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Physical Conditioning for Scale Prevention during Desalination by Reverse Osmosis

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Master's Thesis 2005:64

Cover page: Desalination system in Cranfield University pilot plant

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Abstract

Desalination by reverse osmosis (RO) is the favoured method for potable water production from seawater. However, the membranes are subject to fouling by scaling species, principally calcium carbonate, which reduce the operating flux. Traditionally this scale has been controlled by the addition of chemicals to the system which are effective but add to the chemical load in the waste stream and so having a detrimental impact on the environment.

Candidate non-chemical methods for enhancing desalination by reverse osmosis choose the application of external magnetic or electromagnetic fields (Baker and Judd, 1996; Baker *et al*., 1997; Lipus, 2001). These so-called physical conditioning methods are highly contentious, and have never been satisfactorily proven. It has also been suggested that these methods can be enhanced by using a "distribution plate", which is claimed to work by inducing cavitations. This is the basis of the *Grahamtek* system (Grahamtek et al. 1997), and it is this system that formed the basis of the study.

The objective of the study was to assess the impact of the two conditioning methods, based on a flow distribution plate coupled with electromagnetic scale mitigation, during desalination by RO primarily with respect to membrane permeability. Three different feed waters, deionized water, salt water and hardened saline water, have been investigated and the impacts studied included both desalination performance, based on membrane permeability, and retentate water quality. In addition, various side experiments were conducted, and these included a "rapid scaling test", developed in-house to study calcium carbonate precipitation.

No impact of conditioning on either deionized or saline water was evident on the application of both physical conditioning and the distribution plate, either synergistically or in isolation. Some data from the side experiments indicated possible impacts of physical conditioning on scaling of hardened saline water. These included crystal shape and size of the calcium carbonate, retentate pH and conductivity, particle zeta potential and the rapid scaling test transient. However, the limited number of measurements performed meant that these changes could not be regarded as statistically significant and performance of the RO process itself was unaltered by physical conditioning.

Key words: scale, reverse osmosis, calcium carbonate, desalination, physical conditioning, permeability, distribution plate
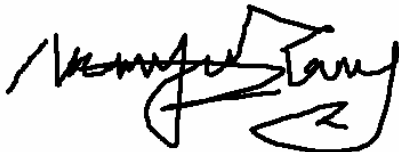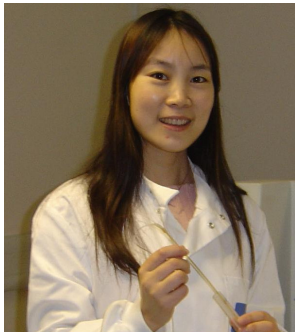
ACKNOWLEDGEMENTS

ABBREVIATIONS

APC	Antiscale physical conditioning
DI	Deionised
DO	Dissolved oxygen
DPD	Diethyl-p-phenylene diamine
FP	Feed pressure bar
GRP	Glass fibre reinforced plastic
ICP-MS	Inductive coupled plasma-Mass spectrometry
LSI	Langelier Saturation Index
NTU	Nephelometric Turbidity Units
OP	Osmotic pressure
PCD	Physical conditioning device
PLC	Programmable logic controller
PF	Product flow rate
PP	Product pressure bar
QP	Normalized product flow rate
RO	Reverse osmosis
RP	Reject pressure bar
RSI	Ryznar Stability Index
SEM	Scanning electron microscope
SW	Spiral wound
TCF	Temperature correction factor
TMP	Transmembrane pressure
TDS	Total dissolved solid

TABLE OF CONTENTS

1. Introduction and literature survey

Water is a very important resource for the human life. The Earth is mostly covered by water but most of it is not potable. 97% of water is salt water from oceans; 3% is fresh water but less than 1% of this is usable from river and groundwater[1]. With the development of industry and agriculture more and more water is becoming polluted. The rapid increase in population exacerbates water shortage, since the limited supply of fresh water cannot meet the future demand. Water availability and security is now a critical global priority, and the search for new water more the urgent than ever.

Desalination offers the opportunity of converting highly saline water, such as seawater, into drinking water. This option is considered more sustainable than the use of freshwater, since the proportion of water provided globally is so high. Its use is limited more by the energy demand of the technology than the environmental impacts, although the latter cannot be ignored completely.

1.1 Desalination

By the early 1960s, people were already using the thermal technologies to desalt water for potable supplies. Membrane processes such as Reverse Osmosis and Electrodialysis were introduced in the late 1960's. The total capacity of world's desalination facilities available at present was in excess of 20 million m^3/day[1]. With the development of the membrane technology coupled with reduced of costs of construction and operation, membrane desalination has become the most cost effective and environmentally friendly means of desalting compared the distillation.

There are several ways of conducting desalination. The techniques used can be classified into three process-based categories:
- distillation, such as multi-stage flash
- adsorption based on chemical bonds such as ion exchange
- membranes processes such as reverse osmosis or electrodialysis

Distillation is the oldest type of desalination process and involves phase changes to lead to the pure water separate from the feed water by physical means[2]. Ion exchange is a process by which contaminant dissolved inorganic salts such as Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} are exchanged with more innocuous ions such H^+ and OH^-. At low salinities, ion exchange is marginally more economical than RO for producing high purity water for industrial, pharmaceutical, and health care applications[3] (Zahid Amjad, 1999). However, it is not appropriate for brackish or concentrated waters.

1.2   Reverse osmosis

Reverse Osmosis technique is considered the most promising seawater and brackish water treatment process (Furukawa, 1997). It is a process whereby the natural phenomenon of osmosis is reversed by the application of pressure to a concentrated solution in contact with a semipermeable membrane (Amjad, 1993). If the applied pressure is in excess of the water's natural osmotic pressure, the salt water will flow through the membrane to the pure water side and more concentrated salt water remains on the side to which pressure was applied.

1.2.1 Membrane materials and configurations

There are two major membrane materials which industry employs for desalination purposes. They are cellulose acetate membranes and thin film composites membranes, the latter incorporating aromatic polyamide membranes. A comparison of these two membranes is listed in Table 1.2.1.

Cellulose acetate membranes were the first commercial RO membranes to be developed (Zahid Amjad, 1993) in the 1960's. They have low chemical stability and easily to hydrolyse at pH values above 7.5. They are also readily biodegradable, and hence vulnerable to microbial attack. However, they have reasonable tolerance to fouling, and are also resistance to attack by low concentrations of chlorine, allowing them to be sanitised.

Thin film composites find widespread use. They are used both for potable water treatment, along with cellulose acetate, and for high-purity water production. They are often used in larger system because their low energy consumption associated with their high permeability. But the fouling occurs more quickly than other type of membrane due to higher flux rates. Aromatic polyamide membranes are suited for treating TDS waters because of their high salt rejection and chemical stability. They are not readily biodegradable and do not hydrolyse.

Table 1.2.1 Membrane property comparison

	Cellulose Acetate (CA)	Thin film composites (TFC)
Water flux rates	high	higher
Salt rejection	low	high
Tolerate to chlorine	yes	no
Tolerate to foulants	high	low
Chemical stability	low	high
Bio-fouling	poor	excellent
Cost	low	high

There are generally four types of membrane configuration employed for desalination purposes: hollow fiber membrane, spiral wound membrane, tubular membrane and plate and frame membrane.

Spiral wound membrane is relatively inexpensive and has reasonable resistance to fouling. It is by far the most widely employed configuration in reverse osmosis treatment and is available in a wide variety of membrane materials. However, spiral wound modules achieve low recoveries in small systems because single elements operate at only about 8 to 10 percent recovery due to the limits imposed by concentration polarization-promoted fouling. Tubular membranes have high flow velocities and large flow channels, making them less readily fouled (due to the large shear imposed by the crossflow associated with the high Reynolds numbers) and more easily cleaned than the spiral wound configuration. However, the high flow rates impose a high energy demand. Plate and frame membrane modules are similarly fairly resistant to fouling. They can also be disassembled for cleaning. However, they are also very costly. Hollow fibre membrane modules have high area to volume ratios, and can produce a relatively high recovery for single element. However, they are very sensitive to fouling by colloidal and suspended matter due poor hydrodynamic conditions involved.

1.2.2 RO advantages and disadvantages

RO plants demand less energy than distillation plants, have lower capital costs and have a smaller footprint. They are also modular, and so can be expanded more readily than an evaporative process. On the other hand, the conversion achievable by RO is limited by the osmotic pressure of the waste brine, and the process cannot be directly steam-driven (and so cannot operate using waste steam). Its performance is also greatly affected by membrane fouling, since this can change not only flow through the membrane but the membrane rejection properties as well.

Fouling comprises mineral scale formation, gel-layer formation, colloidal deposition and pore plugging, and biological fouling. Scaling and gel-layer formation, which respectively relate to sparingly soluble inorganic and organic matter, is exacerbated by concentration polarization, which refers to the accumulation of rejected materials next to the membrane surface. Fouling impairs membrane performance and shortens its life.

1.3   Scaling background

Scalants are low-solubility salts whose precipitation onto the membrane is promoted by the conversion of water into permeate and further encouraged both by concentration polarisation and the pH shift produced by carbon dioxide permeation. The scale formed can reduce the membrane permeability and permselectivity. As with

colloidal and particulate fouling, scaling is also a problem in membrane filtration processes. Any water containing calcium carbonate close to or beyond its thermodynamic saturation limit, as is the case for many dairy and pharmaceutical effluents, can produce calcite (the most common crystal form of calcium carbonate) at the membrane surface.

Scale formation propensity is usually apparent from chemical thermodynamics, and specifically the solubility product K_s (Table 1.1) although it can never be unequivocally predicted. The solubility product represents the maximum value of the product of the molar concentrations of the two component ions of the salt. If the solubility is exceeded then the salt will precipitate. The general rule of thumb to avoid precipitation is that the ionic product should not exceed 80% of the solubility product. The appropriate constants for thermodynamic equilibrium appropriate to some of the more common scalants, such as salts of the divalent alkaline earth elements of magnesium, calcium and barium, are normally included in CAD packages for designing RO arrays. The thermodynamic relationships include, in the case of calcium carbonate formation, data pertaining to hydrolysis. The significance of this is outlined below.

Calcium carbonate is very insoluble in water and readily precipitates to form a scale on pipework, heat transfer surfaces and membranes. The equilibrium constant for the dissolution reaction is represented by:

$$K_s \quad = \quad [Ca^{2+}][CO_3^{2-}] \hspace{5cm} 1.1$$

and so:

$$[CO_3^{2-}] \quad = \quad K_s / [Ca^{2+}] \hspace{5cm} 1.2$$

When carbon dioxide dissolves in water it forms carbonic acid which dissociates producing acid and bicarbonate ions thus:

$$CO_2 \text{ (dissolved)} \quad + \quad H_2O \Leftrightarrow H^+ + HCO_3^- \hspace{3cm} 1.3$$
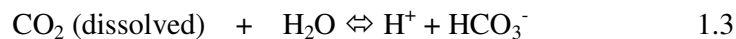
This is the origin of the pH shift in reverse osmosis. Because the membrane allows free passage of carbon dioxide, the CO_2/HCO_3^- ratio in the permeate is high and that of the retentate low. Since, according to Equation 1.3, the acid (i.e. H^+) concentration relates directly to the CO_2/HCO_3^- ratio, the retentate pH is correspondingly high whilst that of the permeate is low.

Bicarbonate ions further dissociate to carbonate:

$$HCO_3^- \quad \Leftrightarrow \quad H^+ + CO_3^{2-} \hspace{4cm} 1.4$$

for which the equilibrium constant is:

$$K_2 \quad = \quad [H^+] [CO_3^{2-}]/ [HCO_3^-] \qquad\qquad 1.5$$

and so:

$$[CO_3^{2-}] = \quad K_2 [HCO_3^-] / [H^+] \qquad\qquad 1.6$$

Table 1.1 Solubility products for some common scalants at 20°C (Cranfield university lecture, 2004)

Salt	Formula	Solubility product, K_s
Aluminium hydroxide	$Al(OH)_3$	8.5×10^{-23}
Barium sulphate	$BaSO_4$	9.2×10^{-11}
Calcium carbonate	$CaCO_3$	4.8×10^{-9}
Calcium fluoride	CaF_2	3.2×10^{-11}
Calcium hydrogen phosphate	$CaHPO_4$	2.0×10^{-7}
Calcium hydroxide	$Ca(OH)_2$	8×10^{-6}
Calcium sulphate	$CaSO_4$	2.3×10^{-4}
Cadmium sulphide	CdS	1.4×10^{-28}
Cobalt sulphide	CoS	3.0×10^{-26}
Chromium hydroxide	$Cr(OH)_3$	2.9×10^{-29}
Copper sulphide	CuS	1.0×10^{-44}
Dolomite	$CaMg(CO_3)_2$	6.8×10^{-18}
Ferrous hydroxide	$Fe(OH)_2$	4.8×10^{-16}
Ferric hydroxide	$Fe(OH)_3$	3.8×10^{-38}
Ferrous sulphide	FeS	4.0×10^{-19}
Lead sulphide	PbS	5.0×10^{-29}
Manganese hydroxide	$Mn(OH)_2$	4.0×10^{-14}
Manganese sulphide	MnS	1.4×10^{-15}
Magnesium ammonia phosphate	$MgNH_4PO_4$	2.2×10^{-13}
Magnesium carbonate	$MgCO_3$	1.0×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	3.4×10^{-11}
Mercuric bromide	Hg_2Br_2	5.2×10^{-23}
Mercuric chloride	Hg_2Cl_2	3.5×10^{-18}
Mercuric sulphide	Hg_2S	1.0×10^{-45}
Nickel hydroxide	$Ni(OH)_2$	8.7×10^{-19}
Nickel sulphide	$AgBr$	7.7×10^{-13}
Silver chloride	$AgCl$	1.5×10^{-10}
Silver sulphide	Ag_2S	1.6×10^{-49}
Zinc hydroxide	$Zn(OH)_2$	1.0×10^{-17}
Zinc sulphide	ZnS	1.0×10^{-23}

Equations 1.2 and 1.6 can be combined to give:

$$[H^+] \quad = \quad K_2 [Ca^{2+}] [HCO_3^-] / K_s \qquad\qquad 1.7$$

Thus:

$$pH_s = \quad (pK_2 - pK_s) + pCa + pAlk \qquad\qquad 1.8$$

where Alk represents the molar bicarbonate concentration or alkalinity. In this equation the term "pH_s" represents the pH at which the water is in equilibrium with calcium carbonate, and is thus sometimes referred to as the saturation pH. The value of $(pK_2 - pK_s)$ is dependent on temperature and ionic strength.

The Langelier Saturation Index is defined as:

$$LSI = \quad pH - pH_s \qquad\qquad 1.9$$

Where pH is the actual measured pH of the water and pH_s is the calculated value. The LSI effectively measures the degree to which the water is either supersaturated or undersaturated with calcium carbonate, and thus its propensity for forming scale (ASTM D3739). A negative LSI indicates corrosive water which will dissolve calcium carbonate scale and a positive LSI indicates a scale forming one. The LSI is widely used and there are several nomograms available for rapid calculation.

Whilst the LSI is a good predictor of scaling it is a bit unreliable in the range -1 to +1 and gives no indication of the relative scaling potential. The Ryznar Stability Index gives more quantifiable results and is defined as follows:

$$RSI = \quad 2pH_s - pH \qquad\qquad 1.10$$

An RSI of 7 indicates water more or less at equilibrium. As the value falls the water becomes more scaling and as it rises the water becomes more corrosive. The Langelier and Ryznar saturation indices can be used to predict scaling in most waters but they become unreliable when the total dissolved solids content approaches 5000 mg/l. Above this level the Stiff & Davis index (ASTM D4582) or a similar method must be adopted.

1.3.1 Chemical scale control

The simplest means of preventing scale formation in RO systems is to operate at a conversion sufficiently low that the reject stream is not so concentrated that solubility problems are encountered. This, of course, has economic implications for the operation of the plant which may be unacceptable, and in such cases some form of scale prevention must be used. Where calcium carbonate or some other hydrolysable

scalant is the main problem, i.e. those salts containing hydroxide (OH^-) and carbonate (CO_3^{2-}) which therefore have associated pH-dependent solubility due to hydrolysis reactions (i.e. reaction with acid, H^+) of these anions, it is often possible to adjust the LSI by acid dosing. This converts bicarbonate into carbon dioxide which can be removed by degassing either of the feed or the permeate. Depending on whether hydrochloric or sulphuric acid is used there will be an increase in sulphate or chloride concentration. Increasing the sulphate may give rise to calcium sulphate precipitation.

Scale-inhibiting chemicals can be used to delay precipitation of some salts by interfering with the crystallization process forming microcrystals which do not cause fouling and which will not show significant agglomeration at least until the concentrate stream has left the RO unit. Most of the commercially available chemicals work well on calcium carbonate, provided that the LSI in the concentrate stream is less than +2, but less well on other salts. The most established scale inhibitors are termed "glassy polyphosphates", typically sodium hexametaphosphate (*Calgon®*). These work by absorbing into the nanoscopic protonuclei forming during the incipient stages of precipitation and destabilising the subsequent crystal nuclei. They are not the most effective chemicals for the application and revert quite quickly in solution to orthophosphate, producing calcium phosphate sludge which can cause blocking of separators and small bore pipes. Since the development of Calgon, more effective threshold chemicals, including phosphonates, have become available. Polycarboxylic acids, such as polyacrylates and polymalonates, operate by blocking crystal growth sites preventing the growth of nuclei into crystals whilst chelating chemicals react with potentially insoluble cations like calcium to form a soluble complex. Dosage rates are typically of the order of 5-10 mg/l and, whilst some indication of the efficacy of these reagents may arise from the scale inhibition mechanism, it is generally the case that only pilot trials yield reliable information as to their suitability for a particular duty.

Where scale-inhibiting chemicals are unable to cope with the concentrations involved, and where chemical dosing is to be avoided for some reason, then pretreatment of the water is necessary to remove the scale-forming salts. This would normally only be necessary at LSI levels >3. This may be by sodium cycle ion exchange softening, ion exchange dealkalisation, lime or lime-soda softening or even a nanofiltration process if divalent ions are to be selectively removed. Some scalants, such as silica, are particularly recalcitrant.

1.3.2 Physical conditioning

Physical conditioning represents an unusual and highly contentious type of scale control, involving no chemicals and little energy. This method is thought to work through acting at various junctures of the crystalisation process (Table 1.2). As yet, however, no consistent, universally accepted mechanism exists to describe all the

effects observed. However, suppliers of most of the devices make similar claims regarding their efficacy, these being:

- reduction of the amount of scale formed,
- production of a less tenacious scale (due to a change in crystal morphology),
- removal of existing scale, and/or
- retention of the antiscaling properties of the treated water for an extended time following treatment.

Although their scientific basis remains enigmatic, their use has increased over the past years due to their low environmental impact (in terms of chemical use and waste). Many authors also report large saving in energy, cleaning and process downtime costs (Donaldson and Grimes, 1988) from the installation of magnetic water conditioners in real systems. Publications of physical conditioning studies have dramatically increased in the past five years (Table 1.2 and Table 1.3).

The observed impacts are often contradictory, as indicated in table 1.2. However, there is some consensus that treated crystals are easier to remove from solid surfaces, in either the calcite or aragonite form. The associated "magnetic memory" of water is equally controversial, lasting anything from a few seconds to hundreds of hours. There are many proposed theories that attempt to explain the mechanisms of this phenomenon, though none are fully proven. Some of the more recent theories do contain credible equations, resulting in their increased plausibility, yet rather large assumptions remain in all cases. Colic and Morse (1999) present one of the more convincing theories of a mechanism for the magnetic memory by regarding perturbations of the gas/liquid interface.

There are fundamentally three different types of antiscale physical conditioning (APC) devices, these being magnetic, electronic and electrolytic. Of these, the latter is at least consistent with established science. Electrolytic conditioners operate through the use of a sacrificial electrode usually zinc which is sometimes supplemented with iron. Dissolved zinc and iron and known scale inhibitors, impacting significantly on the crystal form even at concentrations as low as a few ppb (Coetzee, 1996).

However, the mechanisms offered for magnetic, electrolytic and electrostatic conditioners remain highly contentious and often inconsistent with the energy available. Magnetic devices were originally reviewed extensively by authors such as Baker and Judd (1996), and identified reported effects summarised in Table 1.2 and mechanisms acting at the four levels indicated in Table 1.3. Most electronic devices apply alternating electronic fields, and the scale mitigating impacts are claimed to relate to the frequency and amplitude of the signal transmitted to the solution through perturbation of intermolecular or even intramolecular forces. This may be manifested as an electrostatic effect, such that the natural surface charge at the particle:solution interface is altered thus promoting or inhibiting particle agglomeration. However, the fact that there has been no evidence reported of significant and consistent changes in

zeta potential, the most readily determined particle parameter directly relating to surface charge, suggests that interfacial effects, if arising at all, are not long-lived.

Table 1.2   Impacts (1997 – present)

Impact	Reference
Enhanced nucleation	Chibowski *et al*. (2003), Colic and Morse (1998), Euvrard (1997), Holysz, Chibowski and Chibowski (2002), Holysz, Chibowski and Chibowski (2003), Holysz, Chibowski and Szczes (2003), Lui (1999), Wang et al. (1997)
Reduced nucleation	Barret and Parsons (1998), Chibowski *et al.* (2003, 2003b), Colic and Morse (1998), Euvrard (1997), Holysz, Chibowski and Chibowski (2002), Holysz, Chibowski and Chibowski (2003), Holysz, Chibowski and Szczes (2003), Khalil *et al.* (1999), Parsons *et al.* (1997)
Enhanced growth	Baker and Judd (1996), Baker *et al.* (1997), Barret and Parsons (1998), Chibowski *et al*. (2003), Colic and Morse (1998), Fan and Cho (1997), Lipus, Krope and Crepinsek (2001), Lui (1999)
Reduced growth	Chibowski *et al.* (2003), Cho *et al.* (2003), Colic and Morse (1998), Holysz, Chibowski and Szczes (2003), Parsons *et al*. (1997), Wang *et al.* (1997)
Reduced scale deposition	Baker *et al*. (1997), Barret and Parsons (1998), Busch *et al.* (1997), Chibowski *et al*. (2003b), Cho *et al.* (1998, 2003), Dallas (2001), Euvrard (1997), Gabrielli (2001), Holysz, Chibowski and Szczes (2003), Khalil *et al.* (1999), Lipus, Krope and Crepinsek (2001), Lui (1999), Parsons et al (1997a), The U.S. Department of Energy (1998),
Change in crystal mor-phology (aragonite: calcite)	Baker *et al*. (1997), Chibowski et al. (2003b), Cho *et al.* (1999, 2003), Coey and Cass (2000), Hall (2002), Holysz, Chibowski and Chibowski (2003), Kobe *et al*. (2001, 2001a), Lipus *et al.* (1998), Parsons et al (1997)
Change in solution pH	Chibowski et al. (2003, 2003a), Colic and Morse (1998), Higishitani and Oshitani (1998), Holysz, Chibowski and Szczes (2003), Lipus et al (1998), Parsons *et al.* (1997, 1997a)
Change in zeta potential	Chibowski et al (2003a), Colic and Morse (1998), Goldsworthy *et al.* (1999), Holysz, Chibowski and Chibowski (2003), Holysz, Chibowski and Szczes (2003), Lipus *et al.* (1998), Lubomska and Chibowski (2001), Parsons *et al*. (1997)
Change in conductivity	Chibowski *et al*. (2003b), Lipus *et al*. (1998)
Change in surface tension	Burgess, Judd and Parsons (2000), Chibowski *et al*. (2003b), Cho *et al.* (2003), Hall (2002), Holysz, Chibowski and Chibowski (2002, 2003)
"Magnetic memory"	Barret and Parsons (1998), Chibowski *et al*. (2003a, 2003b), Coey and Cass (2000), Colic and Morse (1998a), Goldsworthy *et al.* (1999), Higishitani and Oshitani (1997, 1998), Holysz, Chibowski and Chibowski (2002, 2003), Holysz, Chibowski and Szczes (2003), Lubomska and Chibowski (2001)
Accelerated coagulation	Barret and Parsons (1998), Cho *et al*. (2003), Goldsworthy *et al.* (1999), Higishitani and Oshitani (1998), Holysz, Chibowski and Szczes (2003), Leahy *et al.* (2000), Lipus *et al.* (1998), Lipus, Krope and Crepinsek (2001), Parsons *et al.* (1997)

According to Baker and Judd (1996), there are a number of specific impacts of conditioning devices on systems (Table 1.2), which are discussed in more detail below.

Table 1.3   Effects and proposed mechanisms

Effect	Mechanism	References
Intra atomic	Free radical production	Colic and Morse (1998, 1998a)
	Changes in electron configuration	Ghui and Carnahan (2002), Holysz, Chibowski and Chibowski (2003), Lubomska and Chibowski (2001)
Intra molecular	Bond deformation and Molecular bond breaking	Chibowski et al (1994), Cho *et al.* (1997), Colic and Morse (1998), Hall (2002), Higashitani et al (1996), Holysz and Chibowski (1994), Kobe *et al.* (2001a), Leahy *et al.* (2000), Lubomska and Chibowski (2001), Oshitani *et al.* (1999), Ozeki *et al.* (1996)
Inter molecular	Clustering and Changes in coordination of water molecules around ions	Al-Qahtani (1996), Baker and Judd (1996), Chibowski *et al.* (2003b), Colic and Morse (1998, 1998a), Oshitani *et al.* (1999, 1999a), Ozeki *et al.* (1996)
	Water structure changes	Busch et al (1986), Colic and Morse (1998, 1998a, 1999), Chibowski *et al.* (1994, 2003b), Fesenko (1995), Higashitani *et al.* (1996), Higishitani and Oshitani (1997, 1998), Holysz, Chibowski and Chibowski (2002), Leahy *et al.* (2000), Lubomska and Chibowski (2001), Ozeki *et al.* (1996), Weissenborn and Pugh (1996)
	Changes in hydration shell (rupturing/ distorting/ expanding)	Chibowski et al. (2003b), Dallas (2001), Dallas and Koutsopoulos (1989, 1993), Ghui and Carnahan (2002), Higishitani and Oshitani (1998), Holysz, Chibowski and Chibowski (2002), Holysz, Chibowski and Szczes (2003), Lipus, Krope and Crepinsek (2001)
	Charge neutralisation (charge on H^+/OH^- ions)	Busch *et al.* (1986), Chibowski and Holysz (1995), Higishitani and Oshitani (1997, 1998), Holysz and Chibowski (1994), Leahy *et al.* (2000), Lipus *et al.* (1998), Lubomska and Chibowski (2001)
	Electrolytic dissolution	Busch and Busch (1997), Busch *et al.* (1986), Herzog *et al.* (1989)
	Improved ion collision frequency	Cho *et al.* (1997), Goldsworthy *et al.* (1999), Lipus *et al.* (1998), Lui (1999)
Interfacial	Solid-liquid	Baker and Judd (1996), Barret and Parsons (1998), Burgess, Judd and Parsons (2000), Chibowski and Holysz (1995), Dallas and Koutsoukos (1989), Lipus, Krope and Crepinsek (2001), Lubomska and Chibowski (2001), Ozeki *et al.* (1996), Parsons *et al.* (1997)
	Gas-liquid	Colic and Morse (1998, 1998a, 1999), Lubomska and Chibowski (2001), Weissenborn and Pugh (1996)
	Importance of dissolved gasses	Colic and Morse (1998, 1998a, 1999), Lubomska and Chibowski (2001)
	Double-layer distortion (Lorentz Force)	Baker and Judd (1996), Coey and Cass (2000), Goldsworthy *et al.* (1999), Leahy *et al.* (2000), Lipus *et al.* (1998), Lipus, Krope and Crepinsek (2001), Parsons *et al.* (1997)

Effects on crystallinity

Physical conditioning can change crystal habit. Calcium carbonate arises in three such habits: calcite, aragonite and vaterite. Vaterite was a rare metastable form, whereas calcite is the most common at ambient temperatures (Deer et al., 1982). Aragonite is

the most common form at elevated temperatures, between 60 and 80 °C (Herzog et al., 1989). It is less tenacious than calcite, producing a softer and more readily removable scale. Aragonite can convert to calcite over time, forming a more tenacious encrustation as a result (Herzog et al., 1989). Donaldson (1988) found that the ratio of calcite: aragonite was reduced after magnetic treatment. Parsons et al., (1997) reported that crystallization and dissolution of some compounds could be affected with the application of magnetic field. Raisen (1984) reported that aragonite is produced in the solution following magnetic treatment. Reports of the so-called "magnetic memory", the ability of the magnetically-treated solution to retain conditioned properties for periods between several minutes to many hours, have also related to crystallinity. (Ellingsen and Kristiansen, 1979; Higashitani *et al.*, 1992)

Effects on nucleation and growth

Some theoretical studies support proposed mechanisms for magneticlly-affected crystallisation behaviour, usually with reference to nuclei formation (Sinezuk et al., 1987; Kul'skii et al., 1983). Experimental studies in this area suggest that conditioning can both accelerate nucleation (Koubikiva, 1969) and suppress it (Ellingsen and Vik, 1982) depending on the solution chemistry. When nucleation is suppressed either scaling is reduced or larger crystals are formed. Ellingsen and Vik (1982) and Higashitani (1993) have produced photographic evidence indicating suppression of nucleation of $CaCO_3$ following magnetic treatment. When nucleation is accelerated, more nuclei are produced which are then thought to collide more frequently and generate smaller crystallites which from softer, less teneacious scales. Hence, it would appear that both enhancement and suppression of nucleation can have beneficial impacts on scaling.

Effects on coagulation

Most mineral colloidal particles have negatively charged surface in the water, and it is this charge that stabilises the suspension through electrostatic repulsion. In region next to the solid surface counter-ions form an attached layer known as the Stern layer. Outside this layer ions are not directly bound to the surface but there is an imbalance of counter and co-ions which reduces as the distance from the particle surface decreases. The region where an imbalance exists is known as the diffuse layer. Suppressing the thickness of the diffuse layer, which can be achieved, for example, by increasing the ionic strength or by directly reducing the particle surface charge by adding coagulants, reduces the particle stability and promotes their aggregation. Higashitani et al. (1992, 1993, 1995, 1996 and 1997) have reported the impacts of a magnetic field on the coagulation rate of colloids, which increased following magnetic treatment. Gehr et al (1995) reported that the zeta potential, the potential close to the outer Stern layer boundary, was reduced by 25%, destabilizing the suspension to some extent. Ledion et al.(1988) and Gehr (1995), working on calcium sulphate, have both reported a reduction in zeta potential following magnetic treatment.

Many magnetic treatment device manufactures claim that the principal action of the device is through the formation of hydrophilic crystallites with a modified surface charge which inhibits their attachment to surfaces to form scales (Ellingsen and Vik, 1982). Growth on existing scale is thermodynamically favoured (Nielsen, 1964), such that the size and surface charge of growing suspended crystallites are altered increasing their tendency to remain entrained with the bulk of the solution (Crolet and Ledion, 1988).

Effects on physicochemical properties of water and solutions
Magnetic effects reported on fundamental properties of water about intra-molecular and molecule-ion interactions have generally been few in number (Baker and Judd, 1996). Bruns et al. (1966) found that the infra red (IR) absorbance of water was changed by about 30% upon application of a magnetic field of around 0.15 T. but Duffy (1977) found that static and dynamic treatment of doubly distilled water produced no changes in absorbance at all wavelengths. The alteration of water properties such as light absorbance, pH, zeta potential or surface tension has been reported following magnetic treatment. Amiri (2003) found that surface tension was reduced follosing magnetic treatment, increasing the solubility of existing scale.

1.4 Enhanced desalination by reverse osmosis

The use of physical conditioning for scale mitigation in reverse osmosis represents an obvious application for such devices. However, there remain very few publications relating to this duty (Table 1.4). Moreover, few authors describe the experimental design in any detail and these reveal significant dissimilarities which make comparison of results difficult. The reported impacts during APC application are proposed to be the result of physical and chemical alterations, which may hinder the transport of particular ions through the membrane but, as with all aspects of physical conditioning, the mechanisms are not yet understood. There is no doubt that if a higher flux can be achieved at lower pressure the cost savings would be significant; Vedavyasan (2000) estimated an associated 8% decrease in total water costs.

Table 1.4   Impacts on reverse osmosis

Impact	Reference
Reduced salt passage	Al-Qahtani (1996), Carnahan *et al.* (1999), Ghui and Carnahan (2002)
Increased particle size on the membrane	Baker *et al.* (1996), Baker (1997)
Greater permeate flux at lower pressure	Carnahan *et al.* (1999)
Membrane flux equilibrium value reached more rapidly	Carnahan *et al.* (1999)
Reduced fouling rate of the membranes	Vedavyasan (2000)
Extended cleaning-in-place (CIP) intervals	Vedavyasan (2000)

In 1996 Al-Qahtani found that the salt concentrations of the permeate from re-circulating seawater through a magnetic field without chemical treatment were usually lower than that for the untreated ones. There were accentuated differences for higher operating pressures. Increases in pH and conductivity in the treated water were also observed. The changes in the salt passage values were postulated to be due to the physical alterations, such as clustering or nucleation, of certain types of ions. This alteration might then hinder the transportation of those ions through the micro-porous structure of the membrane. It was alternatively proposed that the effect of the magnetic device was to cause chemical interaction between certain types of ions, producing entities more readily rejected by the membrane.

Baker *et al.* (1996) found that magnetic pretreatment enhanced precipitation in the pre-filter units and also provided some improvements in the salt rejection decline, though no significant changes in the permeate flux were evident. In his thesis (Baker, 1997), Baker found that there was no change in a once through system with single magnetic exposure of the water. However, under recirculation the grain size of the deposit was reproducibly increased. The findings included:

- occasional improvements in salt rejection decline due to this more porous deposit
- no repeatable substantial improvement in flux decline
- magnetic treatment was promoting enhanced precipitation in the pre-filter units

Antiscale magnetic treatment proved to be unsuccessful in suppressing scale formation on reverse osmosis membranes operated at high recovery using saturated calcium carbonate solutions in both once through and recirculating systems. However, effects were evident under recirculation which could only be attributed to magnetic treatment. These included an increase in particle size on the membrane and increased deposit growth on the pre-filter units. Whilst these changes were found to be statistically significant, they did not correlate with improved process performance.

Graham *et al*. (1997) first proposed the system with a flow distributor as a means of to improve flow distribution and reduce hydrodynamic boundary layer thickness (and thus concentration polarisation). It was implied that this would lower the transmembrane pressure and reduce pressure losses through the system. This system was later supplemented by strategically positioned electromagnetic fields and became the *GrahamTek* system. According to Carnahan *et al.* (1999), the system provides:

- a greater permeate flux achieved with lower pressure
- reduced particulate fouling and biofouling at the membrane surface due to enhanced mixing
- improved salt rejection, since the salt passage through a membrane is concentration related
- more rapid equilibration of the membrane flux when compared with a parallel conventional test.

Sheikholeslami (1999) also reported on the *GrahamTek* system. It was claimed that the electromagnetic field deters the precipitation of sparingly soluble salts and also affects organic components either by negating or partially affecting their ability to interact with the charged membrane surface, which surrounds the membrane elements and affects both ionic and organic species in the feed water, deterring both precipitation and membrane fouling. However, no significant scientific trials had been conducted and the data presented was incomplete.

The basis on which the distribution plate is claimed to work is, at least in part, questionable. The plate has been claimed to promote cavitations, producing micro-bubbles which scour the membrane surface and suppress fouling as a result.

Sheikholeslami (1999) suggested that the flow distributor causes gases to be expelled. Some cavitation could form behind the distribution plate. There will be some bubbles produce. Just many gases dissolved in the solution will find holes to fill them. The bubbles are the gas filled holes. These bubbles from the gases of CO2 and O2 enhance scrubbing at the membrane surface reducing the boundary layer thickness (Harry, K, 2003). These micro bubbles actively scour the membrane surface preventing foulants from settling. The flow distributor improves the cross-flow shear force and easing mass transfer across the membrane surface. Therefore it reduces the concentration polarization and increases the flux of permeate water.

Vedavyasan (2000) offered a cost-benefit approach. Reporting on a small-scale system similar to the *GrahamTek* system, Vedavyasan (2001) concluded that the fouling rate of the membranes is considerably reduced by the presence of a magnetic field. This allows for considerable cost saving in the operation and maintenance of such membrane processes. The transmembrane pressure was 20% lower compared with a conventional system, improving the overall performance of the plant. Another significant observation was that the cleaning-in-place (CIP) intervals were extended three-fold. Should this process scale up then the benefits include higher reliability and improved economics, resulting from lower investments and operating costs which could give an estimated 8% decrease in total water costs?

Ghui and Carnahan (2002) investigated the influence of a magnetic field on the salt permeation through reverse osmosis membranes. They found experimentally that the salt transport across the reverse osmosis membranes was decreased by up to 13% for KCl whereas lower differences were observed for RbCl and NaCl. There was no significant impact of the magnetic field for CsCl. They concluded that the magnetic field could interact with the solute and the membrane at multiple levels:
- bulk effects, such as the Laplace force
- intramolecular effects, such as the rupture or expansion of the hydration shell
- superficial interaction with the membrane interface
- intra-atomic effects due to the interference with the spin magnetic momentum

More likely, there is a synergy of all these effects and each has a different magnitude for any singular ionic species.

1.5 Aims and objectives of study

The antiscale reverse osmosis system under examination in this study is based on the one produced by GrahamTek (patent number US 6,217,773 B1).

The project aims to assess the impact of two conditioning methods, based on the flow distribution plate and electronic scale mitigation, during desalination by reverse osmosis (RO) with specific reference to:
1. membrane permeability and salt rejection
2. bulk liquid chemical parameters (conductivity, pH, etc)
3. particle properties (size distribution and zeta potential)
4. scaling rate, as determined through a bespoke ex-situ test

2. Experimental

2.1 Materials

The desalination pilot plant was provided by Salt Separation Services and is located in the Cranfield University Rig Bay area. The plant uses standard 2.5-inch spiral-wound reverse osmosis elements in three parallel streams, and operates at a feed flow rate of between 900 and 1300 l/hr and a recovery of around 10%. Distribution plates were fitted to two of the modules. The transmembrane pressure or feed water flow rate can be controlled manually by regulating the rejected valve on the rig. All the physical parameters were measured automatically on-line from the screen (Fig. 2.1).

The rig is made up of four components: the feed water tank, pretreatment, reverse osmosis unit and PLC (programmable logic controller) (Fig. 2.2). The cylindrical feed tank was of GRP plastic and had a capacity of 3000 liters. Water was pumped from the tank and through heat exchanger fed by a chiller to maintain ambient temperatures. It then passed through a cartridge filter (5 μm rated, nominal) by a low-pressure pump and fed to three RO modules in parallel by high pressure pumps capable of providing

pressures up to 68 bar. Both the retenate and the permeate streams were returned to the feed tank for the majority of the trials, i.e. the rig was operated as a closed loop. The PLC displayed data via a touch-sensitive screen and provided 3 days of data for downloading. Data logged comprised pH, DO, conductivity, flow rate, pressure (inlet and outlet) and temperature for feed, reject and permeate water.

Fig. 2.1 Desalination rig

The use of pre-hardened water demanded dosing with separate concentrated stock solutions of calcium chloride (2664 mg/L $CaCl_2$, or 2400 mg/L as $CaCO_3$) and sodium bicarbonate (4032 mg/L $NaHCO_3$) at a pH of 7.1-7.3, adjusted to the appropriate pH. One smaller (400L) feed tank was used for this purpose. A submerged pump was used for dissolving the constituents to make up the stock solutions, which were then pumped into the feed tank. General purpose grade reagents were used for the pilot trials.

An electromagnetic physical conditioning device (*Scalewatcher*, provided by Enigma, Fareham, UK) was installed at the feed pipe at the recommendation of the manufacturers. The device is electrically powered and comprises a coil which is manually wrapped around the pipe fed by a power supply. The device operates by

producing a fluctuating magnetic field of fixed amplitude but adjustable frequency (Appendix 1). According to the suppliers it may be necessary to adjust the frequency to achieve significant scale suppression.
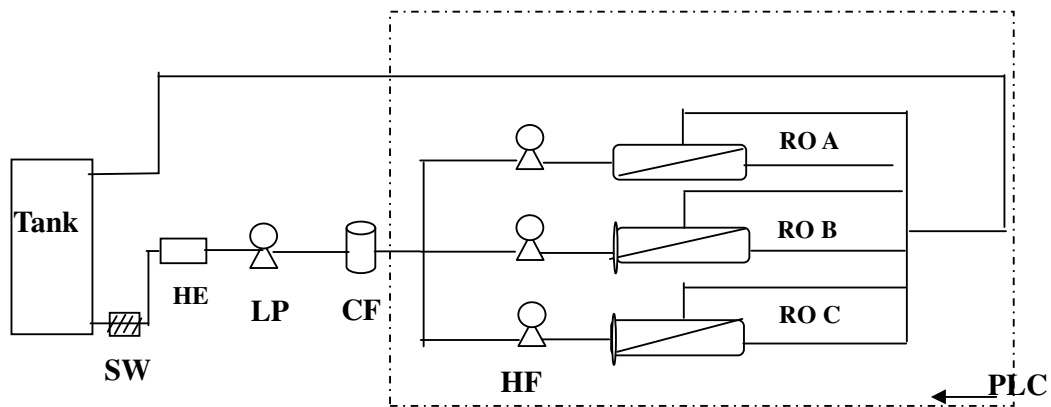

Fig. 2.2 Desalination system

Two of the streams were fitted with a distribution plate. The distribution plate with plastic material comprised a series of 2mm holes (Appendix 2). The membranes elements were the standard spiral-wound sea water desalination type, SW30-2540, provided by Filmtec, and composed of aromatic polyamide thin-film composite. The elements are 1.02 meters long and 61mm (2.5") in diameter and provide an active area of 2.8 m^2 and a stabilised rejection of 99.4%. Distribution plates were installed in lines B and C.

2.2   Methods

Experiments were conducted under the three different pretreatment conditions afforded by the rig as constructed (Table 2.1). The rig offered the capability of comparing the impact of the magnetic field and dispersion plate combined and the dispersion alone on scaling, as manifested in the membrane permeability (i.e. flux per unit mean TMP). Limits on the availability of the hardened water supply meant that the only reasonable mode of operation was recycling of both the retentate and the permeate (i.e. a closed loop), with the heat exchanger used to maintain a temperature of 20°C.

Table 2.1   Physical treatment options offered by rig

Unit					
1		2		3	
Scale Watcher	Dispersion Plate	Scale watcher	Dispersion Plate	Scale Watcher	Dispersion Plate
✘	✘	✘	✔	✘	✔
✔	✘	✔	✔	✔	✔

It should be noted that if the assumption is made that the antiscale physical conditioning does not exert a permanent change in the water, but merely suppresses scaling within the module itself, then recirculation may be used and any differences in performance noted between the units attributed to the antiscale physical conditioning alone. However, if a permanent impact on scaling is exerted by the physical conditioning then either:

a. experiments should be restricted to once-through operation with a supersaturated feed, or
b. experiments conducted with recirculated water must be duplicated to assess treatment with and without the conditioning device(s) under conditions of identical feedwater quality, or profile thereof.

The experimental plan was devised on the basis that recirculatory tests would be conducted to preserve water, chemicals, time and effort. Tests were then duplicated so that data was obtained for both unconditioned and conditioned water.

2.2.1 Pilot trial protocols

Trials were conducted on feedwaters comprising deionised water, saline water (NaCl), and hardened saline water (NaCl + $CaCO_3$).

An initial trial was conducted with water deionised to 5μS/cm using a twin-bed ion exchange process. This test, conducted for just 25 hours, provided baseline data for operating parameters such as flux and transmembrane pressure, as well as allowing a test of the postulate that conditioning directly impacts of membrane permeability. The second trial was conducted using 33 g/l NaCl, again to provide baseline conditions and test the same hypothesis as before at elevated TDS levels and osmotic pressures. A more extensive trial was conducted on water at the same salinity using a mains water source dosed to around 400 mg/L of calcium carbonate (i.e. 8 meq/L). This trial ran for 10 days in closed loop mode using a feedstock prepared by adding a calcium chloride ($CaCl_2$) solution to a solution of sodium bicarbonate ($NaHCO_3$).

Table 2   Water qualities to be studied

Expt.	Feedwater	Test conditions
1	Deionised water only	Recycle
2	Water + NaCl	Recycle
3	Water + NaCl + $CaCO_3$	Recycle

Tap water was used for make-up of both the saline and hardened saline waters so as to provide trace amounts of inorganic matter which the supplier believed may have a synergistic effect with the conditioning device. Due to the sensitivity of the membranes to low levels of chlorine, sodium thiosulphate ($Na_2S_2O_5$) was added at the appropriate

stoichiometric concentration to reduce the total chlorine, present at 0.2 ppm according to a titration analysis conducted by the standard DPD method (Palin,1957) to chloride. The rig operated at a conversion of around 5%-10%, yielding an LSI of around 2.5 in the retentate, according to a standard RO software package (ROPRO 7.0, Fluid Systems).

2.2.2 Bench-scale tests

Supplementary bench-scale tests and analyses were conducted in the form of:
• inductively-coupled plasma atomic absorption spectroscopy (ICP-AES) for assay of metal ions
• particle size distribution measurements, using a mastersizer meter 2000
• zeta potential measurement, using a zetasizer 2000HSA
• crystal investigation by scanned electronic microscope and optical microscope
• hardness and alkalinity measurement
• scaling rate measurement

Scaling rates were measured using a simple test developed within the School of Water Sciences. For this test a continuously stirred 500ml of sample of retentate was immediately titrated against a 0.1 M solution of caustic soda (NaOH). The hydroxide solution was added at a rate of 0.5 mmol every 30 seconds and the response of the solution pH monitored. The onset of scaling is indicated by a diminution in the change in pH. At the point at which no pH change arose on adding the hydroxide dosing was ceased and the pH monitored. The onset of scaling is indicated by a sharp decrease in pH until the scaling produced in the sample. When scaling formed the pH would start to decrease. When pH arrived to the peak value it was the time when the scaling produced. NaOH was stopped dosing and continual to observer the pH change with the time.

3. Results

3.1 Deionised water

In this test deionised water, turbidity 0.45 NTU, was circulated through the rig at an inlet pressure of 20 bar for a total of 25 hours, 16 hours without conditioning followed by 9 hours with the conditioning device switched on. No temperature control was applied for this trial, such that the temperature steadily increased at a rate of 0.5°C/hr throughout the trial. Transients for the transmembrane pressure, TMP (Figs. 3.1-1 and 3.1-2), and flow rate (Figs. 3.1-3 and 3.1-4) indicate no change in the rate of decline of either TMP or flow as a result of applying physical conditioning.

Permeability steadily increased for three streams before treated (Figure 3.1-5) but appeared to reach a plateau at the time at which the physical conditioning was applied. Permeability for both stream A and B was higher than that of stream C, providing no indication of any impact of the distribution plate on permeability.
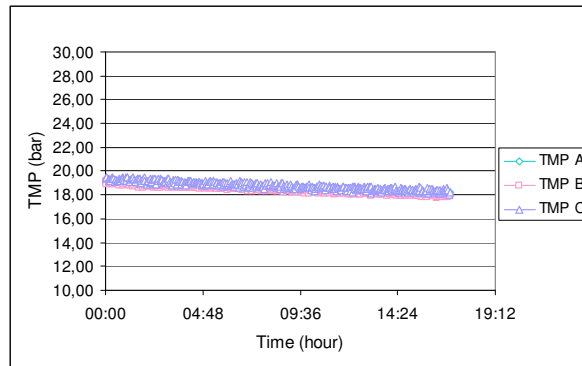
Figure 3.1-1: Transmembrane pressure for three untreated streams, 16 h run
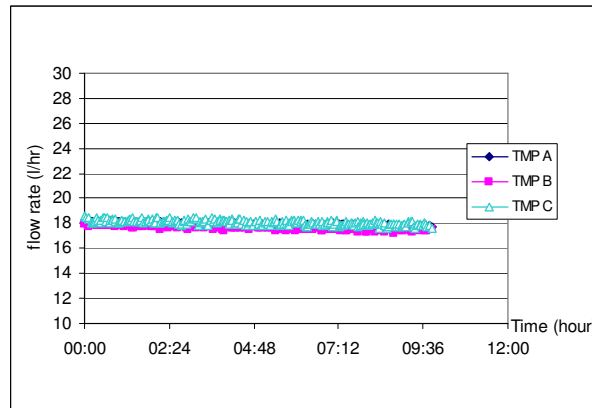
Figure 3.1-2: Transmembrane pressure for three treated stream, 9 h run
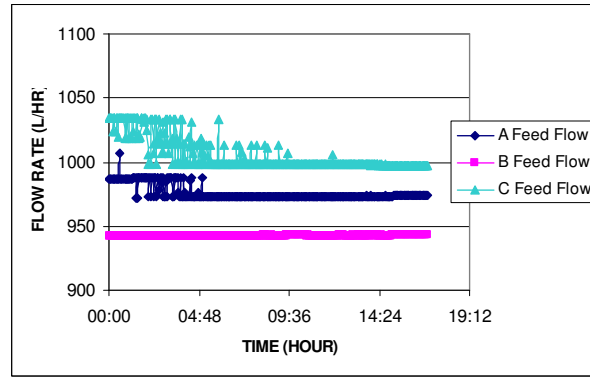
Figure 3.1-3: Feed flow rate for three untreated streams, 16 h run
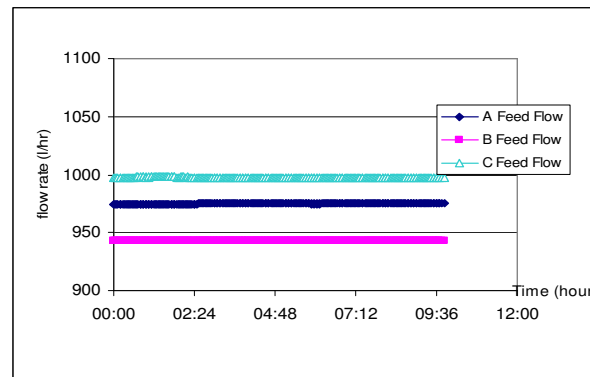
Figure 3.1-4: Feed flow rate for three treated streams, 9 h run

A summary of permeability and recovery data is provided in Tables 3.1-1 and 3.1-2. From these data it appears that conditioning improved permeability following treatment for all three streams. However, improvement was marginal (<10%) and relates to the oversimplistic method (Appendix 3) based on viscosity alone used for correcting temperature effects to produce the normalised values shown in Table 3.1-1. Recovery also increased for the same reason. No significant instantaneous response of permeability to conditioning was observed, and no impact of the distribution plate noted. From this evidence, direct impacts of conditioning on water itself can probably be discounted.
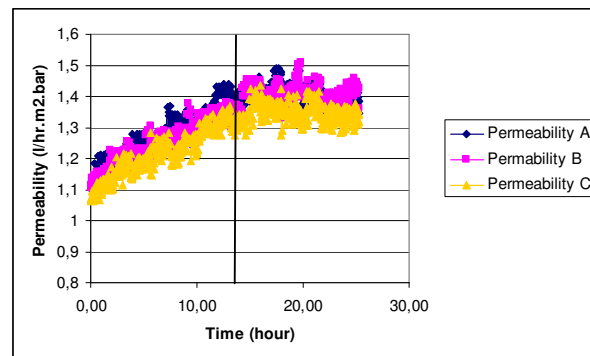
Figure 3.1-5: Permeability for the three streams during the whole treatment
(The line shows time at which physical conditioning was applied)

Table 3.1-1   Flux and permeability data, DI water

Average value Stream	Untreated normalised permeate flux (l/hr.m^2)	Treated normalised permeate flux (l/hr.m^2)	Untreated TMP (bar)	Treated TMP (bar)	Untreated permeability (l/hr.m^2.bar)	Treated permeability (l/hr.m^2.bar)
A	24.1	25.19	18.6	17.9	1.3	1.4
B	23.48	24.8	18.4	17.7	1.28	1.4
C	23.18	24.36	18.8	18.1	1.23	1.35

Table 3.1-2   Recovery data, DI water

Average Value Stream	Untreated feed flow rate (l/hour)	Treated flow rate (l/hour)	Untreated normalised flow rate (l/hour)	Treated normalised flow rate (l/hour)	Untreated recovery (%)	Treated recovery (%)
A	976	975	67.45	70.55	6.91	7.23
B	943	943	65.72	69.45	6.97	7.36
C	1005	998	64.89	68.21	6.46	6.83

The pH (Figs. 3.1-6 and 3.1-7), conductivity (Figs. 3.1-8 and Figs. 3.1-9), and dissolved oxygen (DO) content (Figs. 3.1-10 and 3.1-11) of the reject stream were all monitored throughout the trial. Apart from a small incremental increase in conductivity (Fig. 3.1-9), which did not coincide with the application of conditioning, no unusual patterns of behaviour were evident. DO levels declined with increasing temperatures, but were unaffected by the presence of the distribution plate.
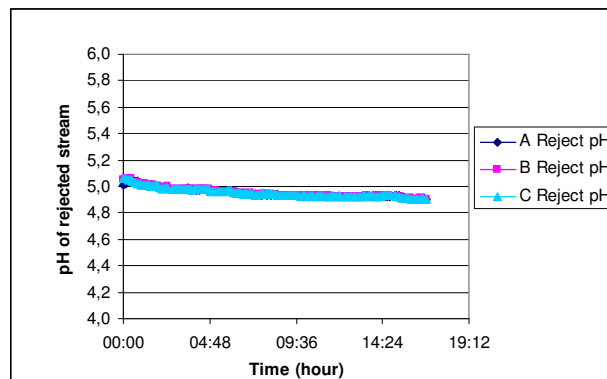
Figure 3.1-6: pH change for untreated reject streams
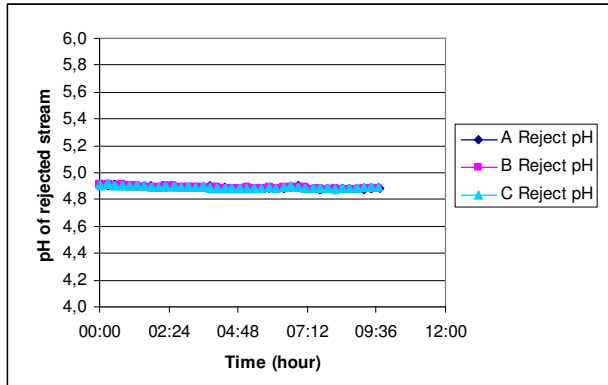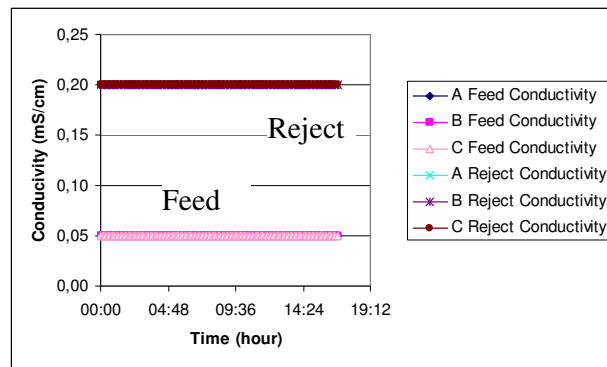
Figure 3.1-7: pH change for treated reject streams

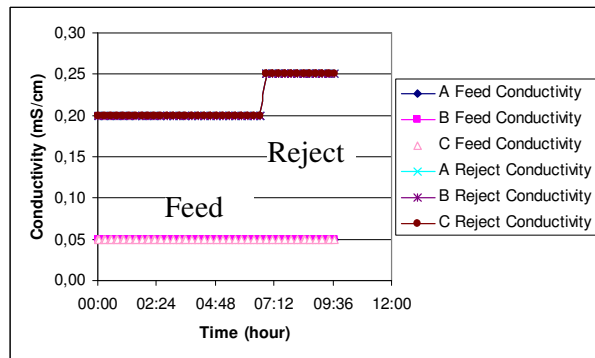Figure 3.1-8: Conductivity change for untreated reject streams

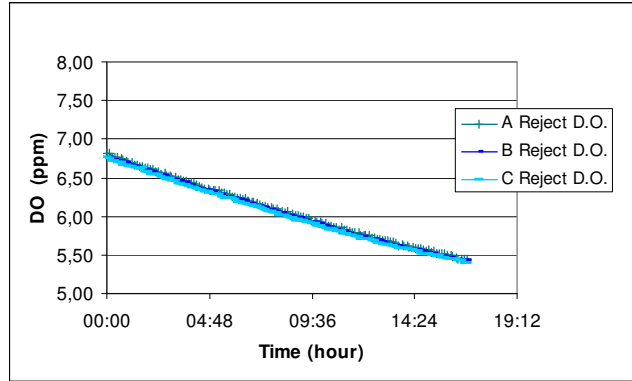Figure 3.1-9: Conductivity change for untreated reject streams

27

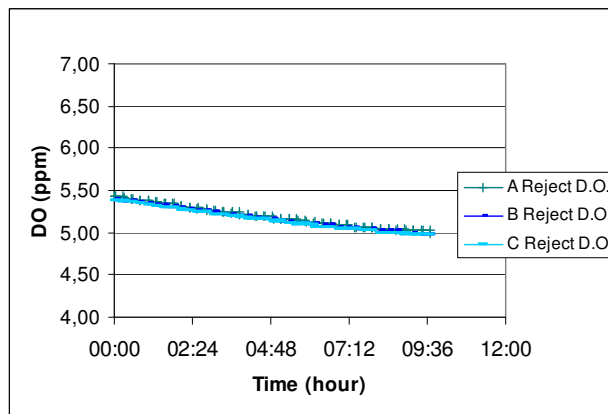Figure 3.1-10: Dissolved oxygen for three streams, untreated

Figure 3.1-11: Dissolved oxygen for three streams with PCD treated

3.2 Saline water

Saline water at a concentration of 33g/l NaCl in mains water of hardness 120ppm to 140ppm was prepared to give a solution of turbidity 0.45NTU. A short-term study of 6 hours was conducted with conditioning applied after 3 hours. The feed pressure was set at 35 bar.

Results for TMP (Fig. 3.2-1) indicate that, as with DI water, there is no instantaneous change in TMP on application of conditioning. The TMP for streams B and C fluctuated more widely than that for stream A, presumably because of the effects of the distribution plate placed in these two streams. This was also reflected in the permeate flow and recovery transients (Figs. 3.2-2 and 3.2-3), which again indicate no impact of either conditioning or the distribution plate on flow or recovery (2.8-3% on average throughout). Similarly, the permeability transients of the three streams largely overlap (Fig. 3.2-4). A study of the water chemical parameters (Figs. 3.2-5─3.2-7) indicates no impact of either the distribution plate or the conditioning device on pH, conductivity or DO levels.
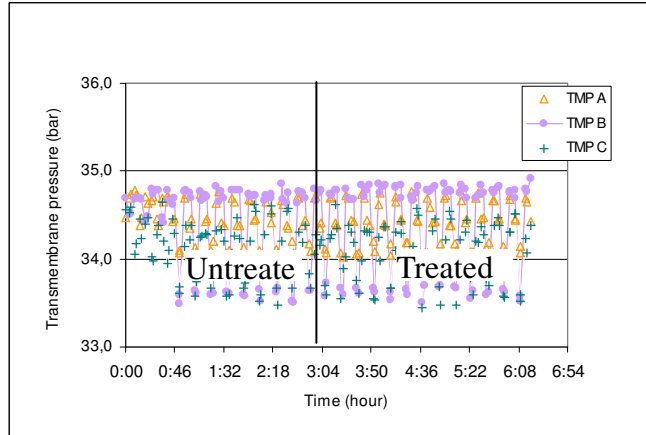
Figure 3.2-1: Transmembrane pressure for three streams during the whole experiment
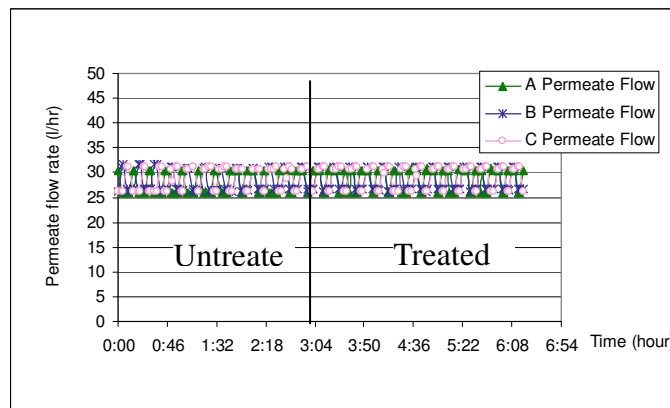(The line shows the time when physical conditioning was applied)

Figure 3.2-2 Permeate flow rate for three untreated streams and treated streams
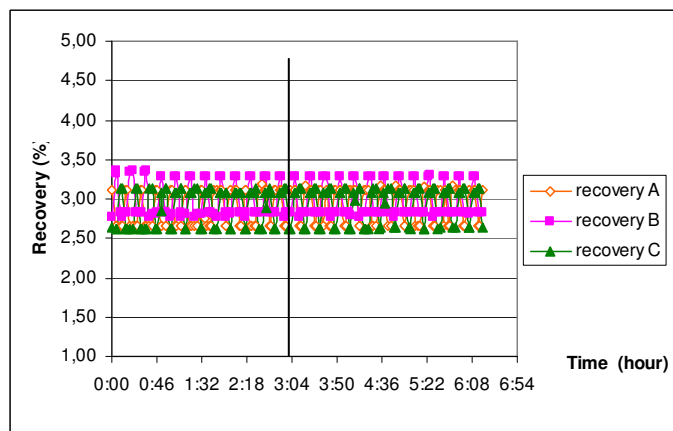(The line shows the time when physical conditioning was applied)

Figure 3.2-3: Permeate recovery for three untreated streams and treated streams
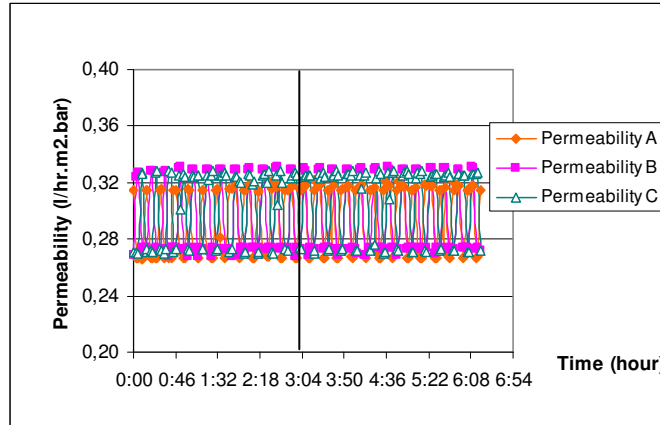(The line shows the time when physical conditioning was applied)

Figure 3.2-4: Permeability for three streams during the whole experiment
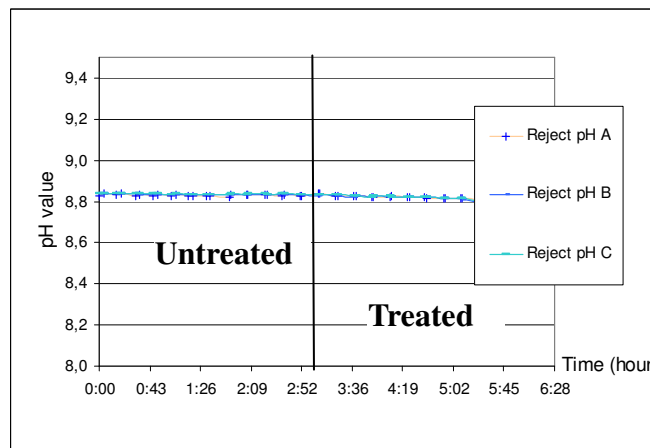(The line shows the time when physical conditioning was applied)

Figure 3.2-5 pH change for three streams during whole experiment trial
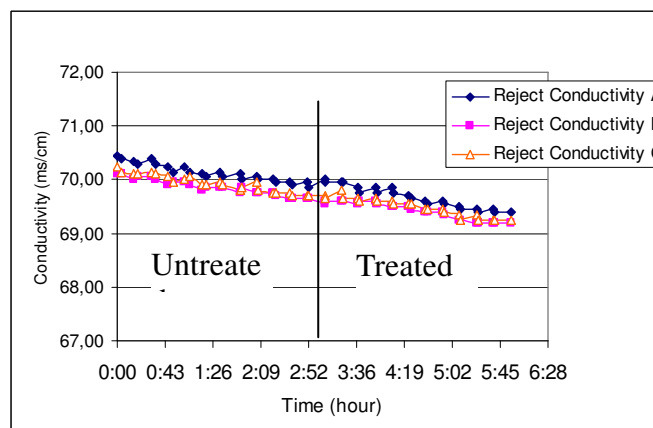(The line shows the time when physical conditioning was applied)

Figure 3.2-6: NaCl conductivity for reject stream A, B and C
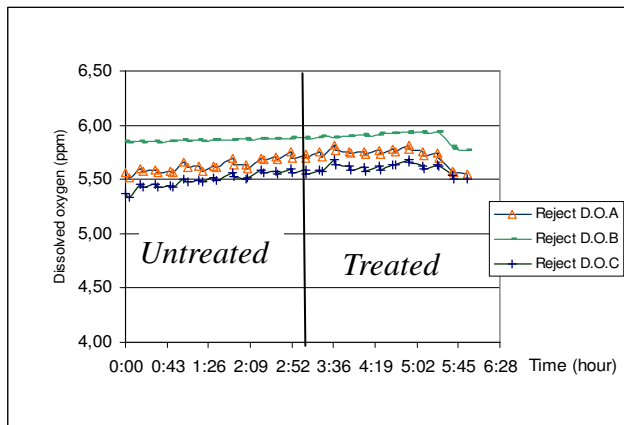(The line shows the time when physical conditioning was applied)

Figure 3.2-7: Dissolved oxygen for three streams
(The line shows the time when physical conditioning was applied)

3.3 Hardened saline water

3.3.1 Pilot plant

The experiment with hardened saline RO water, a basic analogue sea water, was run for 10 days in total, with the first 5 days without conditioning. Due to a data logging malfunction no data was available for the first 8 hours, but a rapid fall in permeability was noted after about 3.5 days which could be attributed to the start of scaling. This was manifested as a drop in flow rate (Fig. 3.3.1-2) at near-constant TMP (Fig. 3.3.1-1) at feed flow rates averaging (943, 900 and 970 l/hour for streams A, B and C respectively). The temperature of feed water was maintained at 20 ± 1 °C throughout. Whilst there was a small difference in the absolute permeability across the three streams, which in this case could not be correlated with the fitting of distribution plates, the rate of decline was similar for all the streams and did not change following the introduction of conditioning.
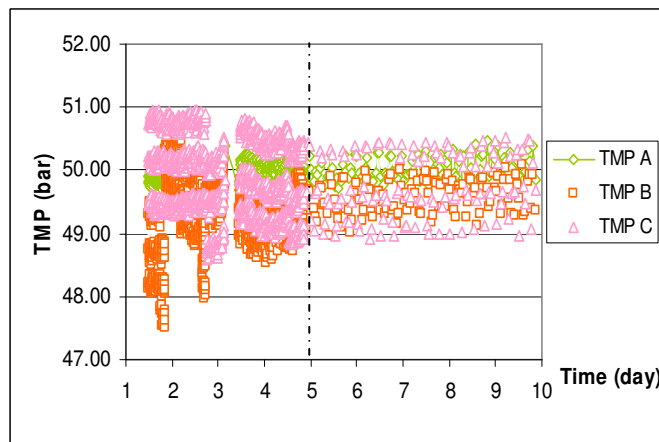
Figure 3.3.1-1: Transmembrane pressure for the three streams:
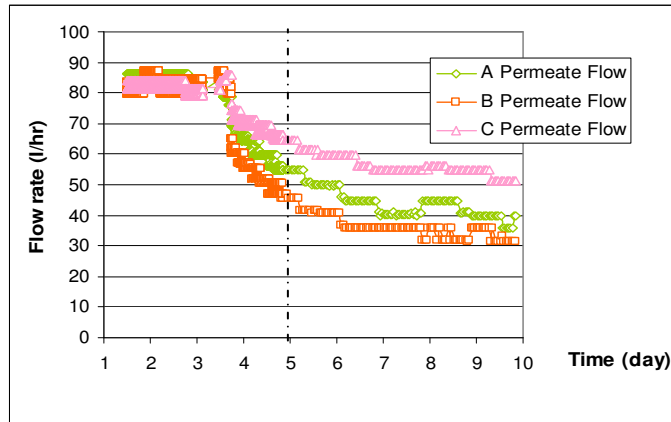conditioning applied at five days

Figure 3.3.1-2: Permeate flow rate streams under the untreated and treated condition
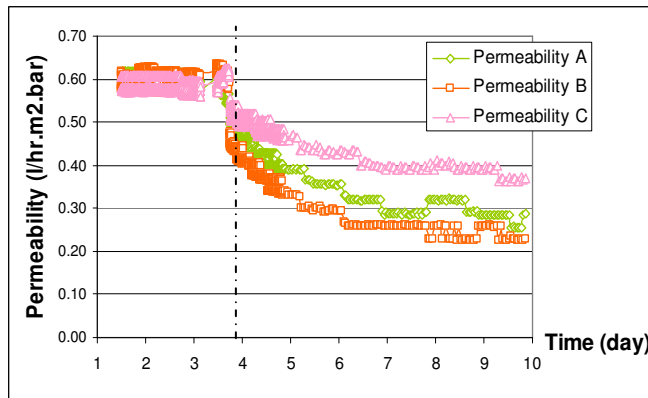(The line shows the time when conditioning was applied)

Figure 3.3.1-3: Permeability for three streams under untreated and treated conditions The line
shows the time when conditioning was applied

The pH of the feed, retentate and permeate streams did not vary between the three streams (Fig. 3.3.1-4). A noticeable drop in pH for all streams was evident following the initiation of scaling which continued for about 12 hours before slowly increasing. This well recognized phenomena is due to the decrease in the CO_2/HCO_3^- ratio (Equation 1.3), as alkalinity is removed from solution through precipitation. The introduction of conditioning had no impact on the subsequent slow but steady incline in pH from 4 days onwards. Conductivity declined by around 5% over the course of the first 7.5 days due to calcium carbonate precipitation but then suddenly increased between 7.5 and 9 days back to around its original value before declining at the same rapid rate (Fig. 3.3.1-5). This was not accompanied by a similar pattern in pH shift, which would be expected if the shift in conductivity relates to calcium carbonate dissolution. It is therefore possible that dissolution of sodium chloride from the membrane surface took place at this time. Small difference in dissolved oxygen concentration between the three streams was apparent, and no

consistent change in the concentration transient resulted from the application of conditioning (Fig. 3.3.1-6).
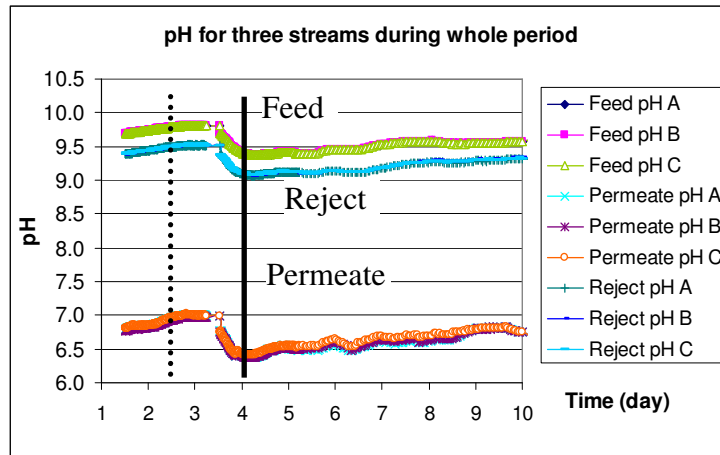

Figure 3.3.1-4 pH changes with the time under untreated and treated conditions
(The solid line shows the time when conditioning was applied,
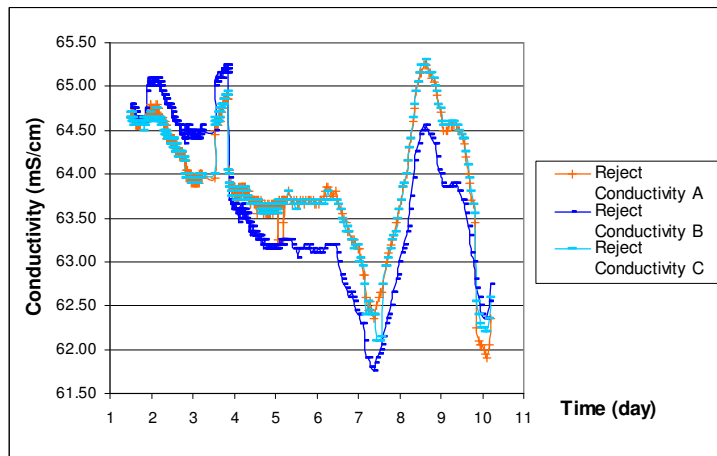broken line shows the time when scale produces)

Figure 3.3.1-5: Conductivity for the three reject streams under untreated and treated conditions
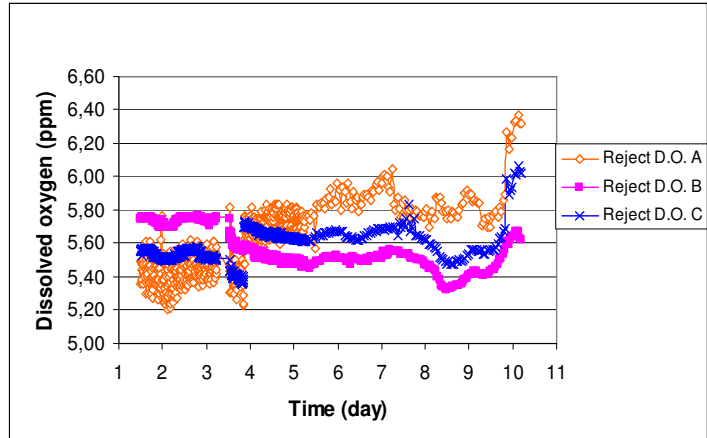
Figure 3.3.1-6: The concentration of dissolved oxygen for three rejected streams under untreated and treated conditions

Alkalinity and hardness transients are respectively shown in Figures 3.3.1-7 and 3.3.1-8. Whilst not a continuous trend, the hardness level shows a decline over the course of time due to precipitation, albeit with a period of a small incline from Days 6 to 8. The alkalinity shows a minimum concentration in this period, increasing from Day 8 onwards. This increase presumably relates to the increasing pH, and thus hydroxide concentration, indicated in Figure 3.3.1-4.
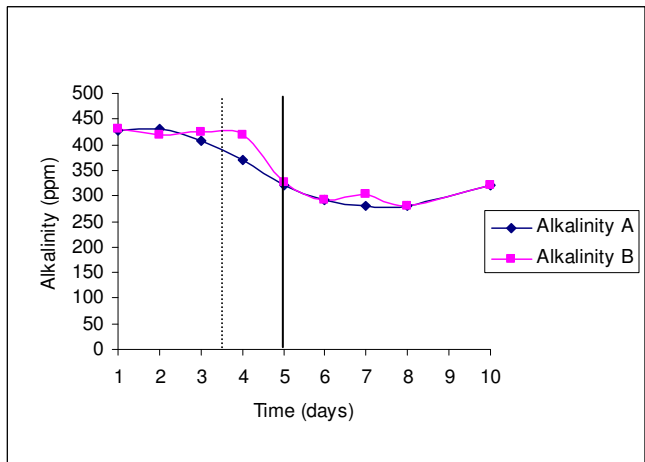

Figure 3.3.1-7: Alkalinity for three rejected streams before streams and treated (dashed line means the scaling producing time, solid line means the beginning treated time)
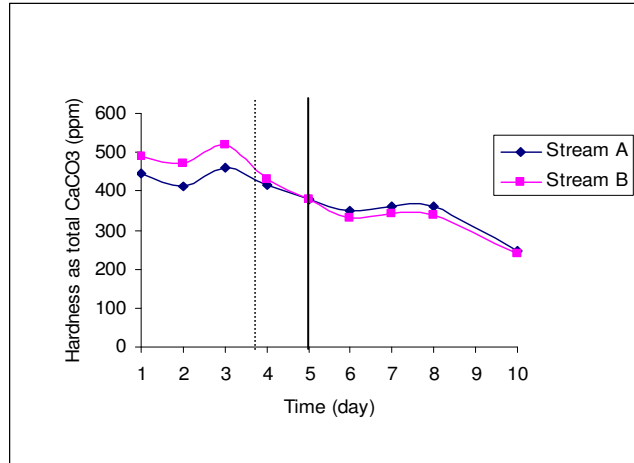
Figure 3.3.1-8: Hardness for three rejected streams before streams and treated (dashed line means the scaling producing time, solid line means the beginning treated time)

Salt passage, defined as the ratio of the permeate to feed concentration in permeate stream to that in the feed streams, was assessed by inductively coupled plasma atomic absorption spectroscopy (ICP-AES). Results (table 3.3.1) shows the sodium ion increased 6.9% in the rejected stream after treated while the calcium ion decreased 12.6% comparing the 7th day and 8th day. It is consistent with the expected increased rejection for the more highly-charged ions. These data would appear to confirm that the increase in conductivity arises from dissolution of sodium chloride, rather than the calcium concentration which continues to decline. It can thus be concluded that no impact of conditioning on hardness levels took place.

Table 3.3.1 salt rejection and salt passage for the sodium ion concentration
by ICP test (Na^+: g/l; Ca^{2+}: mg/l)

	Element	Feed	Rejected	Permeate	% Salt rejection	% Salt passage
Untreated (2nd day)	Na^+	10.66	12.08	0.0976	99.1	0.92
	Ca^{2+}	226	272	1.03	99.5	0.46
Just Treated (the 7th day)	Na^+	9.4	9.56	0.0506	99.5	0.54
	Ca^{2+}	167.8	175	0.404	99.8	0.24
Treated (the 8th day)	Na^+	9.2	10.22	0.0399	99.6	0.43
	Ca^{2+}	134	153	0.332	99.8	0.25

3.3.2 Supplementary analyses

Scanning electron micrographs of air-dried samples of retentate revealed large crystals of sodium chloride which had essentially the same cubic crystal structure as the calcite (Figs. 3.3.2-1 and 3.3.2-2). EDAS (Electron Dispersive Analysis System) used to distinguish between the two crystals (Fig. 3.3.2-3), revealed that some unusually-shaped circular crystals arose in the

35

conditioned rententate sample. Similar crystals observed in magnetically-treated retentate by Baker et al (1997) were attributed to vaterite, whose size appeared to change with time. The diameter of vaterite was around 3-5μm following the introduction of conditioning and increased to 8-10μm after 8 days (Figs. 3.3.2-4-3.3.2-5). It was noticeable that no aragonite was formed, consistent with its arising only at elevated temperatures.

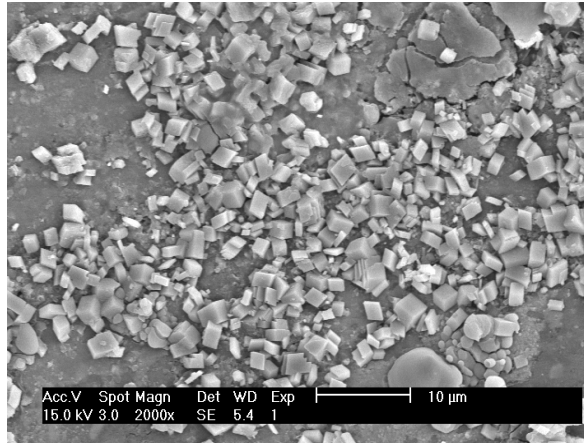Figure 3.3.2-1 before treated (CaCO3)   Magnification 2000X
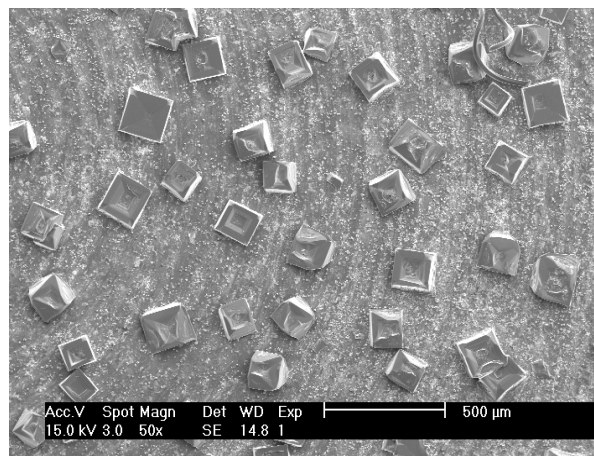

Figure 3.3.2-2 before treated (NaCl) Magnification 50X
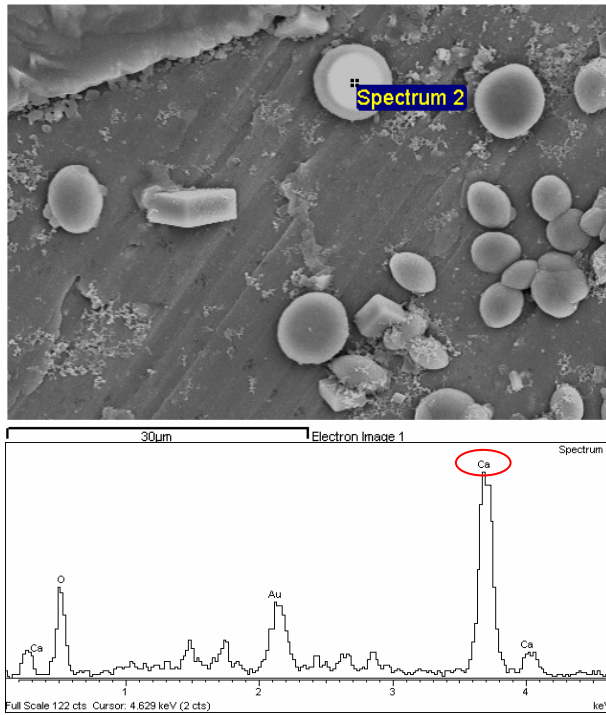
Figure 3.3.2-3 spectrum analysis for calcium carbonate crystal by SEM
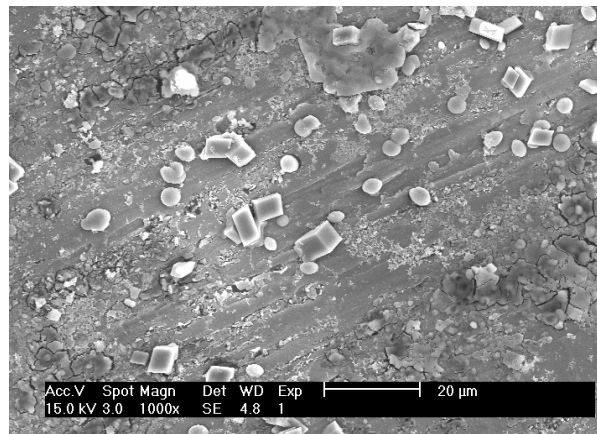
Figure 3.3.2-4:   after treated the 1st day Magnification 1000X
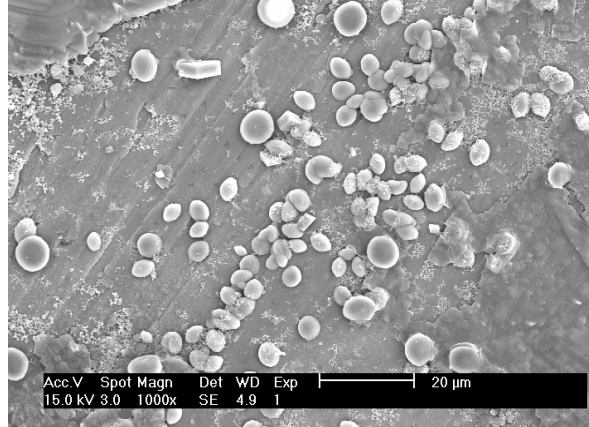
Figure 3.3.2-5:   after treated the 3rd days Magnification 1000X

Also the size of vaterite was variable. Figs 3.3.2-4 and 3.3.2-5 showed the crystal shape and size after conditioning was applied. Both the amounts of round shape crystals and size increased with the time during the three treated days.

The SEM studies were supplemented with optical microscopic analysis. These indicated disc-like crystals (Figs. 3.3.2-6-3.3.2-11) which again varied in size (2-12 μm) from sample to sample. It would be expected that larger particles would be removed by the prefilter protecting the high-lift pumps. The size of round crystals was largest in stream B while smaller ones were present in streams A and C.
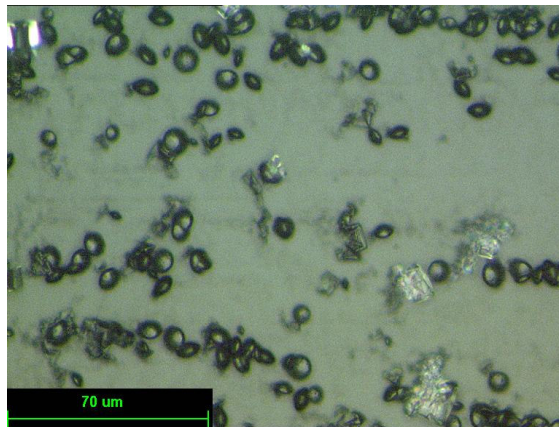
Figure 3.3.2-6: the 2nd day treated from stream A: Magn.400X
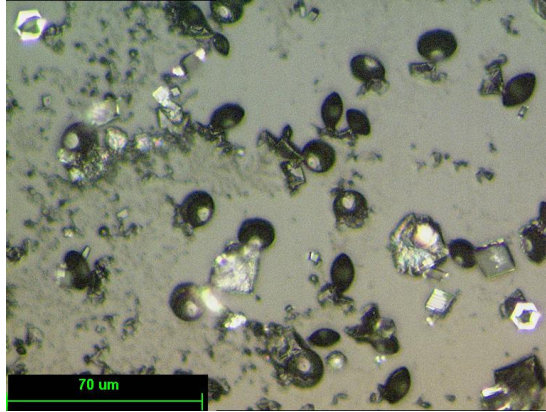
Figure 3.3.2-7: the 2nd day treated from stream B : Magn.400X
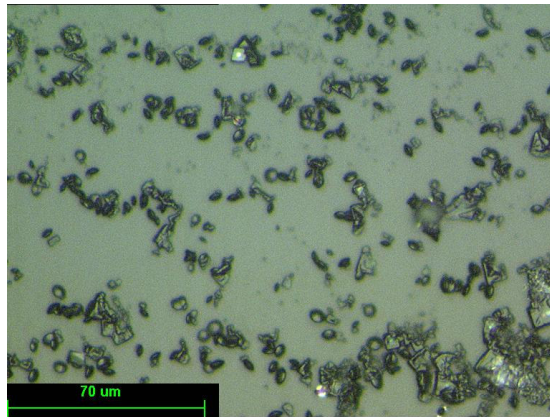
Figure 3.3.2-8: the 2nd day treated from stream C: Magn. 400X
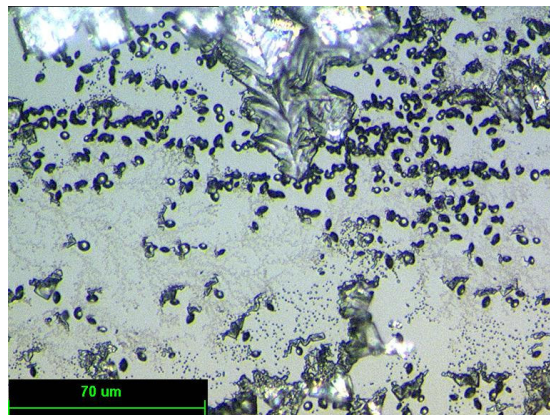
Figure 3.3.2-9: The 5th day treated from stream A: Magn.400X
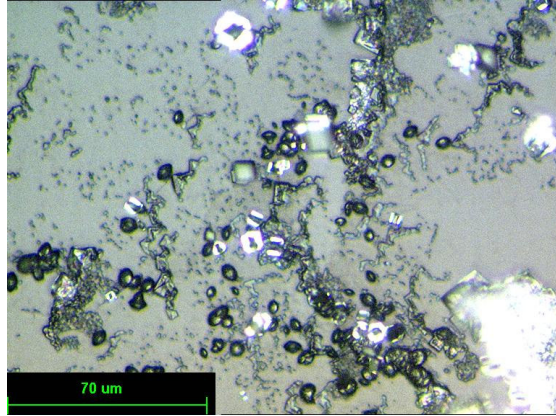
Figure 3.3.2-10: The 5th day, treated, from stream B: Magn.400X
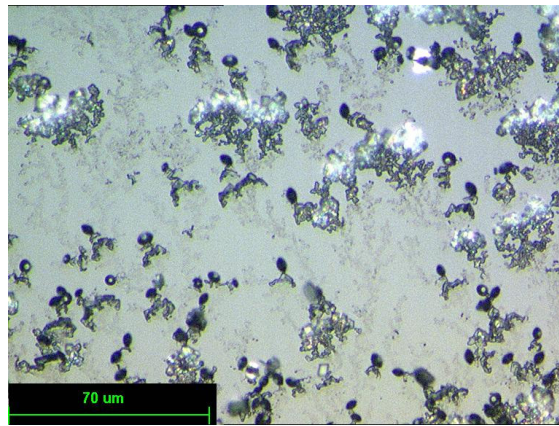
Figure 3.3.2-11: the 5th day treated from stream C: Magn.400X

The measurement of zeta potential indicated a tendency towards higher surface charges following conditioning (Fig. 3.3.2-12). However, the pattern was not consistent, with apparently anomalously low values recorded on Day 8. More measurements would need to be made in order to establish whether this trend is significant.
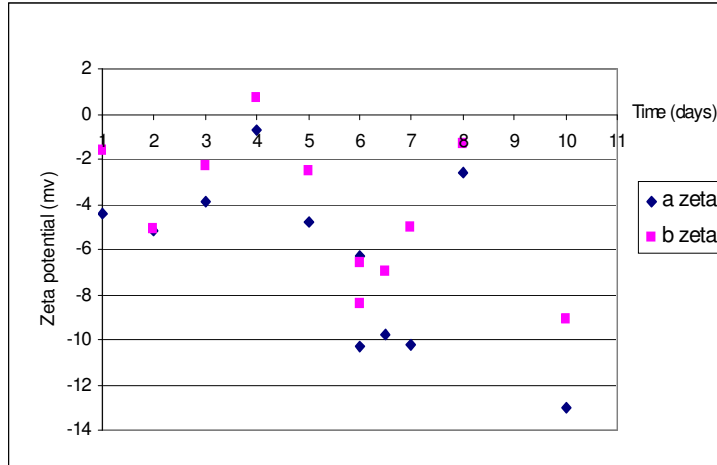
Figure 3.3.2-12: zeta potential for rejected stream A and stream B
during whole procedure.

Results from the rapid scaling test, Section 2.2.2, are shown in Figures 3.3.2-13 –
3.3.2-17 for Days 4, 5, 6, 8 and 10 respectively. The first two of these refer to an
untreated solution whereas the remainders are treated. Figures 3.3.2-13, 3.3.2-14 and
3.3.2-17 all display the classical trend of a rapid decrease in pH at the point at which
scaling takes place due to the change in the alkalinity/CO_2 ratio. However, the plots
obtained following one and three days of treatment show an unusual and unexpected
sudden increase in pH close to the point of incipient scaling.
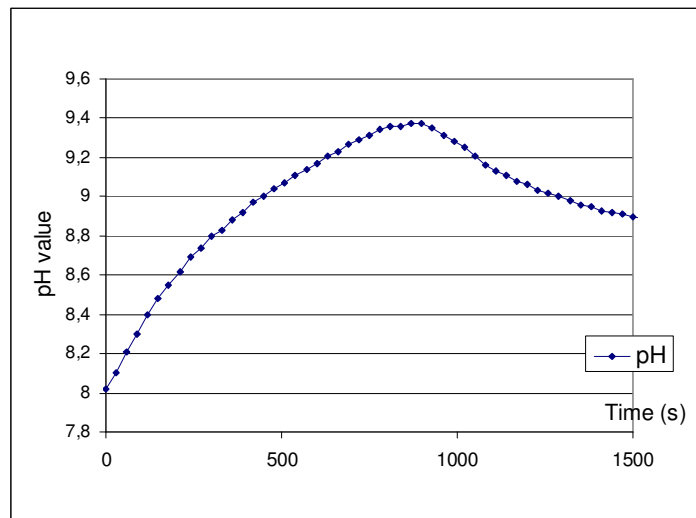
Figure 3.3.2-13 Rapid scale pH change through adding 0.5mmol of NaOH every 30
second for rejected stream at untreated 4th day
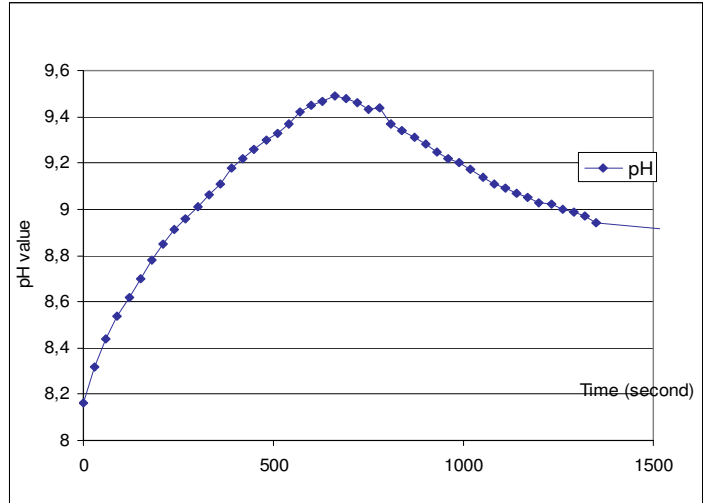
Figure 3.3.2-14 Rapid scaling test pH changes through adding 0.5mmol of NaOH every 30 second for rejected stream on the 5th untreated day
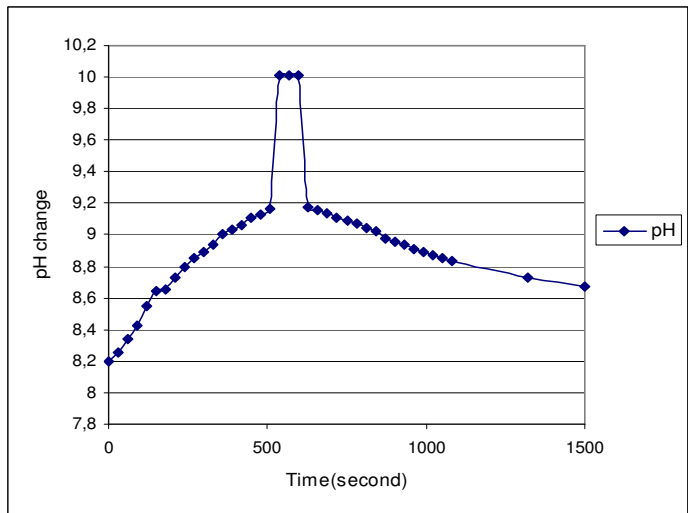
Figure 3.3.2-15 Rapid scaling test pH changes through adding 0.5mmol of NaOH every 30 second for rejected stream on the 1st treated day
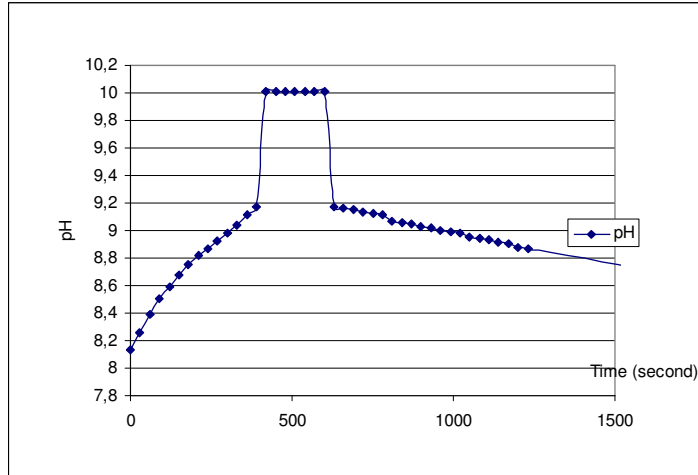
Figure 3.3.2-16 Rapid scaling test pH changes by dosing 0.5mmol of NaOH every 30 second for rejected stream on the 3rd treated day
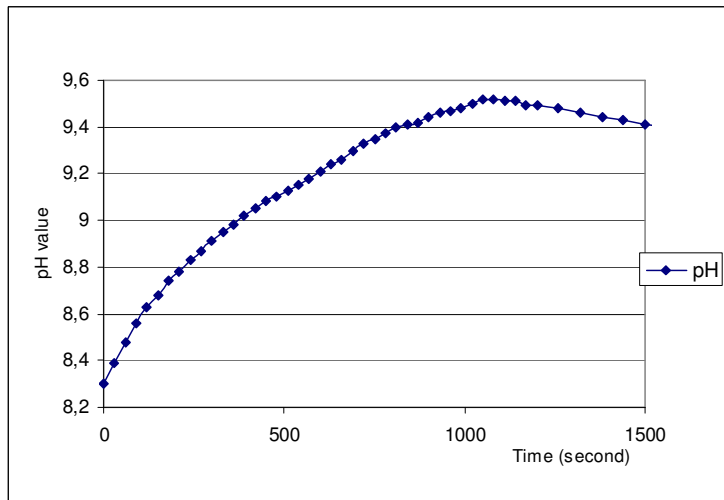
Figure 3.3.2-17 Rapid scaling test pH changes through adding 0.5mmol of NaOH every 30 second for rejected stream on the 5th treated day

4. Discussion

In both deionized water and saline water experiments neither the membrane permeability nor the water quality changed following application of either the distribution plate or physical conditioning. The latter is consistent with the notion that the primary action of physical conditioning is on the scaling process itself, rather than on the membrane-solution interface.

Whilst perhaps not entirely unexpected, this is an important finding. According to Table 1.3, a significant body of work has been conducted supporting either intra-atomic, intramolecular or interfacial effects. Moreover, some authors (Al-Qahtan, 1996; Carnahan *et al.*, 1999; Ghui and Carnahan, 2002, Busch, 1986; Benson,1994), some of which are listed in Table 1.4, have specifically reported conditioning impacts on salt passage in reverse osmosis processes. Ghui and Carnahan (2002) have recently reported on studies of the influence of a magnetic field on the salt permeation through reverse osmosis membranes. These authors found experimentally that the salt transport across the reverse osmosis membranes was reduced by up to 13% for KCl whereas lower differences were observed for NaCl.

Clearly, according to the current study, there are no apparent direct impacts acting at the membrane:soliution interface, such that either permeability and/or ion selectivity are significantly affected – though small and probably insignificant changes of 6.9% were recorded for NaCl. Moreover, any intra-atomic or intermolecular effects that may be taking place do not appear to affect the membrane separation process. Such an impact would certainly be expected if there were any changes specifically in the hydrated ion size, as suggested by the research groups of Chibowski and Carnahan.

For hardened saline water the application of physical conditioning appeared to change certain properties relating to water quality without having any impact on membrane permeability, broadly reflecting the results reported by Baker et al (1997) for magnetic conditioning. As with the previous trials, permeability was not affected by the use of the distribution plate, contrary to reports of Sheikholeslami (1999) and Graham et al (1997). These authors suggested that microbubble formation would take place from precipitated dissolved gases.

However, a review of basic hydraulic theory reveals that the distribution plate used in the current study is unlikely to promote precipitation. The plate is perforated plate, containing 45 holes of 0.0025m in diameter which in total provide a small cross sectional area of 2.2×10^{-4} m^2.

From Bournoulli's equation:

$$P_{Up-stream} + \frac{1}{2}\rho v_{Up-stream}^2 = P_{Jet} + \frac{1}{2}\rho v_{Jet}^2$$

as $\frac{1}{2}\rho v_{Up-stream}^2$ is close to zero, and the equation can thus be simplified to:

$$P_{Jet} = P_{Up-stream} - \frac{1}{2}\rho v_{Jet}^2$$

The upstream pressure in this system is approximately 50 bar (50 x 10^5 Pa). Assuming ρ = 1145 kg.m^{-3}, and a feed flow rate of 24 m^3.day^{-1} (2.78 x 10^{-4} m^3.s^{-1}), and thus an in-orifice velocity of 1.26 m/s.

$$P_{Jet} = (50 \times 10^5) - (\frac{1}{2} \times 1145 \times 1.26^2) = 50 \times 10^5 - 909,$$

resulting in a pressure drop of <10 mbar as the water flows through the orifices. If the gas dissolved in the water is at equilibrium at atmospheric pressure (1 bar), the amount of air that will dissolve at this pressure at 20°C is given by the Henry's Law constant of 0.046 atm.l mg^{-1} for air:

$$P = 0.046 \; C = 0.00909$$

where C therefore takes a value of ~0.2 mg L^{-1}, an insignificant change in the overall dissolved air concentration.

For dissolved gasses to come out of solution the pressure must drop to below 1 atm absolute. It is therefore very unlikely that a large enough pressure drop is created to cause dissolved gasses to come out of solution and form microbubbles. To create these bubbles a velocity through the orifices in the region around 100 m.s^{-1} would be required instead of 1.26m.s^{-1}. In a lower pressure system, such as 1 to 2 bar, cavitation could be caused, but it is most unlikely at the elevated pressure required for reverse osmosis. This would defeat the object of having a high-pressure pump to supply the membranes and therefore is not a viable option. Bubbles could form if the gas was forced into the water under higher pressures, but this was not the case in the current study.

The possibility exists that there may be localised cavitation immediately behind the plate. However these bubbles would immediately dissolve on leaving that region, and would not provide scouring bubbles along the membrane surface. Another alternative is that nanobubbles, as proposed by Vinogradova *et al.* (1995), may be formed and remain as bubbles through the system. These exist in all water systems and are often too small to be detected. However, their size are unlikely to be sufficient to cause

scouring along the membrane should they exist. On the other hand, according to the DO measurements of the current study, there may have been some effect of the distribution plate on dissolved gas precipitation, since the DO levels in streams B and C were less than that recorded in stream A (Fig.3.3.1-6). Clearly, though, such precipitation was not sufficient to impact on membrane permeability through scouring. Indeed, impacts of air scouring, which are known to be beneficial in submerged filtration processes such as membrane bioreactors, could most easily be studied by injecting air directly into the stream using an air compressor, rather than relying on cavitation.

The only other possible benefit of the perforated distribution plate is to improvement of flow distribution, such that the entire membrane area is utilised. This would increase the overall permeate flow rate from the module. However, it is postulated that this improvement would be insignificant with regards to the extra energy requirements to maintain the pressure. Theoretical considerations indicate that there will be no change to the permeate flux with or without the distribution plate at any given transmembrane pressure.

The marginal effects on crystallinity possibly corroborate findings of other authors, such as Baker et al. (1997), Wang et al (1997) and Northern agrotech, 1990. Baker assumed that the appearance of round crystals amongst the characteristic cubic calcite crystals following magnetic conditioning were attributable to vaterite formation. Similar spherical crystals were observed by Wang, and the experiments conducted by Northern Agrotech in Israel on milk revealed that oval crystals were formed following conditioning. Similar patterns were observed in the current study but, as with the study of Baker et al, no impact on permeability accompanied these minor changes in crystallinity. Changes reported in the aragonite:calcite balance (Coey & Cass 2000; Hall 2002; Holysz, 2003, Kobe, 2001) following conditioning apply only to elevated temperatures, where aragonite formation is energetically favoured.

Many authors (Baker & Judd 1996, Baker *et al.* 1997, Barret & Parsons 1998, Chibowski *et al*. 2003a, Colic & Morse 1998a, Fan & Cho 1997, Lipus *et al.* 2001, Lui, 1999) have reported impacts of conditioning on crystal growth kinetics, with both enhancement and, perhaps more frequently, suppression (Chibowski *et al.* 2003, Cho *et al.* 2003, Holysz *et al.* (2003), Parsons *et al.* 1997, Wang *et al.* 1997) being reported. In the current study the measured size of the vaterite crystals was varied and followed no consistent pattern, possibly due to the nature of the measurement method. Crystal growth appeared to be rapid during first 3 days but following 5 days of treatment the vaterite size fell to 2-4 μm. Perhaps more significantly, there was no indication of significant amorphous crystal growth following conditioning, which would naturally lead to a less tenacious scale.

Particle charge data were limited in this study, and somewhat scattered. Conditioning tended to increase the particle charge, thus tending to make them more stable, but

there was an anomalous reading which rendered any possible trend insignificant. Zeta potential for the rejected bulk solution was a little variable. Zeta potential effects have also been reported by other authors (Gehr, 1995; Gabrielli, 2001; Holysz, 2002, Parsons, 1997) for both magnetic and electronic conditioners.

pH effects have often been reported in the literature (Haitham, Al-Qahtani, 1996; Busch, 1986; Benson, 1994, Wang et al, 1997). In the current study no impact of scaling was observed in the pilot rig. On the other hand the alkalinity decreased slightly following conditioning, and this would normally be expected to be accompanied by a decrease in pH. However the shift was not significant. Also, the pH of the retentate was lower than the feed (9.1 vs. 9.35), indicating a lower alkalinity which is contrary to expectations based on the expected increased alkalinity due to its rejection by the membrane. It must be assumed that this is due to scaling on the membrane.

The rapid scaling test used in this study yielded expected pH trends for three of the tests but very unusual, and inexplicable, trends for two of them. These two anomalies sample 3 and 4 (table 4.1) both referred to conditioned samples. On the other hand, the very last sample tested was also a conditioned sample and gave a conventional pH response. The anomaly was a very sharp increase in pH from 9.2-10.01 (figs. 3.3.2-15 and 3.3.2-16) at some sub-critical point followed by an equally sudden drop marking the actual critical point (i.e. incipient scaling) after adding a further small amount of hydroxide between 0.1 and 0.3mmol (table 4.1). This indicates that the samples retain a level of enhanced supersaturation for some extended time finite period lasting, in one this case, between 60 and 180 seconds (figs. 3.3.2-15 and 3.3.2-16). Moreover, the actual concentration of hydroxide added and the pH at the critical point follow a consistent pattern for these two anomalies (Table 4.1). The critical point was reached at lower NaOH levels and the pH at the critical point higher than for the other samples. Clearly, this unusual behaviour demands further exploration.

Table 4.1:   Summary of rapid scaling test data

Sample	Conditioned?	Conventional pH response?	Critical point, min	NaOH molarity at critical point, mmol	Total NaOH (mmol) from beginning to critical point	pH at critical point
1	N	Y	15	0.05	1.5	9.37
2	N	Y	11.5	0.05	1.15	9.49
3	Y	N	9	0.1	0.9	10.01
4	Y	N	7	0.3	0.7	10.01
5	Y	Y	18	0.05	1.8	9.51

No other patterns in water quality behaviour could be discerned, including conductivity, alkalinity and hardness. Small changes in conductivity appeared to be

attributable to dissolving sodium chloride and these were not significant. Haitham (1996), conducting magnetic conditioning recirculation experiments on RO membranes with the seawater, reported increased conductivity following conditioning. The author suggested that conditioning might cause certain physical or/and chemical changes to the nature of the ions reducing their passage through the membrane. Changes in hardness which have been reported have all related to calcium carbonate precipitation, as previously outlined.

5. Conclusions

From the results of the study conducted it can be concluded that, over the period of time tested (10 days) and using a simulated saline seawater (24 g/l NaCl) with hardened water (400mg/l $CaCO_3$), there was no significant impact of a distribution plate or electronic conditioning either individually or in combination. Given the marked similarity of the system studied (i.e. an AC electromagnetic field applied to the membrane module combined with flow through an upstream perforated plate), it must be concluded that there is no evidence to support the reported efficacy of the *Grahamtek* commercial system. Moreover, additional application of the conditioning device to the feed pipe, in accordance with the supplier's recommendations, had no impact on scale control at the membrane surface and only marginal impacts on water quality.

A number of caveats need to be added concerning minor differences in the system studied and the Grahamtek system. Firstly, in the commercial system the holes on the distribution plate are drilled at a 45-60° angle to the surface, rather that 90° as in the current study. This may enhance cavitation. However, it is hard to conceive how cavitation could be significance given that the microbubbles cannot be sustained at the operational pressures involved. Secondly, the Grahamtek system comprised three coils wrapped around the membrane module providing three overlapping magnetic fields. It is possible that the efficacy of the system critically depends on the interaction of the electromagnetic fields, but there is no scientifically credible reason to suspect this should be the case.

There are a number of other departures from actual desalination conditions prevailing in a full-scale plant which should not be overlooked.
- The rig was operated as a closed, with complete recirculation of both retentate and permeate. This is obviously unrepresentative of a real situation, but literature evidence suggests that multiple passages through a conditioning device actually promote the conditioning effects (Baker and Judd, 1996).
- An analogue water was used, although the hardened saline water used to represent seawater was at least based on main water. Micro-contaminants, constituents present in low concentrations, which may promote conditioning in actual seawater (or even actual hard water) through some synergistic effect were therefore absent from the water. It has recently been shown (McAdam, 2005) that scaling in analogue hardened waters is less readily suppressed than that in naturally hard waters.
- Full-scale rigs operate at conversions of at least 30% by using multiple-element modules. This means that the scaling propensity at the outlet of the RO module in a full-scale system is considerably higher than that in the pilot plant.

It should additionally be acknowledged that the trial conducted was relatively brief (12 days in total) and the measurements made generally too few in number for any statistically significant trend to be obtained. This applies especially to the zeta potential measurements and the rapid scaling tests. Particle size distribution measurements were also made, but these were so few in number and gave such obviously variable data that they have been omitted from this thesis.

Further work should be based on extended trials supplemented with a larger number of tests, particularly the rapid scaling test on the retentate. It would also be fruitful to collect data from apparently successful existing operational desalination plant based in London. According to data provided by the water company and the plant supplier (rather than the conditioning device supplier), a nanofiltration plant is currently being used to treat a borehole water having an LSI of 0.79 in the feedwater and an estimated value of 1.4 or more in the retentate. Such a high scaling propensity would normally demand chemical dosing, either with acid and/or threshold inhibitors. The plant, which has been fitted with the same conditioning device as that used in the current study, has apparently been operating for over a year without chemical dosing. Clearly, this case merits further study.

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Appendix1

Scalewatcher physical conditioning device

Scalewatcher Enigma unit (electronic-magnetic device):
Scalewatcher enigma unit was manufactured by the scalewatcher industrial. A scalewatcher uses the same principle as magnets but uses powerful high frequency signals that are designed to effectively treat all water conditions and flow rates. The electronic unit works by sending out a modulated signal which changes the electrical and physical properties of scale-forming calcium molecules. This action stops any further build-up of scale by preventing the molecules from adhering to themselves or any other surface. The solubility of the water is also increased therefore existing scale is dissolved back into the water and gradually removed.
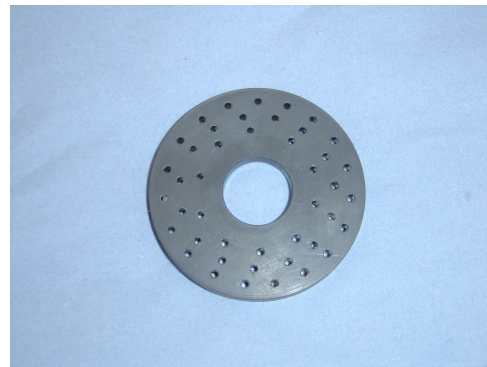
Appendix2

Distribution Plate

The plate used by GrahamTek contains up to 84 holes and one
central hole, placed before the element. The central hole is for
the permeate passage. The holes in the plate are arranged
circular array.

GrahamTek Design[1] defined the feature of distribution plate is
incorporated at the front end of the spiral wound membrane elements and generates a
higher flux with improved recoveries through the continuous disruption of the
concentration polarization on the membrane surface releasing micro-bubbles, thereby
improving the cross-flow shear force, easing mass transfer across the membrane
surface. The micro bubbles generated, actively scour the membrane surface
preventing foulants from settling.

The Cranfield university pilot plant distribution plate only has 45 holes (10, 15, 20).
The holes in the plate are arranged along a number of lines radiating out from the
centre of the plate that has its centre at the centre of the plate.

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[1] http://www.grahamtek.com/tech/
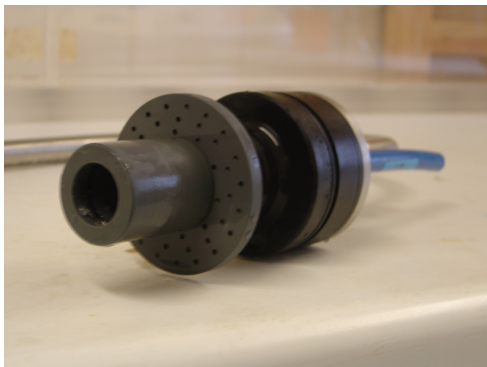
Appendix3

The calculation of normalized flow rate for DI water

1 The recovery of the plant
R=PF/FF

Where PF is the product flow (m3/hr)
FF is the feed flow (m3/hr)

2 Calculate the concentration of the feed water (CF)
CF=SF*[ln [1/(1-R)]/R]
Where R is plant recovery
SF is salinity of feed water (TDS mg/l)

3 Calculate the osmotic pressure of the feed water (OP)
For water with a salinity of less than 20000 mg/l
OP=CF*(T*320)/491000
For water with a salinity of more than 20000mg/l
OP={[(0.0117*CF)-34]/14.23}*[(T+320)/345]

4 Transmembrane pressure
transmembrane pressure (TMP) is defined as
TMP=[(Pf+Pr)]/2-Pp
Where Pf, Pp and Pr are the pressures for the feed, permeate and reject streams respectively.
Pressure drop: pressure differential between feed and reject streams.

5 Calculation the normalized product flow(QP)
Qpps=[FPs-[FPs-RPs]/2-PPs-OPs]
Qppa=[FPa-[FPa-RPa]/2-PPa-OPa]
QP=[Qpps/Qppa]*[TCFs/TCFa]*PF

Subscript s= standard condition
Subscript a=actual operating condition

Table: Example for QP change (normalized product flow rate)
for stream A with the different temperature

Time (hour)	Feed A Flow(l/hr)	Permeate Flow A (l/hr)	QP A	TMP A	Temperature	TCF s 25/TCF a
0,00	987	51	59,83605	19,04	18	1,23751
0,04	987	51	59,56229	19,13	18	1,23751
1,36	972	55	63,71968	19,16	18	1,23751
1,40	987	55	63,55385	19,21	18	1,23751
1,44	972	55	64,47675	18,94	18	1,23751
1,48	987	55	64,30696	18,99	18	1,23751
3,56	988	56	63,95785	18,93	19	1,19966
3,60	973	56	64,72004	18,78	19	1,19966
3,64	973	57	65,38494	18,81	19	1,19966
3,68	973	56	64,292	18,90	19	1,19966
3,72	973	57	65,24082	18,96	19	1,19966
3,76	988	57	64,95336	18,94	19	1,19966
5,52	973	60	66,91803	18,70	20	1,16320
5,56	973	60	66,91803	18,70	20	1,16320
5,60	973	60	66,47369	18,83	20	1,16320
5,64	973	60	64,63905	18,78	21	1,12810
5,68	973	60	64,42459	18,84	21	1,12810
7,32	973	64	70,10878	18,71	21	1,12810
7,36	973	62	67,66532	18,70	21	1,12810
7,40	973	64	70,34373	18,65	21	1,12810
7,44	973	61	67,27256	18,51	21	1,12810
7,48	973	64	70,95404	18,50	21	1,12810
9,28	973	64	68,77261	18,53	22	1,09428
9,32	973	65	68,88096	18,54	22	1,09428
9,36	973	64	69,38122	18,36	22	1,09428
9,40	973	65	69,25455	18,44	22	1,09428
9,44	973	64	68,54889	18,58	22	1,09428
9,48	973	64	66,50742	18,58	23	1,06169
9,52	973	64	66,67949	18,54	23	1,06169
13,16	974	69	72,72657	18,29	23	1,06169
13,20	973	69	72,97598	18,23	23	1,06169
13,24	973	69	71,17055	18,13	24	1,03028
13,28	973	69	70,68308	18,25	24	1,03028
13,32	973	69	70,58639	18,28	24	1,03028
16,00	974	71	72,89327	18,19	24	1,03028
16,04	974	71	72,8432	18,20	24	1,03028
17,86	975	74	73,98	18,1	25,0	1
17,90	975	74	74,29	18,1	25,0	1
17,94	975	74	74,49	18,0	25,0	1

19,78	975	74	71,39	18,1	26,0	0,961697
19,82	975	74	68,81	18,1	27,0	0,925101
19,86	975	74	69,01	18,0	27,0	0,925101
19,90	975	74	69,69	17,8	27,0	0,925101
19,94	975	74	69,64	17,8	27,0	0,925101
19,98	975	74	69,14	18,0	27,0	0,925101
20,02	975	74	69,00	18,0	27,0	0,925101
21,66	975	76	71,64	17,8	27,0	0,925101
21,70	975	76	71,34	17,9	27,0	0,925101
21,74	975	76	68,60	17,9	28,0	0,890128
21,78	975	76	68,46	17,9	28,0	0,890128
23,50	975	76	69,41	17,7	28,0	0,890128
23,54	975	76	69,46	17,7	28,0	0,890128
23,58	975	76	68,94	17,8	28,0	0,890128
23,62	975	79	68,71	17,8	29,0	0,856695
25,22	975	79	69,20	17,7	29,0	0,856695
25,26	975	79	68,89	17,8	29,0	0,856695
25,30	975	79	66,64	17,7	30,0	0,824726