – concentration polarisation, solute nucleation, cake formation and steady state. The rate of deposition at each stage was found to depend on the operating parameters including applied pressure and cross flow velocity. A number of researchers [15,16] have opined that nucleation is an important step for crystallisation and hence cake formation. It was also reported that the flux reduction is significant only after the cake formation and the induction period of nucleation stage for calcium sulphate depended on cross flow velocity. Based on these studies, crystal growth appears to be the critical step and its rate is depicted mathematically by [12]

$$\frac{\mathrm{d}M}{\mathrm{d}t} = KS(C_\mathrm{w} - C_\mathrm{s}), \tag{1}$$

where K is the rate constant of crystallisation, S is surface area of active sites, C_w is wall concentration near membrane surface (for surface crystallisation) and bulk phase concentration (for bulk crystallisation), C_s is the saturation concentration of calcium sulphate at that temperature.

In view of these observations, it is felt that the scaling could be prevented on the membrane surface if we maintain appropriate hydrodynamic conditions (which ensures less residence time on the separation zone, optimal super-saturation and a feed nearly free from foulants such as colloids or suspended matter) to minimise surface crystallisation and hence to obtain higher recovery without significant scaling on the membrane surface.

Even though several studies have been conducted using NF and RO membranes on scaling of calcium sulphate, most of them are based on test cell having small membrane area of about 150 cm^2 or less. The present study is an attempt to evaluate the potentiality of the membrane process in the treatment of effluents containing saturated calcium sulphate solution and to extend the benefit of the studies for real time application in the field. The experiments were carried out in a single commercial element with a view to scale up the performance for field applications, which is feasible considering the modularity of membrane processes. Commercial spiral elements use both feed and product spacers in certain geometries and the feed spacers are expected to act as turbulence promoters. This could result in changes in flow pattern, considerably different from the reported test cell studies.

Treatment of the calcium sulphate saturated effluents through NF only the first step in the overall scheme, would produce a stream containing less calcium and sulphate species and significant amount of chlorides as the permeate. Further treatment is required to remove the supersaturated calcium sulphate from the concentrate of NF. Permeate from NF also needs to be processed through RO to recover reusable water. The concentrate from RO has to be suitably disposed. An attempt has been made also to indicate the possible approaches so that we can approach towards ZLD.

3. Materials and methods

3.1. Membranes

Film Tech make NF membrane element NF-90-4040 has been used for NF experiments. At standard conditions (i.e., 2,000 ppm $MgSO_4$ at 5 bar pressure) the membranes exhibited 98% percent solute rejection. For sodium chloride the percent solute rejection was found to be 80%, at corresponding conditions (2,000 ppm NaCl, 5 bar). The membrane area was about 7.6 m^2. Indigenously developed back-washable spiral polysulphone based 60KD MWCO UF membrane element [17] was used for the filtration of feed solution before using as feed for NF experiments. After each experiment membrane was flushed with RO treated service water (<5 ppm) until the conductance of the discharge stream from NF element indicated constant low conductivity. Depending on the feed flow rates and operating pressure, the water required for flushing varied from 50 to 100 l. Wherever the original pre-experiment pure water permeability (PWP) was not obtained, the membrane was cleaned with dil. hydrochloric acid at around pH 5. The experiments were conducted initially with higher flow rates towards and later at lower flow rates. For each flow rate the data was collected at three different pressures starting from lower pressure. This sequence was adopted to minimise permanent scaling, if at all formed, that could affect the membrane performance.

3.2. Preparation of test solutions

Pure calcium sulphate solution was prepared by dissolving excess quantity of calcium sulphate under vigorous stirring, allowed to settle overnight and filtered through UF. The resultant solution was free from turbidity and used in the experiments. For $CaSO_4$-NaCl system, the solution was prepared by dissolving calcium chloride and sodium sulphate in 500 l water corresponding to a feed composition of 705 ppm calcium, 2,000 ppm of sulphate, 958 ppm of sodium and 1,242 ppm of chloride. The solution was left overnight to allow for any precipitation. Before using in the experiment, the solution was filtered through ultrafiltration (UF) element and is collected into the feed tank.

Calcium, chloride and sulphate concentrations were measured by standard analytical methods [18]. TDS was determined by evaporation. Sodium was estimated by difference. Conductivity measurements were also made as soon as the samples were taken for initial estimation of the trend.

The schematic diagram of the experimental set up is shown in Fig. 1. The prepared feed is filtered through UF and is stored in the feed tank. The feed then is pumped through the NF module through the high pressure pump. Provisions were made for bypassing part of the feed for studying different flow-rates, recycling the concentrate and collection of permeate independently. The tanks are calibrated in terms of volume.

Rotary Vane pump (Procon make) rated at 15 lpm flow 15 bar pressure was used. By suitably manipulating the valves (by pass valve/concentrate recycle) the requisite pressure and flow were maintained. The fluctuations in flow measurements were about ± 0.25 lpm and that of pressure was about ± 0.5 bar. Concentrate was continuously recycled back to the feed tank till the

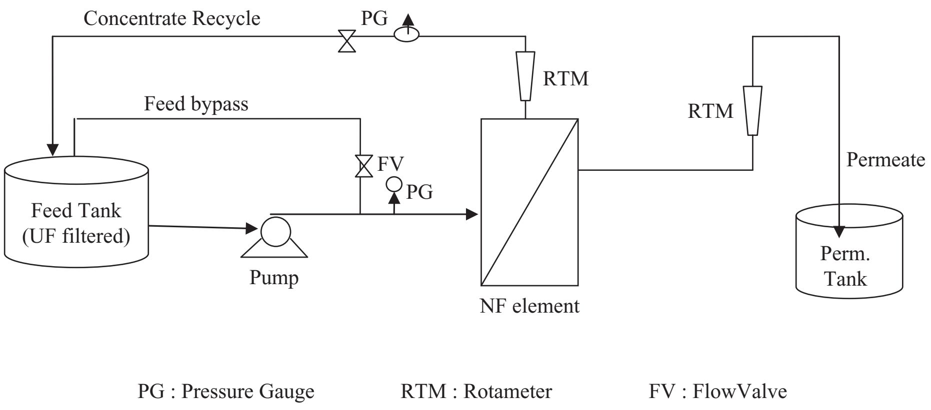


Fig. 1. Schematic diagram of the experimental set up.

desired recovery is obtained. Product water is collected in the product water tank.

All the experiments were conducted with 500 L feed solution and on a batch-recycle mode. The tanks (both permeate and feed tank) were calibrated and readings of volume can be easily noted at 10 l interval. Considering the hold up in the membrane element and the associated piping (about 5 l), the permeate volumes were considered for estimating recoveries. In each experiment, data were collected (permeate rate, product quality) for different recovery points. The product samples were drawn ensuring that it is representative of the permeate tank solution.

3.3. Terminologies used

Pure Water Permeability (PWP): Pure water permeability (PWP) is defined as the amount of water permeating through the membrane per unit time at the given operating pressure when pure demineralised water is used as feed. PWP is a linear function of operating pressure (P) for a given membrane element at a given temperature. PWP is used as an indicator for the loss in permeate rate of the membrane and its restoration has been considered to indicate the restoration of the membrane to its original characteristics.

The PWP measured at the beginning of the experiment when the membrane surface is clean and fresh is denoted by PWP_0. After the conclusion of one experiment say one flowrate at one pressure, the solution is drained and demineralised water is used and PWP (before flushing) is measured without flushing, at the flowrate and pressure employed for the experimental run and is denoted as PWP_{bf}. After thoroughly flushing of the membrane again the PWP (flushed) is measured and is denoted PWP_f. In certain cases when the initial PWP was not restored, acid cleaning at pH 5 was carried out.

The PWPs and the permeate rate (PR) observations were converted to dimensionless number designated as Normalised Flux (Nflux) defined as

$$\mathrm{Nflux_{bf}} = \mathrm{PWP_{bf}}/\mathrm{PWP_0}$$

$$\mathrm{Nflux_{f}} = \mathrm{PWP_{f}}/\mathrm{PWP_0}$$

$$\mathrm{Nflux_{pr}} = \mathrm{PR}\,/\,\mathrm{PWP_0}$$

where PR is observed permeate rate under specified conditions (at 90% recovery).

Recovery (Rec): The experiments were conducted in a recycle mode, in which the water permeating through the membrane is collected separately and the concentrate is recycled back to the feed tank. With time the level of water in the feed tank would reduce and the permeate tank would increase. The tanks are calibrated in advance with respect to levels.

$$\text{Rec.} = (\text{Permeate Volume})/(\text{Initial Feed Volume})$$

$$\text{Rec.}(\%) = (\text{Permeate Volume})/(\text{Initial Feed Volume})\text{x}100$$

Solute Rejection (SR):

$$\text{SR} = (\text{Feed ppm} - \text{Permeate ppm})/\text{Feed ppm} \times 100$$

Degree of supersaturation [19]: Degree of supersaturation (Ω) is best expressed in terms of solubility product (K_s°)

$$\Omega = \left(\frac{IP}{K^\circ s}\right)^{1/\gamma}$$

where the coefficient γ in the exponent is the stoichiometric number of ions in the formula for gypsum, and *IP* is the ion activity product of Ca^{2+} and $SO4^{2-}$ ions.

4. Results and Discussions

The study presented is based on bench scale experiments with a view to extend the same for real-time application in the field. The flow characteristics have been represented directly in terms of litres per minute (lpm). We have refrained from designating the flow in terms of Reynold's number due to the fact that our estimates of the same could not take into account the effect of feed spacers which induces turbulence. However, we have calculated the Reynold's numbers using the cross sectional area available for flow and thence calculated hydraulic diameter. The estimated values range from 132 for a feed flow of 4.5 lpm to 381 at 13 lpm comparable to the values reported in literature [20]

4.1. Studies on nano-filtration for the removal of calcium sulphate species

4.1.1. Selection criteria of operating pressure and feed flow rates

The objective of the experiment is to minimise surface crystallisation of gypsum ($CaSO_4{\cdot}2H_2O$). At higher operating pressures, the specific recovery (permeate rate/feed rate) would be higher making the environment conducive for surface crystallisation. Considering that the osmotic pressure of the feed is less than 3 bars, the experimental investigations were carried out from 5 bar onwards, taking into account the estimated concentration at 90% recovery. As per the design guidelines for RO and NF achieving about 90% recovery in single pass, the membrane system would require more elements in series with staggered configuration [21] to maintain minimum required flow rates (as specified by the membrane element manufacturers) and possible only for very large capacities. As our study deals with nearly saturated to supersaturated solutions, the tolerance to the change of feed flow rates would be less. Based on these considerations it is felt appropriate to opt for a batch system with recirculation to achieve high recovery without compromising on the envisaged basic hydrodynamic parameters albeit at higher energy cost. Accordingly, all the experiments have been carried out at the batch recycle mode at different feed flowrates ranging from 4.5 to 13 lpm with an objective to arrive at a sustainable flow rate and pressure which would minimise surface crystallisation providing the maximum recovery at minimum possible energy cost.

4.1.2. Parametric studies for the optimisation of operating pressure and feed flow rate

The experiments were conducted in the range of 5–9 bars in three steps and for four flow rates ranging from 4.5 lpm to about 13 lpm. Even though the selection of 4.5 lpm feed flow rate is not apparently justified, the experiments were conducted as the last batch to assess the scaling phenomenon under hostile conditions which is likely when one envisages a series of modules for obtaining higher recovery in one pass.

The permeate rate is function of net driving force as seen from Eq. (1) [22]

$$N_p = A(P - \pi_b + \pi_p), \tag{2}$$

where N_p is the permeate flux ($m^3/s\ m^2$), A is the membrane constant ($m^3/s\ m^2$ bar), P the operating pressure, π_b & π_p are boundary layer and permeate osmotic pressure. Since the membrane element used is the same, the membrane area (7.6 m^2) is constant in all NF experimental runs. Hence for detailed data analysis we consider permeate rate and membrane constant A in terms of lpm and lpm/bar respectively.

Boundary layer concentration can be expressed as

$$N_p = k \ln\left(\frac{C_b}{C_f}\right),$$

where k is the mass transfer coefficient in the boundary layer, C_b and C_f, the concentrations at the membrane surface and in the feed solution, respectively. The membrane surface concentration is then given by:

$$C_b = C_f \exp\left(\frac{N_p}{k}\right),$$

where the ratio $\frac{N_p}{k}$ is a function of the pressure difference and the crossflow velocity. Specifically high flux (at high pressure) will lead to higher membrane concentrations (and hence more rapid crystallisation) while high crossflow velocity leads to high mass transfer coefficients, which leads to lower membrane concentrations.

A typical observation of permeate flow as a function of recovery at different pressures for the NF membrane element with saturated calcium sulphate solution as feed at a flow rate of 9 lpm is presented in Fig. 2.

The permeate flowrate decreases with recovery but there are two discernible patterns. In the initial phase, the rate of decrease in the permeate rate is steady.The slopes of all the curves corresponding to different operating pressures are constant upto a particular recovery leading to the inference that permeate flow rate is only

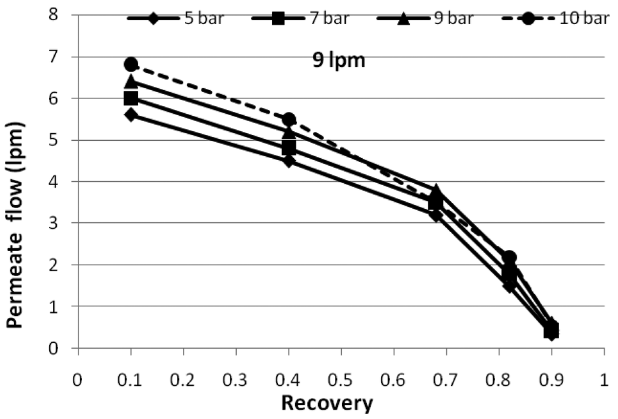


Fig. 2. Effect of operating pressure on recovery at 9.0 lpm feed flow rate.

a function of osmotic pressure in this region. Since the osmotic pressure of the bulk solution is constant for a given recovery at given feed flow rate, the permeate flow rate is only a function of the operating pressure minus osmotic pressure. The significant fall in permeate rate observed at higher recoveries in the second phase, can be attributed to the additional resistance due to scaling. The onset of scaling can be identified from the point of inflexion. The point of inflexion appears to be a function of the operating pressure.

Fig. 3 presents a similar observation for the least feed flow rate of 4.5 lpm where the points of inflexions can be seen distinctly suggesting that lower the operating pressures, higher is the recovery at which the inflexion occurs. It has also been observed that the permeate flowrates are higher at lower pressures beyond certain recoveries indicating the predominance of scaling resistance over the loss in permeate rate due to osmotic pressure.

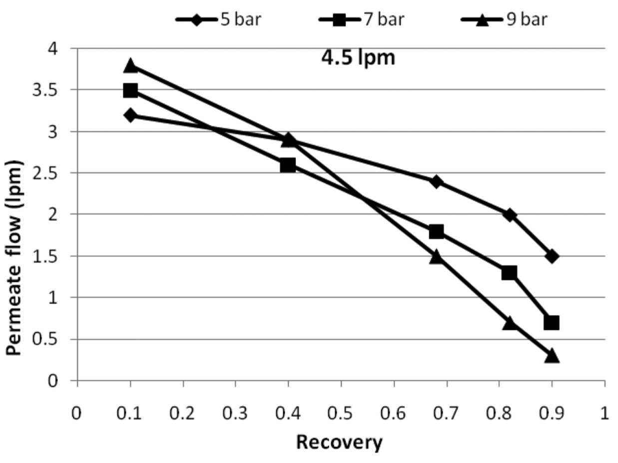


Fig. 3. Effect of operating pressure on recovery at 4.5 lpm feed flow rate.

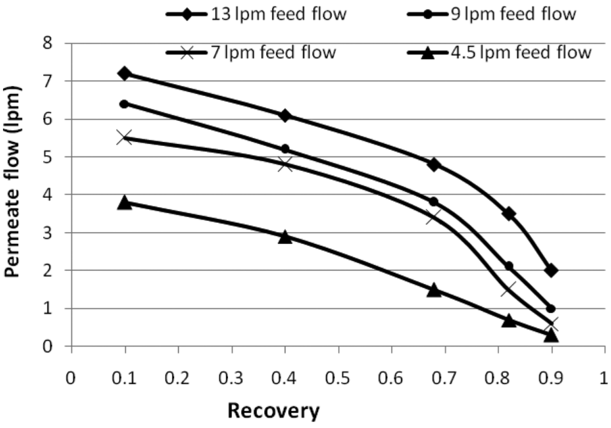


Fig. 4. Effect of feed flow rate on permeate flow at 9 bar pressure.

The point of inflexion advances towards lower recovery with increasing pressure a clear indication of scaling effect. As the pressure increases the specific flux of the membrane increases. Consequently the boundary layer concentration would be higher leading to higher degree of supersaturation and hence scaling.

The variation of permeate flowrate as a function of feed flow rate is depicted in Fig. 4 at 9 bar pressure. The permeate flowrates show a steady decrease with recovery for 9 and 13 lpm feed flowrates. However, for lower feed flow rates (7 and 4.5 lpm) there is an observable change in slope corresponding to the recovery of 0.7 and 0.4, respectively. With higher flowrates, the boundary layer concentration increases slowly and hence the onset of scaling is shifted to higher recoveries.

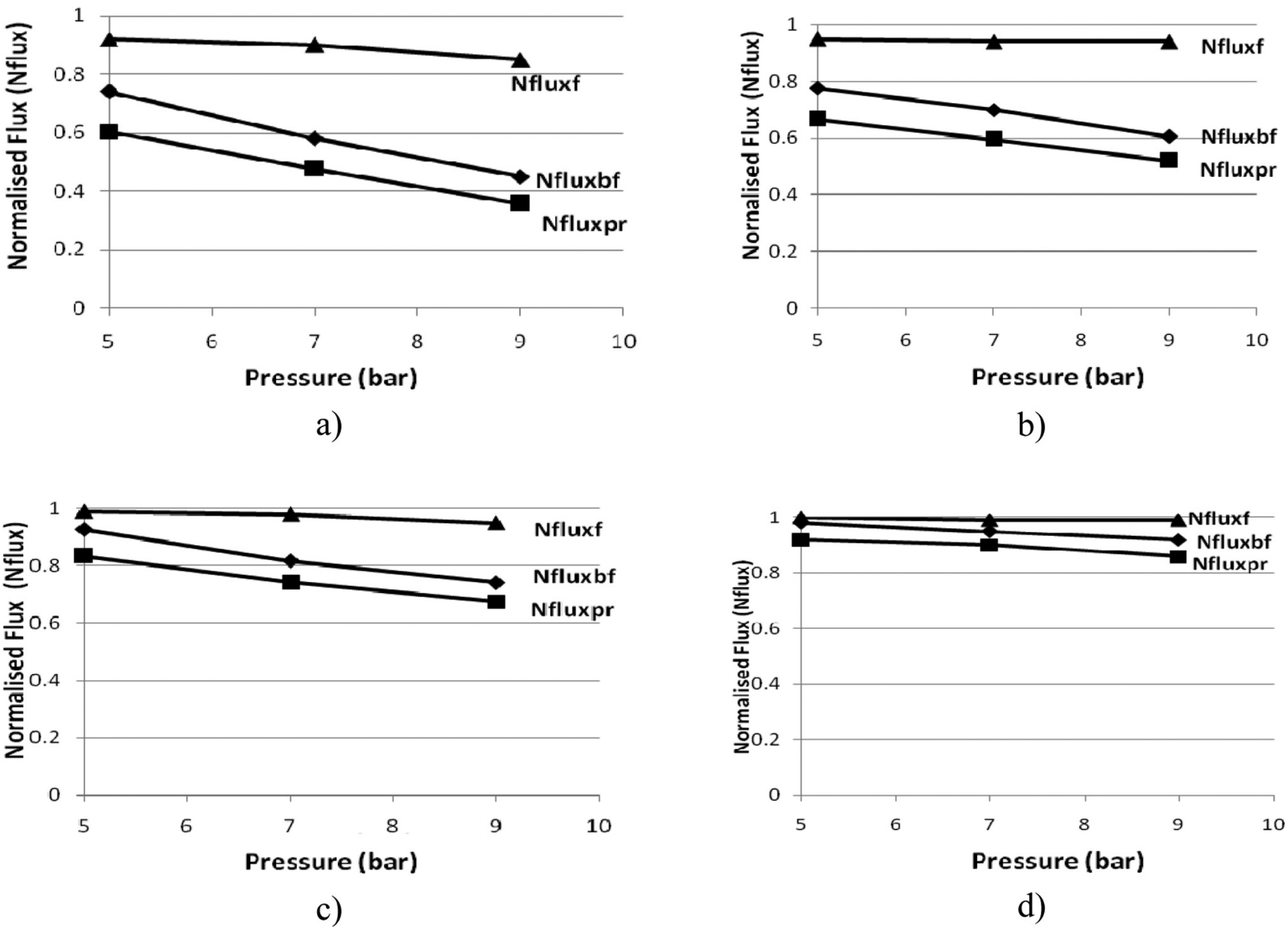
Based on the study of permeate flow rates as a function of operating pressure and feed flowrate it can be concluded that scaling is a function of both feed flow rate and operating pressure.

Rearranging Eq. (1) we obtain

$$\pi_b = P - N_p/A + \pi_p. \qquad (3)$$

Recalling π is *iCRT* where *i* is the number of species *C* is the molar concentration, *R* gas constant and *T* temperature, π_b and thence the concentration at the boundary can be estimated.

The degree of supersaturation, i.e., the ratio of concentration of the solution to the saturation concentration can be calculated based on the boundary layer concentration, from Eq. (1), knowing measured values of product rate, product concentration and membrane constant. With the length of the membrane being one metre and the velocities vary from 0.00172 to 0.00496 m/s, the residence time vary from 581 to 201 s. The estimates of the boundary layer concentration at the



a)

b)

c)

d)

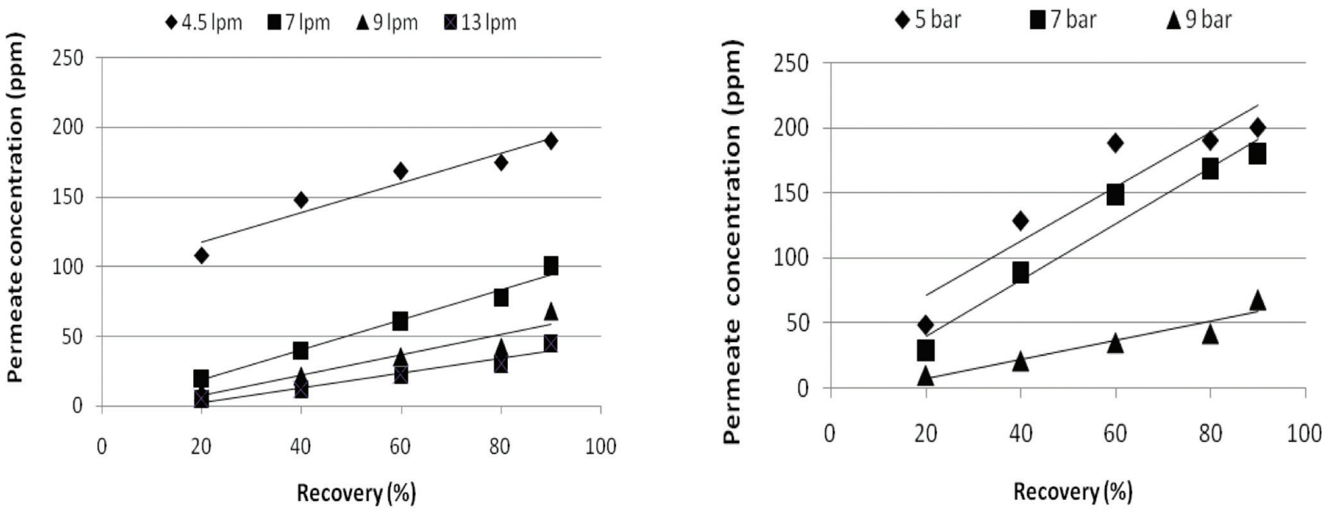
Fig. 5. Normalised flux as a function of operating pressure at 0.9 recovery for different feed flowrates: (a) 4.5 lpm, (b) 7.0 lpm, (c) 9.0 lpm and (d) 13.0 lpm [corresponding to apparent Reynold's Number 132, 205, 264, 381, respectively].

point of inflexion using the above methodology indicates a molar concentration of about 0.07 moles/litre of calcium sulphate in flowrates ranging from 4.5 lpm and above corresponding to a degree of supersaturation around 12.5 (except 5 bar pressure 4.5 lpm) confirming the formation of scale [23].

4.1.3. Analysis of decline in permeate rate in terms of scaling

The Normalised Flux (Nflux), a dimensionless number representing the drop in permeate rate due to different factors under various experimental conditions was plotted as a function of operating pressure. Nflux_{pr} describes the loss in permeation rate due to all possible factors such as osmotic pressure, scaling, feed flow rate, pressure drop, etc. It is the ratio of actual permeate rate at specified conditions to the initial fresh membrane performance at the same pressure. Nflux_{uf} describes loss in permeate rate due to physical factors such as scaling, fouling, etc. and includes both soft and hard scales and is calculated as a ratio of PWP before flushing (with least disturbance to the membrane environment to the extent possible) to the initial PWP. Nflux_{f} describes the loss in flux due to hard scales which cannot be removed by simple flushing and is calculated as the ratio of PWP after flushing to the initial PWP. Nflux_{f} is an indicator of hard scale and it is condition one would like to avoid in operating a membrane based system. Figs. 5a) to 5d) describe respectively the behaviour of Nfluxs as a function of operating pressures at flow rates of 4.5, 7,9 and 13 lpm. All the permeate rates (PR), PWP_{f} and PWP_{uf} correspond to the recovery of 0.9, the terminal point of our experimental run in all the cases. Perusal of the plots of Nflux versus Pressure for different flowrates allows us to observe that

1. Original flux (Nfluxf) is restored for the cases 5, 7 and 9 bar operating pressures for 13 lpm feedflow rate and 5 and7 bar operating pressures for 9 lpm



(a) (b)

Fig. 6. Permeate quality with recovery at constant pressure (a) and constant flow rate (b).

feed flow rates. In the case of 7 lpm feed flow rate the permeate rate could be nearly restored at 5 bar operating pressure but not restorable for 4.5 lpm under all experimental conditions.

2. The difference between Nfluxuf and Nfluxf describes the loss in permeate rate due to scaling.
3. The difference is higher at higher pressures and lower flow rates.
4. The slope of the Nfluxpr lines decreases with increasing flow rates.
5. The difference between Nfluxpr and Nfluxuf is nearly constant for all the operating pressures.

The above observations lead us to infer that scale formation does occur at all operating pressures and flow rates studied but manageable at higher flowrates and moderate pressures.

Permeate Quality: The product quality in terms of calcium has been shown Fig. 6 as a function of different flowrates at constant pressure and different pressures at constant flowrate. As expected the quality shows improvement with flowrate and operating pressure.

The observations indicate that product quality is best at 13 lpm 9 bar pressure, the quality is acceptable at around 50 ppm for 9 lpm feed flowrates and 9 bar pressure at 0.9 recovery.

The solute rejection increases with increasing flow rate resulting in less concentration of calcium and sulphate species in the permeate due to more efficient back diffusion of the solute species from the boundary layer. Deposition of calcium sulphates at lower flow rates further reduces the reject concentration. Mass balance based on volume and concentration of feed, permeate and reject streams indicate more deposition at lower flow rates. Based on the conductivity of flushed water we could get a nearly total mass balance within an error of less than 5%. However reject stream on standing reveal more deposition in case of higher flow rate.

4.2. Experimental study with simulated solution

In order to extend the results to realtime applications simulated effluents containing a mixture of sodium chloride and calcium sulphate have been prepared. The trace chemical species have not been added for the present studies as field experiments have been planned. Moreover, with prior UF treatment no trace species which can foul the membranes is expected to be present such as manganese and iron. Heavy elements, if at all present would report only in the concentrate which can be either recycled or disposed of suitably in conformity with environmental regualtions. As our focus specifically is to assess the recovery of water from saturated calcium sulphate streams, it is felt appropriate to restrict the study to mixed systems containing the major solute species. The experimental observations based on the simulated effluents with respect to recovery and product quality are presented in Figs. 7 and 8.

4.3. Assessment of experimental results for field trials

The main objective of the experiments were to assess the possibilty of recovering water as much as possible. The suspected difficulties in achieving the same were scaling of calcium sulphate dihydrate on membrane surface as the feed is nearly supersaturated. However, the experiments for the recovery of water

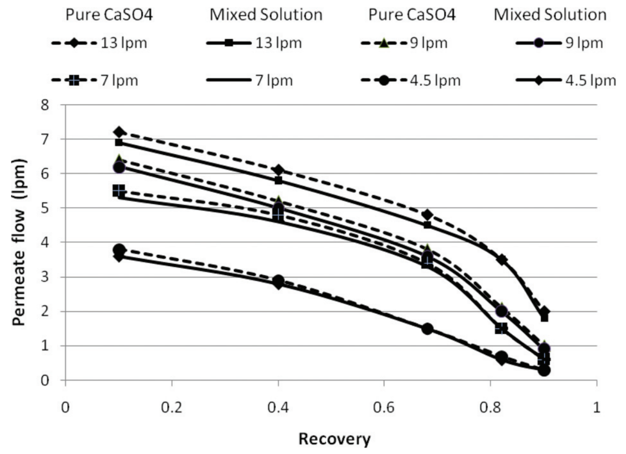


Fig. 7. Permeate flow as a function of recovery at 9 bar pressure at different flowrates.

were carried out with the knowledge that the calcium sulphate scaling requires significant induction period depending on the degree of supersaturation. Our experimental studies have indicated that there are two distinct controlling factors: namely the osmotically controlled decline in permeate rates and the other scale controlled decline. It has also been found that onset of scaling occurs at distinct recoveries based on feed flowrates and operating pressures. Under the present experimental runs it has been found that the scales do not occur upto a recovery of 0.6 for flow rates 9 and 13 lpm in the pressure ranges of 7–9 bar. Higher flowrates may extend the point of inflexion corresponding to the scaling but in a recycle system it would mean higher energy consumption. Similarly lower pressures delay the onset of scaling. In simple terms specific recovery controls the scaling point which is a function of feed concentration. The quality of product in terms of calcium content also is less than 50 ppm under these conditions.

4.4. Suggested scheme for field implementation

Higher recoveries should be targetted in the NF experiment to reduce the ultimate waste volume. As far as NF experimental run is concerned the operating pressure and feed flowrates have to be chosen to avoid precipitation on the membrane surface. Lime treatment has been found to be effective in removing calcium and sulphate species from the supersaturation levels to below saturation limits as reported Lorax consultants [24] and confirmed by our experimental studies. In view of this it is proposed that the concentrate coming out of the NF element be passed through lime column (where the the concentration of calcium and sulphate species would be brought down to less than the saturation levels) and can be mixed with the incoming feed thus leading to higher net recovery of water. It is likely that sodium chloride concentration would go up along with other trace elements

In order to operate the system in a sustainable manner, it must be ensured that the concentrate coming out of the NF membrane and the specific recovery of the module (containing a few membrane elements in series) are well within the limits corresponding to the scaling point at the operating conditions of pressure and feed flow rate. The concentrate then shall be passed through the lime column and circulated back to feed tank. The resultant solution would be rich in sodium chloride but less in calcium sulphate content. When the net recovery is about 90%., the batch can be stopped and the permeate processed through brackish water RO system for the recovery of water for reuse. The concentrate of RO which is rich in sodium chloride can be used for softener regeneration or disposed off. Fig. 8 depicts the scheme which can minimise the waste generation. The concentrate of NF in real effluents can be recycled into the process if any valuable is to be recovered.

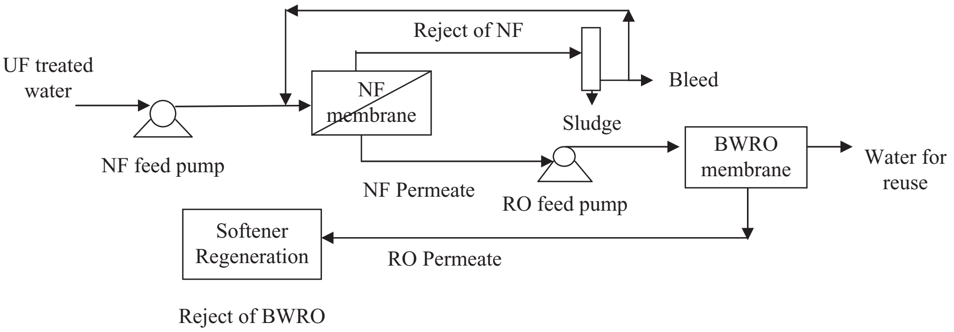


Fig. 8. Flow sheet of approach towards zero liquid discharge.

5. Conclusions

The bench scale experiments with actual NF element has indicated that it is possible to develop a working system using NF for the treatment of calcium sulphate saturated effluent such as one arising out of uranium Mill effluents. It is also demonstrated that supersaturated calcium sulphate solution when passed through lime column can provide a stream containing below saturation level of calcium sulphate. It is also realised that due to long induction period required for the crystallisation of calcium sulphate a recirculation type system with minimum change in flow velocity and minimum solution contact time with membrane surface will be best suited. It has been found proper combination of NF-RO and lime column we can minimise the actual discharge to environment.

The present experimental campaign has indicated the technical feasibilty of recovering water from spent streams containing saturated composition of calcium sulphate. However for realtime applications pilot experiments are needed particularly to optimise the operating points such as feed flow rate, operating pressure, specific module recovery, bleeding fraction if required to be done.

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