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# Processing of Desalination Reject Brine for Optimization of Process Efficiency, Cost Effectiveness and Environmental Safety

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Additional information is available at the end of the chapter

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## 1. Introduction

Reverse Osmosis (RO) is currently confirmed and generally approved as the most feasible technology for desalination of brackish groundwater being the most economic for its range of salinity over a wide range of production capacities, and in view of its lowest requirements of energy, and its application ease.

The currently acceptable norm of recovery of desalted water in projects of brackish water reverse osmosis (BWRO) ranges usually between 65 to 85 % according to raw water quality, level of chemical pretreatment and concept of plant design/operation, would it be intended to be a sophisticated facility of low operation cost or vice versa. The balance of 15 %, or above, the desalination reject stream in which the RO rejected components are concentrated, is disposed as a wastewater (WW). Among the disposal options selected to get rid of the desalination reject stream are: 1) Sewer stream, 2) Land application including percolation, 3) Deep well injection and, 4) Evaporation ponds. The last option is the most common in the Middle East in view of:

- The rather common high temperature
- The low ambient humidity
- The relatively low cost of land in desert areas

Disposal of RO reject water aims, in most of the alternatives, to just get rid of that stream without further water recovery which wastes the cost of initial pumping and chemical treatment. It is, therefore, evident that the increase of desalted water recovery is a main factor in determining the process cost effectiveness. On the other hand, a too high recovery would

lead to most, if not all, the membrane fouling problems and the subsequent decline of performance and eventually membrane damage [1]. The present work investigates the promotion of the RO desalination efficiency and cost effectiveness.

Desalination reject stream (DRS) represents, in fact, a WW disposal problem. It includes, in addition to increased salinity, higher concentrations of polyvalent ionic species [2] due to the preferential high rejection of e.g. hardness components, heavy metal cations (HMCs) [3] or radioactive isotopes [4], organics [5]. DRS includes also the residual pretreatment chemicals of the primary desalination step, i.e., coagulants as iron or aluminum salts or polyelectrolytes, disinfection by products, antiscalants [6].

In big RO desalination facilities, however, the surface area of evaporation ponds may attain several millions of square meters and represents, therefore, one of the main cost factors of the desalination projects [7] due to the cost of land and of installation of ponds, digging, lining, construction of dykes [8].

Besides the considerable cost of installation of evaporation ponds and their annual maintenance, they may cause considerable environmental threat through:

1. Possible leak of concentrated brine and possibly contaminated water to pollute the groundwater reserves.
2. Flooding of ponds which was reported for many existing desalination plants in view of inadequate initial design or operation problems. Flooding of contaminated reject would contaminate the neighboring habitat.

In view of the increasingly stringent environmental regulations related to disposal of WWs and the high cost of evaporation ponds the present laboratory and pilot investigation work aims to promote RO desalted water recovery and reduction of the disposed brine stream to a minimum value so as to realize:

1. Promotion of the desalination process efficiency and saving of groundwater reserves.
2. Saving of, or lowering the cost of installation and maintenance of evaporation ponds.
3. Conformity with environmental regulations of WW disposal.
4. Reducing environmental risks of pollution of groundwaters.

Processing of DRS is supported by:

1. The progressive development of water treatment chemicals as the introduction of antiscalant of specific action as e.g.  $\text{SiO}_2$  or  $\text{SO}_4^{2-}$  specific antiscalants which enable safe operation of RO at higher recoveries despite the presence of higher concentrations of the scale forming components.
2. The creation of new generations of RO and NF membranes according to the trends of:
  - a. Higher salt rejection
  - b. Lower energy consumption

c. Optimized hydrophilic/hydrophobic characters and fouling resistance

3. The recent introduction of sensitive energy recovery systems capable of recovery of the residual pressure from the BWRO reject stream.

Our previous results of desalination reject processing through laboratory and pilot investigation [7] showed remarkable optimization of recovery of desalted water which increased the total RO process recovery up to  $\approx 95\%$ .

Comparative evaluation of performance and cost of several alternatives of brine processing was conducted as e.g. application of high rejection, low energy, secondary RO together with use of specific antiscalants or partial softening NF of reject stream prior to secondary RO [7]. A primary cost analysis showed that the studied reject processing is quite cost effective even without consideration of the reduced surface area of evaporation ponds and consequently their cost.

Superior rejection of polyvalent cations from the reject stream was observed by NF as compared to hot lime softening (HLS) together with absence of chemical dosing stoichiometric to deposition of hardness components and, consequently, absence of sludge formation which represents itself a daily disposal problem. NF, on the contrary of HLS, does not require subsequent filtration. NF also leads to partial desalination of the brine stream while HLS results in increase of the concentration of some components like sodium and carbonate ions, and does not modify other components not included in the softening reactions as  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions and, therefore, results in increase of total dissolved solids (TDS).

As for the reject streams, where radioactive isotopes and/or HMCs were concentrated upon primary BWRO, treatment by NF and low energy RO revealed, under adequate application conditions, more efficient than conventional methods of WWs treatment [4]. In fact, several technical challenges remain with regards to the efficiency and cost of conventional methods for rejection of these contaminants. NF and Low energy reverse osmosis (LERO) were evaluated in this respect in comparison with methods of chemical precipitation, chelating ion exchange resins (IER's), hot lime softening and coagulation/settling/precipitation. Membrane methods gave higher rejection of radionuclides and HMC's ranging from zero to 20 pCi/L could match the maximum contaminant level (MCL) of the US Environmental Protection Agency (US-EPA) for drinking water. NF and LERO, on the contrary of the other methods, are continuous processes which are not shutdown for regeneration, do not suffer from interference of similar valence ions with contaminant separation and are not limited by high pH dependence.

Investigation of desalination reject processing (DRP) is of economic and strategic interests in view of the huge daily production rate of such stream. In Riyadh region alone, according to data from the National Water Company [9], if the main desalination facilities, Wasiea, Buwaib, Salboukh, Manfouha, and Malaz are operated at original design rate, the yearly rate of reject stream amounts to 30 million  $\text{m}^3/\text{year}$  which is expected to increase to more than 45 million  $\text{m}^3/\text{year}$  upon installation of the new Wasia project. It is, therefore, expected that the total BWRO reject in KSA, in view of the planned giant projects in Ha'il, Tabuk, etc..., would amount to  $>$  hundred million  $\text{m}^3/\text{year}$ .

## 2. Literature survey

Processing of brine concentrate of water desalination has been conducted for various purposes. For salt extraction, Sommariva et al [10] Smith and Humphreys [11] considered the processing of the desalination reject up to zero discharge using concentrate disposal processes among which solar/evaporation ponds until crystallisation. They stated that evaporation ponds are preferred in presence of strong solar radiation, low precipitation, and low cost desert land. Produced salts were proposed for use in agriculture, forestry, fauna, and algae production, and energy production. Ahmed et al [12] investigated salt production from reject brine by SAL-PROC technology which consists in multiple evaporation and/or cooling steps.

*For the purpose of environmental protection*, Shahalam [13] evaluated the removal of nitrogen and phosphorus from RO reject of refining effluent of biological processes treating municipal WW. While RO is proven to be effective in producing high quality effluent water for non potable uses e.g. for irrigation purposes, its reject contains too high amounts of P and N compounds harmful for the environment if the feed to RO units is effluent stream from municipal and industrial WW treatment plants. Brine treatment included activated sludge treatment and then granular medium filtration. Heijman et al [14] considered the pretreatment of RO and NF reject so as to attain recovery as high as 99% aiming to overcome the problem of reject disposal. A complicated and expensive sequence of steps is proposed and pilot tested that consisted of precipitation of hardness components at high pH, sedimentation, cation exchange resin, and then NF. As for desalination by NF or RO of surface water a more complex processing was tested, i.e. cation exchange resin, then Ultrafiltration (UF), NF followed by treatment by granular activated carbon (GAC). A recovery of 97% was achieved. For a still high recovery up to 99% SiO<sub>2</sub> removal was conducted by co-precipitation with Mg hydroxide at high pH. The total treatment scheme included double barrier against pathogens (UF and NF) and against micropollutants (NF and GAC). Furthermore, the resulting suspended particle concentration is low and the biological stability is expected to be excellent.

According to Jeppesen et al [15] disposal of highly concentrated brines poses significant environment risks. Extraction of some metals from this stream can multiple environmental and economic benefits. Removal of P has little economic benefit but may become interesting in view of environmental restrictions. This study showed that recovery of NaCl from brine can significantly lower the cost of potable water production if employed in conjunction with thermal processing systems. The high ammonia, sulphate, TDS and HMC's render the RO brine hazardous if dumped untreated [16]. Denitrification of RO brine concentrate was conducted by Anaerobic Fluidized Bed Biofilm Reactors with GAC media.

*The main purpose for most of the research work related to reject processing was to promote the desalted water recovery by various techniques.* Queen et al [17] treated the RO brine by NF for removal of polyvalent cations then it goes to the concentrate compartment of an Electrodeionization unit (EDI) while the initial RO permeate goes to the diluate compartment. Overall consumption of feed water was, therefore, reduced. However, on site reject treatment by EDI was reported to be effective only for small RO treatment units [18], while

for large reject stream rates the cost can be very high. A modified evaporation system that consists of forced air thermal evaporation using turbine technology so as to create a high wind speed and generate a very high air temperature was used. This system is approved by US-EPA. It can operate in high humidity, low temperature conditions, and can evaporate up to 126 GPM at the cost of just discharge to sanitary sewer. Evaporation of RO reject was also investigated in underground rock salt mining operation [19].

*In case of inland communities which have no ready sink for RO brine the disposal cost will increase significantly the cost of RO treatment, specially with the limited recovery to avoid scale deposition.* Coral et al [20] studied the minimization of RO reject through vibratory shear enhanced process (VSEP) without softening. They stated that strategies to minimize brine volume include 1) pre RO softening to remove hardening components and achieve higher recovery, 2) two stage RO interrupted by brine softening, 3) innovative technologies for extraction of water from RO brine without softening e.g. VSEP. The same technology was used by Arnold [21] for optimization of water recovery from RO brine issued by Central Arizona Project and by Cates et al [22], in both cases, however, no cost analysis was conducted and no justification was given for selection of such expensive technique.

Electrodialysis (ED) [23] was also applied for treatment of brine resulting from RO treatment of textile effluent for the purpose of reduction of TDS with the recovery of acids and bases. The WW of textile dyeing was first treated by coagulation/precipitation for color removal followed by RO. RO reject was then treated by ED. This treatment was qualitatively reported to enable the protection of environment from contamination by dyes and the related additives and to promote the reject water recovery.

Capacitive deionization (CDI) was used for SWRO reject treatment [24] instead of blending the brine with secondary effluent and discharge to the sea. The objective of the project was to increase water recovery to more than 95% at the required water quality. Correspondingly the volume of the brine will be reduced to less than 5%. For inland RO facilities where disposal of untreated RO brine has adverse environmental impacts, this approach would represent a cost effective alternative for the management of the brine stream. Results of pilot testing have met expectation. Lee et al investigated the treatment of RO brine towards sustainable water reclamation practice [25]. RO brine generated from water reclamation contains high concentrations of organic and inorganic compounds. These authors concluded that *cost effective technologies for treatment of RO brine are still relatively unexplored*. The proposed treatment consists of biological activated carbon (BAC) column followed by CDI for organic and inorganic removal. 20% TOC was removed by BAC while 90% conductivity reduction was realized by CDI. Ozonation was used to improve the biodegradability of RO brine. The laboratory scale O<sub>3</sub> + BAC was able to achieve three times higher TOC removal compared to using BAC alone. Further processing with CDI was able to generate product water with better water quality than the RO feed water. The O<sub>3</sub> + BAC reduced better the fouling in the successive CDI step [26].

Duraflow Company [27] employed a three step approach to define a pretreatment process compatible with the recovery of RO brine using a secondary RO. The objective was to

remove all components detrimental to secondary RO and realize suitable values of Silt Density Index (SDI).

The three step approach includes:

- I. RO brine analysis to determine the components
- II. Chemistry Development which is based on type & concentration of fouling substance identified in the RO brine, a chemical treatment process is developed to counteract each of the fouling factors:
  1. Cold lime Softening
  2. Colloidal silica removal by adsorption on  $Mg(OH)_2$
  3. Activated Carbon for organic reduction & oxidant destruction
  4. pH optimization for the selected treatment & the secondary RO
- III. Microfiltration to the adequate SDI then secondary RO

Kepke et al [28] considered the options of RO brine concentrate treatment:

1. Deep well injection
2. Natural treatment systems (Wetlands)
3. Electrodialysis/Electrodialysis reversal
4. VSEP membrane System
5. Precipitative softening/RO
6. High efficiency RO (pretreatment step [may be several] +secondary RO)
7. Mechanical evaporation
8. Evaporation ponds
9. Landfill

They defined high efficiency RO as a combination of the hardness removal pretreatment which include Lime soda softening followed by filtration and weak cation exchange resin.

This type of RO treatment is relatively new. It has not been used for water reuse applications but has been applied in the power stations and mining industries. The advantages of this process over Conventional RO include reduction in scaling, elimination/reduction of biological and organic fouling due to high pH where  $SiO_2$  solubility is high. The expected recovery would attain 95%.

IER's were also applied in desalination brine reclaim. This did not only optimize system efficiency through additional permeate recovery but also reduced the amount of water and salt required for softener resin regeneration. Some of the salt in the last part of the brine cycle is used for the next regeneration of the exhausted resin.

According to the survey report “Managing Water In The West” [29] by the Southern California Regional Brine-Concentrate Management, the concentrate disposal technologies include 1- the volume reducing and 2- the zero liquid discharge, and 3- the final disposal technologies:

The available volume reducing technologies include:

- Electrodialysis/Electrodialysis reversal
- Vibratory Shear - Enhanced Processing
- Precipitative Softening and Reverse Osmosis
- Enhanced Membrane System
- Brine Concentrator

Technologies which may be useful in this application but are still under development include:

- Two-pass Nanofiltration
- Forward Osmosis
- Membrane Distillation
- Capacitive Deionization

The zero liquid discharge technologies, on the other hand, include:

- Thermal processes
- Enhanced Membrane and Thermal processes
- Evaporation Ponds
- Wind-aided Intensified Evaporation

Final Disposal Options include:

- Disposal to Landfill
- Ocean Discharge
- Deep Well Injection
- Discharge to Waste Water Treatment Plant

Wiseman [29] underlined the criteria for evaluation of the desalination reject processing technology and the related pilot testing as follows:

1. Does the technology/pilot have regional applicability? Is the pilot implementable from regulatory, environmental, and funding perspectives?
2. Is the technology ready to be pilot tested?
3. Does the project have regional benefits?
4. How much water supply is saved by the project?



5. Does the project improve water quality or provide environmental benefits?
6. Can the technology be implemented for a full-scale project?
7. Are there barriers to full scale project implementation (regulatory, environmental, or funding)?

### 3. Objectives, Aim and Scope of the Present Work

The main objective of the present research program is *the optimization of RO process efficiency and the decrease of consumption of the limited groundwater reserves through upgrading of the recovery of desalted water by adequate application of the most developed technologies of desalination membranes and chemicals.*

This chapter focuses on assessing the feasibility of increase of total RO recovery from the brine concentrate stream generated from RO by either secondary RO of the reject stream or by back recycling of reject to the initial RO feed, without significant sacrifice of permeate quality or excessive increase of product unit cost. Increase of total RO recovery means parallel decrease of the surface area of evaporation ponds required for disposal of the final reject stream which will enable a considerable saving in cost of plant installation.

In case of highly concentrated reject streams, the work includes an evaluation of the pretreatment processes required for attaining the highest possible recovery as e.g. removal or reduction of scale forming and gel forming ionic species and other membrane foulant components.

Other than promotion of process cost effectiveness, this investigation is also directed at promoting the environmental safety in relation to final reject disposal particularly in evaporation ponds, the commonly used approach for disposal of BWRO reject stream in Saudi Arabia. Reduction of the reject rate is expected to reduce the possibility of leak from these ponds and the pollution of groundwater reserves, also to control the frequent flooding of evaporation ponds to pollute the neighbouring habitat.

### 4. Experimental

Both laboratory and pilot NF testing were conducted.

*The laboratory experimental system:*

It consists of six test cells with circular turbulent agitation at the level of surface of membrane coupons installed in a test circuit which consisted of a low pressure pump, pressure gauge, cartridge filter, flowmeter and thermostated feed tank. Membrane samples were stored dry and thoroughly rinsed with deionized water before use. They were compacted in the distilled water at 120 psi, prior to testing, until steady flux is obtained, then conditioned by soaking in the testing solution for one hour. The testing feed pressures

ranged from 80 to 100 psi. Tangential cross flow velocity ranged from 0.005 to 1 m/s and feed flux from 120 to 720 L/m<sup>2</sup>.d.

*The pilot testing unit:*

Fig (1) shows schematic representation of the mobile pilot unit designed so as to enable conduction of NF and RO runs over a wide range of operation conditions, feed pressures, flow rates, pretreatment steps, and feasibility of reject recycling. Percent recovery was 85% except when otherwise stated. Both permeate and reject streams were recirculated back to the feed tank in order to keep steady feed water composition and concentration. Ionic concentrations were determined by ICP-AES (Parkin-Elmer, Boston, USA). Feed water temperature was thermostated at 25 C and pH was adjusted to the range 7.5 to 8.

Pilot site testing should enable:

- Direct connection to reject header or collection tank of existing desalination facilities for continuous treatment.
- Conduction of RO/NF pilot testing using:
- Conduction of desalination runs with different pretreatments for determination of the optimum recovery i.e. highest possible recovery attained under safe and steady operation performance.
- Optimization of operation conditions towards lower production cost, lower power and chemicals consumption.
- Investigation of reject treatment in different production sites in order to determine effect of reject characteristics and validity of selected technologies.

Chemical precipitation of radionuclides according to:



- Chemical precipitation of hardness components of reject stream by coagulation/settling.
- Conduction of NF runs for comparison of radionuclides and hardness rejection by NF to that obtained by chemical precipitation.
- Recycling of reject stream to the feed stream in the primary RO process.

## 5. General BW RO Reject Characteristics

- In addition to concentrated TDS, RO reject stream usually gets concentrated in hardness components and other polyvalent ionic species which are efficiently rejected in initial RO step as HMCs and radioactive isotopes.
- This stream is already sterilized and have passed already coarse and cartridge filtration.

- The unreacted pretreatment additives as antiscalants already concentrated in reject stream will lower the required dosing for scaling inhibition.
- pH and temperature values lie in the reasonable range for RO operation.
- Treatment of this stream either totally or partially would solve the problem of deficiency of evaporation ponds.
- Care should be taken for components which are harmful to RO process or membranes as Al, Fe, and Mn which become concentrated in the RO reject.

A typical reject streams analysis investigated in the present work is given by table (1)

Component	Concentration, mg/l	Parameter	Value
Ca <sup>2+</sup>	2825.8	TDS	25,017.3 mg/l
Mg <sup>2+</sup>	961.9	pH	7.6
Na <sup>+</sup>	4406.3		
K <sup>+</sup>	48.1		
NH <sub>4</sub> <sup>+</sup>	0		
NO <sub>3</sub> <sup>-</sup>	328.7		
Cl <sup>-</sup>	10,030		
SO <sub>4</sub> <sup>2-</sup>	4837.2		
SiO <sub>2</sub>	181.2		

Table 1. Typical Desalination Reject Water Analysis.

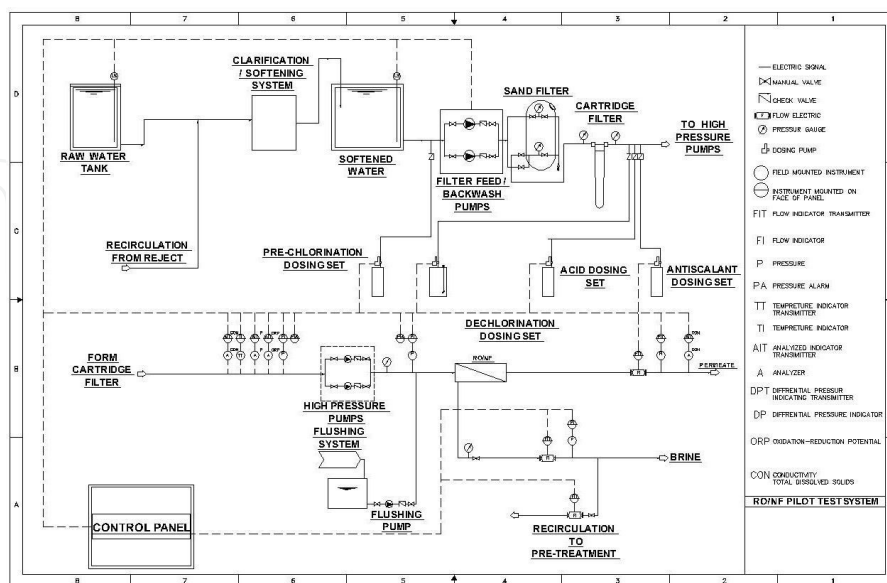


Figure 1. Schematic representation of the pilot testing unit.

## 5.1. Treatment of RO desalination reject stream by secondary RO or NF process

### 5.1.1. Process Definition:

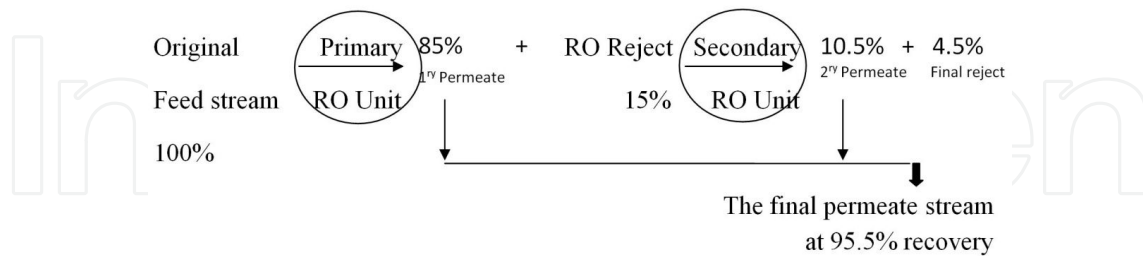


Figure 2.

According to Fig (2), if we consider the rate of feed stream to the initial RO treatment, e.g. raw well water, as 100% which is treated in the primary RO at percent recovery of e.g. 85%, the reject stream of 15% from the original feed will go for further processing in a secondary RO unit at a lower percent recovery of e.g. 70% the secondary permeate will be of 10.5% and the final reject will be reduced to 4.5% as referred to the original feed.

*Upon blending of the primary + secondary RO permeate streams:*

The total RO recovery becomes upgraded to much higher recovery (95.5% in the described case).

The final reject rate becomes reduced to less than the third of previous reject rate and consequently the required surface area of evaporation pond.

The blending ratio is 8:1

*The question is, how much higher is the cost per m<sup>3</sup> of reject processing and what is its effect on the total process cost per m<sup>3</sup> in view of the problems related to the treated reject i.e.:*

1. Higher TDS.
2. The required higher feed pressure.
3. The possible higher cost of additives as specific Antiscalant.

In order to answer to those questions the various alternatives of reject treatment were investigated in detail.

### 5.1.2. Processing of Desalination Reject by Secondary RO:

Table (2) shows the results of RO treatment of three RO reject samples collected from different RO facilities of private sector and government water authorities in KSA of TDS of 33,370.4, 25,017.3 and 16,230.3 mg/l. Treatment is conducted by either brackish or sea water RO.

RO performance	Brine Concentration, mg/l					
	33,370.4		25,017.3		16,230.3	
	BWRO	SWRO	BWRO	SWRO	BWRO	SWRO
Initial Permeate TDS, mg/l	1025.6	292.7	581.3	204.4	485.5	131.2
Percent rejection	96.9	99.12	97.7	99.2	97.0	99.2
Feed Pressure, bar	35.18	43.59	35.3	48.78	29.36	37.09
Percent recovery of reject treatment	50	55	60	70	70	73
Total system recovery	92.5	93.25	94	95.5	95.5	95.95
Final permeate TDS, mg/l	187.0	125.0	122.7	87.3	86.2	52.9
Ratio of final reject to initial reject	0.50	0.45	0.40	0.30	0.30	0.27

**Table 2.** Results of RO treatment of three brine streams by BWRO & SWRO.

The higher the RO reject water TDS, the higher the required RO feed pressure particularly with SWRO. SWRO is shown to be the optimum selection in case of high salinity reject waters. It enables the highest recovery and lowest permeate TDS but required the highest operation pressure. SWRO is also useful in processing of reject water of high concentrations of undesired species as  $\text{NO}_3$  or HMCs. Blending of the secondary RO permeate with the primary one is shown to realize the increase of total RO recovery with only a slight increase in final TDS in view of the low blending ratio. On the other hand, such reject processing in a secondary RO enabled the final reject rate to be remarkably reduced with consequent reduction of disposal cost.

Extent of RO reject processing and reduction of final brine rate is determined by the initial reject TDS and higher applied pressure and consequently the higher recovery realized upon use of sea water RO membrane elements.

### 5.1.3. Comparison of Performance of RO & NF in Processing of Desalination Reject Stream

For this comparative investigation pilot testing unified the main test conditions so that the different results reflect essentially the process behavior. A reject stream of 32,711 mg/l was treated by RO and NF systems having the same array adjusted to produce 1000 m<sup>3</sup>/d, of course operated at different feed pressures, at the maximum attainable steady recovery. Final blending of the primary permeate (that of initial desalination unit) with the secondary

permeate (that of the reject processing unit) was conducted to determine the total system recovery and the final product water quality. Comparison included also the extent of reduction of the final reject rate.

Parameters	Sea Water RO	Brackish Water RO	Nanofiltration
<b>System Performance</b>			
Salt rejection (%)	99.2	97.5	45.3
Permeate TDS, ppm	197.3	622.9	14,818
Fresh water Recovery (%)	71	63	80
% Rejection of some problem making components upon blending of primary and secondary permeate streams	Ca 99.73 NO <sub>3</sub> 92.2 SiO <sub>2</sub> 97.8	Ca 98.53 NO <sub>3</sub> 85.31 SiO <sub>2</sub> 97.85	Ca 89 NO <sub>3</sub> 64.0 SiO <sub>2</sub> 77.2
<b>System cost factors</b>			
Operation pressure, bar	50.87	37.33	14.94
Total system recovery (%)	95.65	94.45	97
Total Permeate TDS, ppm	88.58	129.8	1,899
Final reject rate, m <sup>3</sup> /d	43.5	55.5	30

**Table 3.**

Results of Table (3) show that NF is operated at much higher recovery and much lower pressure than RO so that it could be operated by residual pressure of the reject stream. It is suitable, in fact, for intermediate reject treatment prior to a secondary RO desalination step or recycling in the feed of the primary RO unit. While NF has an only moderate TDS rejection, it rejects efficiently divalent or polyvalent species, organics and colloids [8]. A high hardness reject stream upon NF will, therefore, enable a subsequent RO treatment at a much higher percent recovery and lower operation pressure.

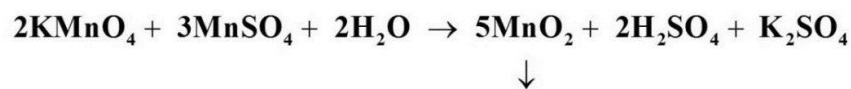
On the other hand, NF reject treatment upon blending would help to raise the primary RO permeate to a required TDS e.g. for drinking water level. The higher recoveries investigated with NF did not lead to higher TDS rejection.

#### 5.1.4. Case Study of a 10,000 m<sup>3</sup>/d BWRO Plant

In this plant the raw feed water have a radioactive contamination of 207.2 + 5.4 pCi/l of combined radium 226+228. It was requested to increase the product rate to the maximum possible value by blending with conditioned feed stream while lowering the radioactivity to < 5 pCi/l the MCL of drinking water of the US- Environmental Protection Agency (EPA), with a final TDS higher than 300 ppm as a regional norm of drinking water TDS. The present plant design failed to realize the

required performance. On the other hand, the same site suffered flooding of evaporation ponds which was reported to be due to an over-estimated evaporation rate.

In fact, according to our previous results [6] the raw well water of TDS of 720.5 mg/l of this plant would be ideal for treatment by NF to produce the requested salinity since NF is characterized by an only modest rejection of TDS, but a rather high rejection of polyvalent ionic species as HMCs and radioactive isotopes [8]. However, in view of the important radioactive contamination, the concerned Water Authority selected RO, of much higher rejection than NF, to be conducted after a partial radionuclide separation by adsorption on the surface of hydrous manganese oxide (HMnO) according to:



Results showed efficient rejection of both radionuclide and TDS to the level of drinking water, however, the value of product TDS was quite lower than 300 ppm.

In order to realize the required final product TDS increase the final product rate and simultaneously decrease the reject rate to the insufficient evaporation ponds partial treatment of the reject stream (already pressurized) by NF was investigated. Table (4) shows the resulting behavior.

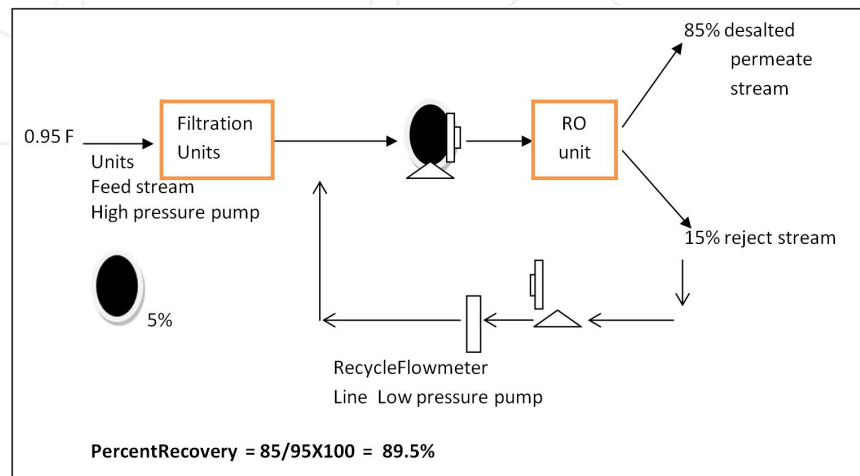
	1	2	3	4	5	6(3+5)	7
<b>Water stream</b>	<b>Initial well water</b>	<b>After adsorption on HMnO</b>	<b>RO permeate</b>	<b>RO reject</b>	<b>Permeate of NF of reject</b>	<b>Final blend product rate</b>	<b>Final reject</b>
Rate m <sup>3</sup> /d	15,552 to cooling towers	14,020 for both RO feed and blending streams	10,000	2,000	1,275 63,75% recovery	11,275	725
TDS ppm	720.5	720.5	70	4149	2508	406	
Ra <sub>228+226</sub> activity	207	82	1	547	26.8	4.08	

**Table 4.**

Results of pilot testing of reject treatment confirmed the realization of higher product rate at TDS > 300 mg/l and Ra activity less than the MCL.

### 5.2. Recycling of treated reject stream to the initial RO feed stream

For the case of already existing desalination facilities and the unavailability of space for additional reject processing unit, partial recycling of reject stream to the main feed stream aiming to upgrade the total recovery rate and reduce the final reject one is evaluated.



**Figure 3.**

The recycling circuit [9] Fig (3) consists of a low pressure pump, a control valve, and a flowmeter. It returns the required fraction of the reject stream ahead of the high pressure pump of the initial feed. The pilot plant was operated at various recycling rates. Upon recycling the reject, the total system working recovery remains at the previous value (85%) but from a higher feed TDS. A state of equilibrium is rapidly attained with a higher permeate TDS.

Water Components	RO feed	RO permeate	RO reject	RO feed 33.3% reject recycle	Secondary / permeate (33.3%)	RO feed 66.6% reject recycle	Secondary / permeate (66.6%)
Ca	284.08	3.2	1,882.22	365.16	4.25	460.83	5.73
Mg	95.85	1.2	641.09	121.72	1.81	154.33	2.3
Na	442.37	10.5	2,934.69	566.02	14.2	714.88	19.37
HCO <sub>3</sub>	134.7	3.5	891.99	173.29	4.20	220.72	6.4
Cl	1010.2	20.1	6,692.61	1,292.95	27.08	1,635.92	36.02
SO <sub>4</sub>	484.5	4.5	3,228.16	623.24	6.08	787.12	7.42
SiO <sub>2</sub>	17.87	0.35	120.85	22.88	0.45	28.95	0.44
TDS	2,506.75	44.3	16,669.03	3,209.88	60.23	4,062.30	76.8

**Table 5.** Variation of secondary feed & permeate TDS with percent recycle.



However, in order to make the calculated percent recovery expressive of the saving in feed water from the wells and of the decrease in final reject stream i.e. representative of the promoted process efficiency, we adopted [9] referring the permeate rate to the lowered raw water feed rate in calculation of recovery.

Table (5) describes a pilot test of BWRO dealing with a groundwater of 2,520.0 mg/l which results in a permeate water of 82.5 mg/l and reject water of 16,790.0 mg/l at 85% recovery. The first three columns give the analysis of each of these streams. Column no. 4 shows the analysis of the increased RO feed TDS upon recycling of 33.3% of the reject stream to initial RO feed one. The corresponding permeate analysis is given by column no. 5 column no. 6 and 7 give the corresponding results for the recycling of 66.6% of the reject stream to the RO feed.

Results revealed that *partial recycling of the reject stream introduced only a moderate increase of the individual ion concentrations in RO feed stream (despite the high reject TDS) in view of the dilution of the recycled fraction of reject upon mixing with the whole feed stream.* In already existing BWRO facilities, therefore, partial reject recycling is shown to raise the percent recovery, lower the consumption of raw feed water, and to lower remarkably the final reject rate and consequently the required land area and cost of installation of evaporation ponds without significant sacrifice of product water quality.

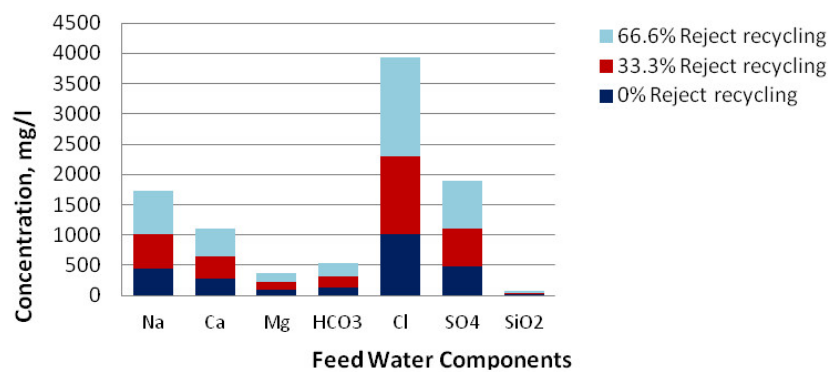


Figure 4. Variation of concentration of component species of the RO feed with percent reject recycling.

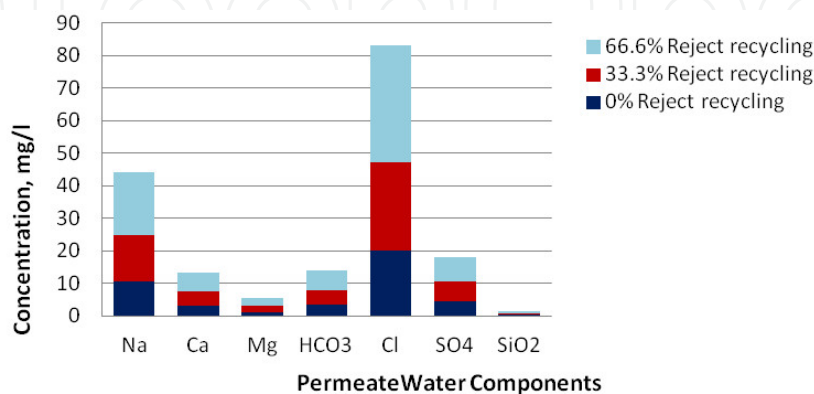


Figure 5. Variation of concentration of component species of the RO permeate with percent reject recycling.

Fig (4) shows the variation of concentration of the RO feed component species with percent reject recycling. These values correspond to an increase of feed TDS from 2,506.8 mg/l to 3,209.9 mg/l by recycling of 33.3% of the reject stream, then to 4,062.3 ppm by increase of recycling to 66.6%. Fig (5), on the other hand, shows the corresponding variation of the concentration of the water species in the permeate stream upon recycling of reject at the mentioned rates. According to these results the increase of permeate TDS parallel to increase of feed TDS upon recycling of reject to original feed stream is limited and did not compromise the drinking water quality. The recycling of 66.6% of the reject raised the permeate TDS only from 44.3 to 76.8 ppm.

As for antiscalant dosing during RO reject processing, in principle the antiscalant which is concentrated in the reject stream is useful for the subsequent reject processing. However, with the higher concentration of certain scale forming components like  $\text{SiO}_2$  in the reject, a different type of antiscalant became required to cover the saturation during the reject processing.

As an example, the general validity antiscalant (Genesys LF) was used in the primary BWRO step of the raw well water of 2,506.8 mg/l ( $1,000 \text{ m}^3/\text{d}$ ) operated at 85% recovery at a dose of 3.03 mg/l. for the reject processing, on the other hand, ( $150 \text{ m}^3/\text{d}$ ) of a TDS of 16,230.3 mg/l and at higher concentration of different components particularly  $\text{SiO}_2$ , a  $\text{SiO}_2$  specific antiscalant was required at a rate of 11.42 mg/l consideration. The difference in price between the different dosed antiscalants did not add much to the general cost/ $\text{m}^3$  (< 1% increase).

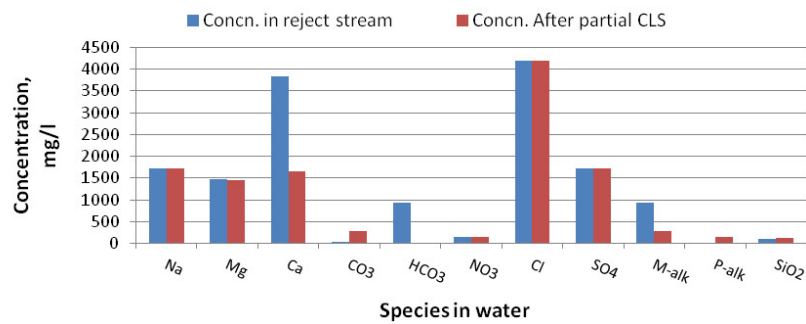
### 5.3. Desalination Reject Processing by Chemical Softening Prior to Recycling or Secondary RO Treatment

After RO of high salinity groundwaters, processing of reject stream by chemical softening or NF aims to remove or reduce the scale forming components accumulated during RO so as to enable the promotion of the total process recovery through subsequent secondary RO step or partial recycling of treated reject to the initial RO feed.

Reject water rather high in Ca, Mg and  $\text{SiO}_2$  can be softened by addition of hydrated lime,  $\text{Ca}(\text{OH})_2$  and sodium carbonate which settles out of water  $\text{CaCO}_3$  and after all of  $\text{HCO}_3^-$  is consumed, the remaining  $\text{OH}^-$  combines with  $\text{Mg}^{2+}$  to deposit  $\text{Mg}(\text{OH})_2$  on which surface  $\text{SiO}_2$  is removed as an adsorption complex (10). Results have shown that for high  $\text{SiO}_2$  reject streams additional Mg may have to be added in order to attain the required  $\text{SiO}_2$  removal.

#### 5.3.1. Partial Cold Lime Softening (CLS)

Fig (6) shows typical results of partial CLS which consists in dosing only hydrated lime to the RO reject water. For each species the first column to the left represents the concentration in the reject water and the second shows the effect of dosing of  $\text{Ca}(\text{OH})_2$ , concentrations are represented as ppm  $\text{CaCO}_3$ . When reject pH was raised from 8.3 to 10.0 by lime dosing, the precipitation which took place resulted in reduction of  $\text{Ca}^{2+}$  content by 56.5%, M alkalinity by 70% the remainder being as  $\text{CO}_3^{2-}$ , and complete consumption of  $\text{HCO}_3^-$ . On the other hand, P alkalinity increased by 140 ppm while other reject water components including Mg and  $\text{SiO}_2$  remained unchanged. TDS was lowered by 26.35% depending on extent of conducted lime dosing.



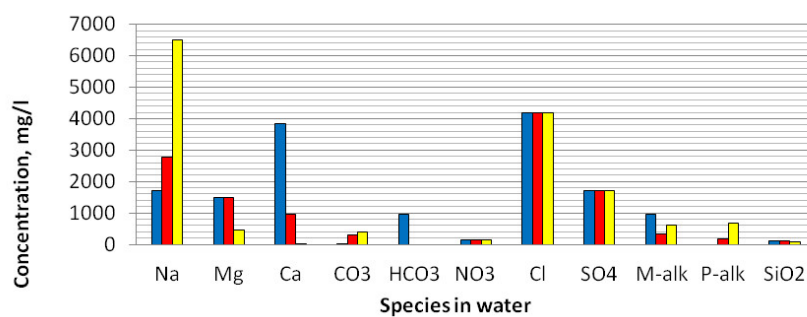
**Figure 6.** Influence of partial CLS on RO reject composition.

According to these results the advantages of the partial CLS are:

1. Ease of operation with only one dosing and coagulation step.
2. Lower cost of chemical dosing than lime-soda ash CLS.
3. Parallel lowering of TDS by precipitation lowers the desalination load on the subsequent reject processing.
4. It is particularly interesting in case of reject streams where Mg and consequently SiO<sub>2</sub> removal do not represent a problem for processing.

### 5.3.2. Conventional Cold Lime Softening

Fig (7), on the other hand, shows the effect of addition of Na<sub>2</sub>CO<sub>3</sub> after the initial partial CLS. For each species the first column to the left represents the concentration in the RO reject water, the second shows the effect of dosing of Na<sub>2</sub>CO<sub>3</sub> at a concentration of 45% of the lime concentration previously added during the partial CLS. This lowered Ca concentration by 75.3%. Mg was practically not removed at this level of alkalinity in view of the absence of additional free OH<sup>-</sup> for deposition of Mg(OH)<sub>2</sub>.



**Figure 7.** Influence of Conventional CLS with different closing rates of CaCO<sub>3</sub> on RO reject composition.

The third bar of Fig (7) belongs to dosing of an excess of Na<sub>2</sub>CO<sub>3</sub> to attain the double of concentration of lime of the initial partial CLS in order to raise alkalinity to a quite higher level.

Such increase of alkalinity did not lead to any further deposition of Ca. *In fact, our CLS results showed a minimum Ca concentration (22 ppm) at which higher lime-soda ash dosing had no effect.* Fig (7) shows in parallel a considerable increase of Na, a lower increase of  $\text{CO}_3$  and a decrease of Mg of 67% in view of the additional free OH.  $\text{SiO}_2$  is lowered by 22% by adsorption on the deposited  $\text{Mg}(\text{OH})_2$ . Complete CLS resulted in decrease of reject water TDS by 7.6% with respect to original reject water TDS.

It is worthy to notice that stoichiometrically equivalent concentrations of coions  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  to those of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , or higher, are required for precipitation of  $\text{CaCO}_3$  and  $\text{Mg}(\text{HO})_2$ . As precipitation advances, however, alkalinity as well as supersaturation are reduced. In order to achieve a steady rate of precipitation and residence time typically between 60 to 90 minutes, we had to keep a supersaturation factor (SSF) of at least three.

Parallel to chemical softening and in the same reactor, components like HMCs which may be concentrated in RO reject were shown to be better precipitated through dosing of sulphide since their sulphides are more insoluble than their hydroxides or carbonates, similarly, chlorine (hypochlorite), added during softening improved removal of  $\text{Fe}^{2+}$  by oxidation to the  $\text{Fe}^{3+}$ , Or sulphite improved precipitation of the soluble  $\text{Cr}^{6+}$  by reduction to  $\text{Cr}^{3+}$ .

#### 5.4. Reject Processing after CLS or NF

After each of partial or conventional CLS or NF of the RO reject stream, further processing was conducted through either partial recycling to the feed stream of the primary RO unit or feeding an independent secondary RO unit.

Fig (8) shows the results of recycling of softened reject stream (partial CLS) in the range of 25 to 75 percent to the feed stream of the primary RO unit. Recycling increased feed TDS which was shown to have only limited influence on permeate TDS. *While at 75% recycling the feed TDS was practically doubled to attain 5461.7 mg/l, treated under mainly similar conditions by the same pilot RO unit operated using High rejection, low energy RO membranes, the permeate TDS showed an only limited increase from 60.9 to 139.3 mg/l which does not compromise its quality for subsequent application.*

According to these results, already present RO facilities, without need of additional equipment or space, can promote the total system recovery and reduce the final reject rate and consequently the cost of the waste disposal through a simple system modification without significant sacrifice of RO permeate quality.

On the other hand, if reject processing aims to increase the final product rate, the softened stream can be treated in an independent secondary RO unit. *The comparison between RO performance of the softened and the unsoftened reject streams shows that presoftening is particularly interesting in case of high TDS, high hardness brines.* Table (6) for an RO reject of 25,017.3 mg/l having a total hardness of 11,007.0 mg/l as  $\text{CaCO}_3$  required a much smaller RO system array to result in a lower TDS permeate at a much higher recovery than the same reject stream after softening (TDS = 18,435 mg/l, total hardness = 8,279.3 mg/l as  $\text{CaCO}_3$ ).

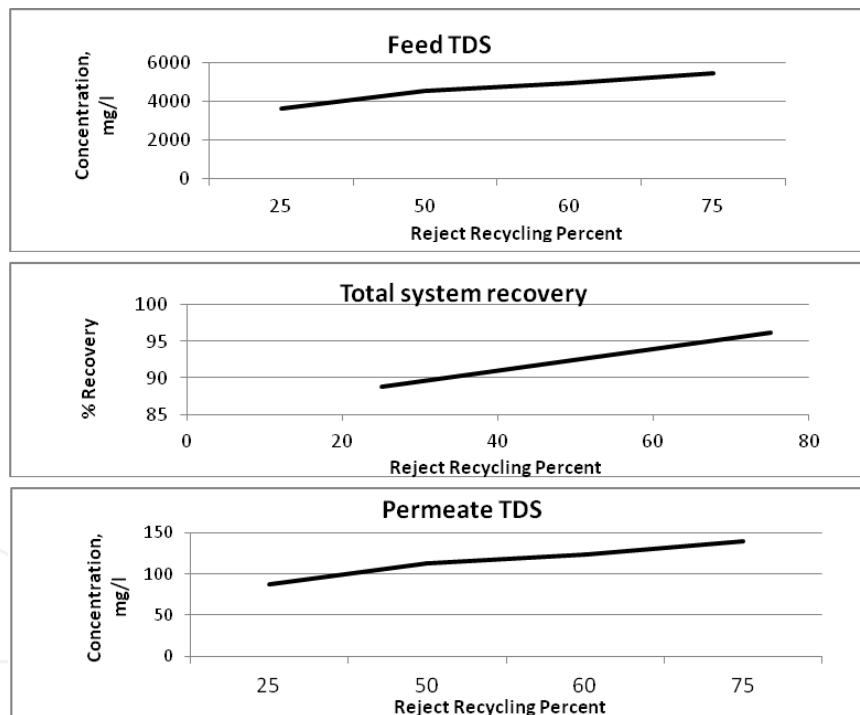
RO Performance	Unsoftened Reject Stream	Softened reject Stream
RO System Array*	(13:6:3)6	(10:5:2)6
Percent Recovery	53%	62%
Permeate TDS, mg/l	763.4	552.3

\*pressure vessels of 6 RO elements each arrayed in three stages.

**Table 6.** Comparison of RO results of presoftened and unsoftened reject.

On the other hand, for NF of reject prior to secondary RO treatment and the efficient dehardening by NF in addition to partial TDS rejection, it enabled recoveries as high as 85% of the secondary RO. This resulted in total process recovery as high as 97.75%.

Results showed that treatments of RO reject by NF prior to recycling or treatment in secondary RO unit is particularly interesting in case of medium salinity and total hardness reject streams while for highly concentrated reject streams CLS is more effective and has a lower cost than NF.



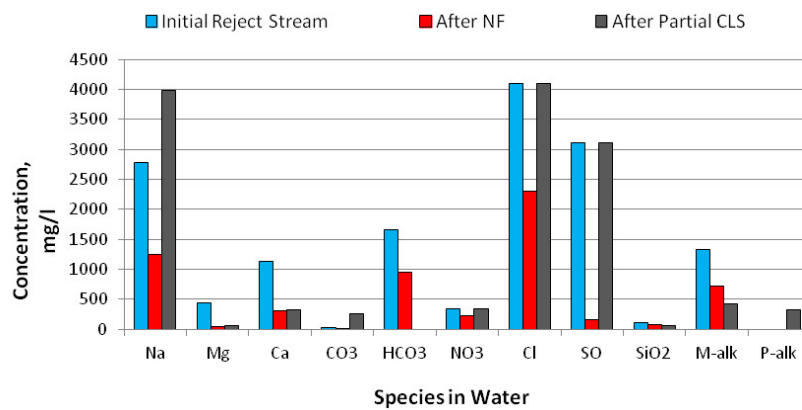
**Figure 8.** Effect of Partial Recycling of Softened Reject Stream.

### 5.5. Comparison between Removal of Scale Forming Components from RO reject by NF and by CLS

Removal of hardness components concentrated in RO reject as Ca, Mg,  $SO_4$  together with  $SiO_2$ , Fe and Mn as well as other possible components like HMC's, was investigated by NF in comparison with precipitation by the conventional CLS.

In order to conduct the comparison of the two methods under similar conditions the extent of rejection recorded by NF was the basis of selection of the dosing rate of lime and soda ash which realize the same Ca rejection. In fig (9) for each species, the first column to the left represent the initial concentration in the reject stream, the second and the third represent the results of rejection by NF, and softening, respectively.

While NF lowered the concentration of all the species to various extents and consequently lowered TDS, softening lowered only that of components included in the softening reactions as  $\text{HCO}_3^-$ , P-alkalinity and  $\text{SiO}_2$  [11]. Softening raised, on the other hand, concentration of  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ , and M-alkalinity. As for  $\text{SiO}_2$ , which is directly rejected by NF, it is removed upon softening by adsorption on  $\text{Mg}(\text{OH})_2$  deposited surface at high pH values, but at a lower efficiency than NF rejection.



**Figure 9.** Comparison between NF & partial CLS in processing of reject stream.

While the chemical softening is usually stated as having lower cost [10], [12] the detailed consideration of all the related cost factors or additional process steps that are not included in NF and which should be added to the cost of softening in order to realize the same performance as NF, revealed the cost advantage of NF reject treatment. Chemical softening but not NF requires stoichiometric or higher dosage of lime and soda ash to reduce hardness, disposal of large amounts of sludge which may include dosage of polyelectrolytes and/or sludge conditioning before delivery to settling ponds and landfill disposal, raising of pH of the reject stream up to > 9.5 for indirect removal of  $\text{SiO}_2$  after deposition of  $\text{Mg}(\text{OH})_2$  and sophisticated installations for chemical dosage, and settling tanks. Our results have shown that CLS is not as complete as by IER or NF for removal of Ca and does not effectively remove organics, or reduce TDS.

The above considerations extend to the treatment of different types of industrial WW's which contain hardness components, HMC's, may be together with organics and suspended solids where NF application will be optimum particularly if complete desalination is not required.

## 6. Conclusions

- Processing of the desalination reject stream, instead of just getting rid of it, is conducted by laboratory and pilot testing in order to promote the desalted water recovery and reduce the final reject disposal problems and costs which will increase the total desalination process efficiency, cost effectiveness and environmental safety.
- Among the investigated processing alternatives the most efficient ones in case of medium concentration brine stream (up to 10,000 mg/l) are (a) (high rejection low energy RO + use of specific antiscalant), (b) partial recycling of reject to the feed stream of the initial RO unit.

In already present RO facilities, reject recycling does not require extra footprint. Results showed that percent reject recycling as high as 75% did not significantly increase the final permeate salinity. For new projects, on the other hand, increase of total product rate was realized through a secondary RO treatment of reject.

- In case of high TDS reject streams up to 33,000 mg/l, reject processing by partial cold lime method, conventional cold lime method or nanofiltration was conducted prior to circulation to initial RO feed or treatment in secondary RO unit. Results confirmed the promotion of total percent recovery without significant sacrifices of total permeate qualities.
- Partial CLS is particularly interesting in case of reject streams where Mg and SiO<sub>2</sub> removal do not represent a problem for processing. Beside ease of operation and lower cost than conventional CLS, a partial CLS lead to higher decrease of reject TDS and does not increase Na concentration.

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