UNIVERSITY OF SOUTHERN QUEENSLAND
AUSTRALIA

INTEGRATED TREATMENT OF BRACKISH GROUNDWATER

A Thesis submitted by

Javier Rioyo, CPEng

For the award of

Doctor of Philosophy

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Dedication

This thesis is dedicated to my parents, sister and brother. Thank you for always being there for me.

Abstract

As freshwater resources become more limited, Australian coastal cities have begun building seawater desalination plants, and inland communities have begun investigating the option of treating brackish groundwater to supplement their water supply. Membrane reverse osmosis (RO) is the leading technology applied in municipal desalination. Despite the advances in technology, membrane scaling is a common problem causing membrane failure, decline in membrane flux and deterioration of product water quality. Since inland plants cannot dispose of RO concentrate into the ocean, they operate at high water recovery in order to minimize the volume of RO concentrate. Antiscalants (AS) are often added during RO pretreatment to prevent membrane scaling. Water recovery percentages (Rw) are then limited by AS efficacy and yet large volumes of RO concentrate are frequently disposed of in evaporation ponds. Therefore, it is important to find novel technologies to combat scaling issues. The integration of a 'High-pH pretreatment' in inland desalination plants is a promising choice for facilitating the removal of scale-forming precursors and other contaminants negatively affecting the desalination process.

In a comprehensive project, this study investigated the efficacy of 'High-pH pretreatment' for membrane scale control and the removal of specific pollutants such as boron. The first phase of the project highlighted the differences between inland and seawater desalination and critically reviewed the existing strategies for RO concentrate minimization towards zero liquid discharge (ZLD) in inland desalination. In contrast to previous studies, the groundwater and RO concentrate collected for these experiments had a magnesium concentration higher than the calcium concentration. Furthermore, no previous studies evaluated the 'High-pH pretreatment' on magnesium-dominated water as this study does. The investigation continued further to assess the efficacy and utilization of two scale control technologies: acid/AS addition and 'High-pH pretreatment'. Therefore, the second phase of this study evaluated 'High-pH pretreatment' of a RO concentrate followed by secondary RO to increase overall water Rw in an existing inland desalination system. The results showed that the lime and soda ash softening treatment followed by pH readjustment and AS addition, allowed the overall water Rw to increase from 80 to 97%. Experimental trials also confirmed $CaCO_3$ and CaO recovery from the precipitated sludge through CO_2 gas injection to selectively dissolve magnesium. This success provided a further opportunity to explore ‘High-pH pretreatment’ of RO concentrate followed by other advanced desalination technologies such as air-gap membrane distillation (AGMD).

In the third phase of the study, two scale control strategies, ‘High-pH pretreatment’ and AS addition, for RO concentrate minimization were further investigated in a lab-scale AGMD system. The results indicated that the first option was more efficient in terms of preventing scale build up in the AGMD system. Following ‘High-pH pretreatment’, pH readjustment and AS addition, the use of AGMD minimized the existing RO concentrate with a TDS level of 10.8 g/L by a concentration factor of 3.2. In addition, the ‘High pH-pretreatment’, using lime and soda ash, facilitated the operation of the AGMD system at a higher temperature, thus permeate flux also increased.

Boron can also be present in groundwater due to natural or anthropogenic sources. It can produce harmful effects on human health depending on both the frequency and extent of exposure. Boron removal is considered to be very complex. In fact, it is largely unclear whether softening pretreatments can enhance boron removal in groundwater desalination systems. Therefore, the final phase of this study investigated the feasibility of ‘High-pH pretreatment’ for boron removal from magnesium-dominated groundwater samples obtained from an existing inland desalination facility. Before commencing the experiments, the brackish groundwater was spiked with 5 mg/L of boron. The results revealed that the lime and soda ash softening treatment achieved 33% boron removal by sorption of hydroxyborate ions onto precipitated magnesium silicate. An additional 9% boron removal was achieved with magnesium chloride addition before the softening treatment, or by a secondary polishing treatment by means of adsorption with MgO. This solution can safely facilitate compliance with strict boron standards in inland desalination plants using RO or electrodialysis technology.

This study evaluated the efficacy of integrating a ‘High-pH pretreatment’ in inland desalination plants treating magnesium-dominated groundwater. The novel approach overcame AS limitations and increased freshwater *Rw* in the inland desalination plant. It also enabled partial removal of other contaminants such as boron. Since groundwater quality is site-specific, selection and optimization of the most suitable treatment for every single process must be based on raw water characteristics.

Certification of Thesis

This thesis is the work of **Mr Javier Rioyo** except where otherwise acknowledged, with the majority of the authorship of the papers presented as a Thesis by Publication undertaken by the student. The work is original and has not previously been submitted for any other award, except where acknowledged.

Student's and Supervisors' signatures of endorsement are held at the University of Southern Queensland.

Javier Rioyo PhD Candidate	Date
Dr Vasantha Aravinthan Principal Supervisor	Date
Professor Jochen Bundschuh Associate Supervisor	Date
Dr Mark Lynch Associate Supervisor	Date

Statements of contributions

The articles produced from this study were a joint contribution of the authors. The details of the scientific contribution of each author are provided below:

Paper I. Rioyo, J., Aravinthan, V., Bundschuh, J., & Lynch, M. 2017. A review of strategies for RO brine minimization in inland desalination plants. Desalination and Water Treatment, 90, 110-123. (Published).

Contributions:

- Javier Rioyo prepared the abstract and outline that described the scope and motivation for the review paper and composed the content of the manuscript. The contribution made by the candidate is 70%.

- Dr Vasantha Aravinthan, Professor Jochen Bundschuh and Dr Mark Lynch assisted with the manuscript compilation, editing, critical revision, and final revision. Overall, their contribution to this manuscript is 30%.

Paper II. Rioyo, J., Aravinthan, V., Bundschuh, J., & Lynch, M. 2018. Research on 'High-pH precipitation treatment' for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility. Desalination, 439, 168-178. (Published).

Contributions:

- Javier Rioyo formulated the research questions and hypothesis, established the research objectives and methodologies, planned and conducted all experiments, data collection, analysis and interpretation, and composed the content of the manuscript. The contribution made by the candidate is 80%.

- Dr Vasantha Aravinthan, Professor Jochen Bundschuh, and Dr Mark Lynch advised on the data analysis and interpretation, assisted with the manuscript compilation, editing, critical revision, and final revision. Overall, their contribution to this manuscript is 20%.

Paper III. Rioyo, J., Aravinthan, V., & Bundschuh, J. 2018. The effect of 'High-pH pretreatment' on RO concentrate minimization in a groundwater desalination facility using batch air gap membrane distillation. Separation and Purification technology. (Under Review, Submitted on 4 February 2019, reference number: SEPPUR_2019_448).

Contributions:

- Javier Rioyo formulated the research questions and hypothesis, established the research objectives and methodologies, planned and conducted all experiments, data collection, analysis and interpretation, and composed the content of the manuscript. The contribution made by the candidate is 80%.

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Paper IV. Rioyo, J., Aravinthan, V., Bundschuh, J., & Lynch, M. 2018. 'High-pH softening pretreatment' for boron removal in inland desalination systems. Separation and Purification Technology, 205, 308-316. (Published).

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CHAPTER 1

INTRODUCTION

1.1 Rationale of study

1.1.1 Background

Australia is the world's driest continent and has always battled drought. One of the worst droughts in recent times was the Millennium Drought from late 1996 to mid-2010, affecting the areas around Perth, Adelaide, Melbourne, Hobart, Canberra, Sydney and Brisbane (BOM, 2015). As a result of drought, climate change and population growth in urban centres, Australia began building desalination plants that purify seawater using reverse osmosis (RO) technology to drought-proof cities located in coastal areas (El Saliby et al., 2009). For inland communities which do not have access to seawater, the desalination of brackish groundwater resources has become more common. Groundwater desalination for domestic supply currently makes up 1.2% of Australia's total desalination capacity, although the number of inland desalination plants is expected to increase in the future (NSW Public Works, 2011). However, cost and concentrate management remain major challenges limiting the construction of new inland desalination facilities (Mickley, 2011).

Groundwater is available for use throughout large parts of Australia. Western Australia, New South Wales, and Northern Territory are the states and territories with more reliance on groundwater resources. The highest concentration of groundwater use is in the Murray-Darling Basin which extends through most of inland south-eastern Australia, including much of the country's best farmland. The Great Artesian Basin also includes aquifers where groundwater is highly developed. However, much of the groundwater is too saline for drinking or agriculture use, requiring prior desalination (Harrington and Cook, 2014). Brackish groundwater has a higher salt concentration than freshwater, but lower concentration than seawater (NSW Public Works, 2011). This research project defines brackish groundwater as having a level of total dissolved solids (TDS) between 1,000 mg/L (the upper limit set by drinking water quality standards) and 10,000 mg/L (the lower limit of saline water). Figure 1.1 shows the proportion of each groundwater region in Australia with salinity (measured as TDS) above 1,500 mg/L.

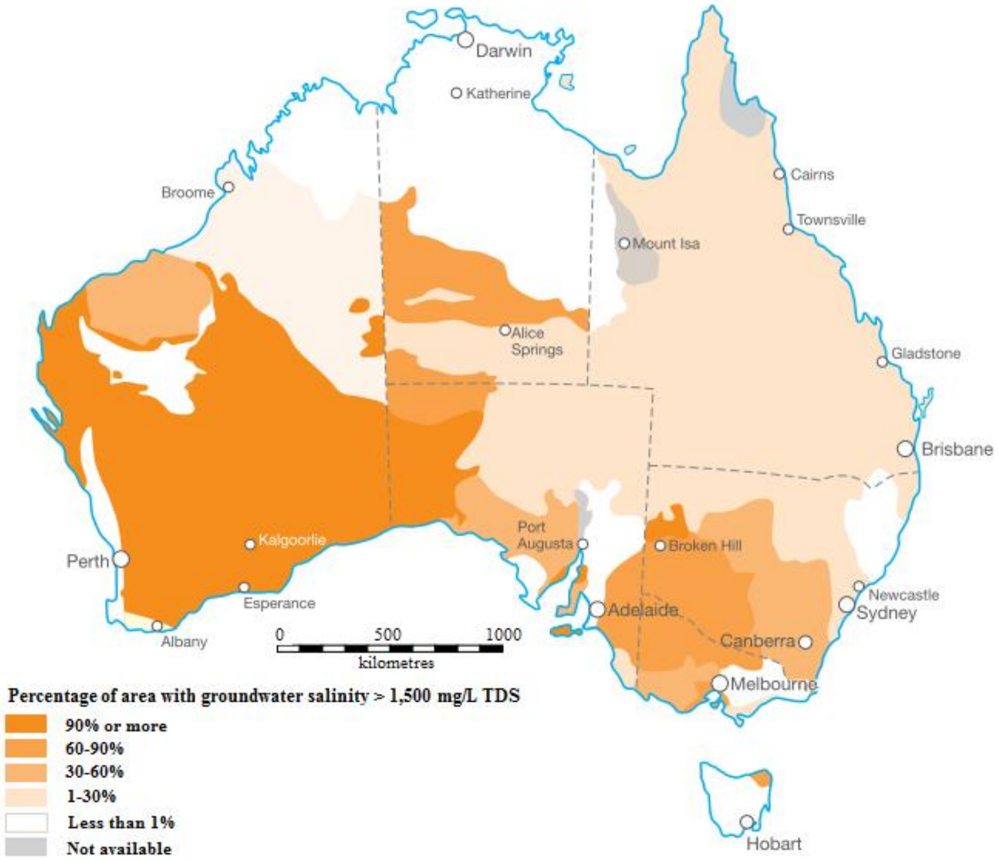


Figure 1.1 Percentage of areas with groundwater salinity > 1,500 mg/L TDS (Harrington and Cook, 2014)

Overall, Australian surface water resources have become limited and tightly regulated. As a consequence, Australia's groundwater is considered to be a major and alternative source of water for many communities, industries, farms and environments. In fact, its use has increased over the past years. Although there is a lack of accurate statistics on groundwater extraction, it has been estimated that total water consumption in Australia is about 15,000 GL/year, with 5,000 GL/year sourced from groundwater, and the remainder (10,000 GL/year) sourced from surface-water (Harrington and Cook, 2014).

1.1.2 Reverse osmosis (RO) technology

RO is the dominant technology in seawater desalination and, in Australia, is almost exclusively employed in inland desalination. RO is a pressure driven treatment process in which a semipermeable membrane rejects salts and other species present in the feed water (NSW Public Works, 2011). Current commercial RO membranes used in seawater and brackish water desalination are operated in crossflow mode. Such RO membranes are almost exclusively made of composite aromatic polyamide in a spiral wound configuration. Polyamide membranes are used in all areas of applications, and are stable in the pH range of 2 to 10, but have very limited tolerance to free chlorine. In past years, the incorporation of variable speed drives and power recovery devices have significantly reduced power consumption and operating costs in RO desalination plants (Wilf, 2007).

1.1.3 Differences between seawater and inland desalination plants

While RO technology can be employed to desalinate both seawater and brackish inland water, there are substantial process differences as listed below:

- Inland plants cannot dispose of RO concentrate into the ocean, which amounts to 15-35% of feed water in plants having a single concentrate stage (Mickley, 2011). The objective of inland desalination plants is, therefore, high water recovery (*Rw)* that also minimizes the volume of RO concentrate. The consequence of high water *Rw* in brackish desalination is the increased scaling propensity which also leads to permeate flux decline and shortening of the membrane's useful life (Rahardianto et al., 2007). In addition, operating pressures are higher in scaled membranes while salt rejection is lower (Amjad, 2010). These problems are currently largely unresolved,
- Inland desalination plants provide higher water *Rw* (75-90%), and require lower operating pressures due to the lower osmotic pressure of brackish water (Greenlee et al., 2009)
- Seawater desalination plants operate at higher pressures to compensate for the higher osmotic pressure of seawater and provide higher salt rejection. Typical

water *Rw* ranges from 35 to 45% (Greenlee et al., 2009) and is limited by maximum feed pressure, energy consumption, and allowable salinity/boron concentration in the RO permeate (DOW, 2007)

- Production capacity and the required investment per unit of production capacity are higher in seawater than in brackish groundwater desalination plants (Greenlee et al., 2009)
- RO treatment to produce drinking water from seawater is considered to be a mature technology with substantial plants operating in Australia and worldwide (Fell, 2014). By contrast, high cost and RO concentrate management remain major challenges limiting the construction of new inland desalination plants (Mickley, 2011).

1.1.4 Fouling, biofouling and scaling in inland desalination

RO filtration is not a panacea in water desalination. Despite its advances, fouling, mineral salt scaling and degradation are common problems in water treatment; causing membrane failure, decline in membrane flux and a deterioration in product water quality due to salt passage (Amjad, 2010). Surface fouling occurs when microbial material, soluble organics, dissolved solids or suspended solids are deposited on the surface of the membrane or on the feed-channel spacers (Greenlee et al., 2009). Biofouling involves the formation of a biofilm from the growth of microorganism on the RO membrane surface (Weinrich et al., 2016). Finally, membrane scaling involves salt precipitation on the surface of the membrane and on the feed channel spacer (Amjad, 2010).

Seawater desalination membranes can be fouled primarily by organic and particulate material (Greenlee et al., 2009; Rodriguez, 2011). Seawater desalination facilities working with open intakes are also prone to biofouling (DOW, 2007). Precipitation is less likely to occur in seawater desalination due to the lower *Rw*, seawater composition, and the higher ionic strength of the solution (Greenlee et al., 2009).

Brackish water desalination membranes are mainly fouled by precipitation and dissolved inorganic salts. Concentration factor (C_F) is defined as the ratio between concentrate TDS concentration and feed TDS concentration. When the water *Rw* is increased, C_F increases more dramatically in brackish water than in seawater desalination plants, enhancing salt precipitation (Greenlee et al., 2009). Sparingly soluble salts that can scale the RO membrane are $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$ and CaF_2. SiO_2 can also scale the RO membrane (Sutzkover-Gutman and Hasson, 2010). Figure 1.2 shows the effect of increasing *Rw* on C_F considering the typical range of water *Rw* for seawater and brackish water operation.

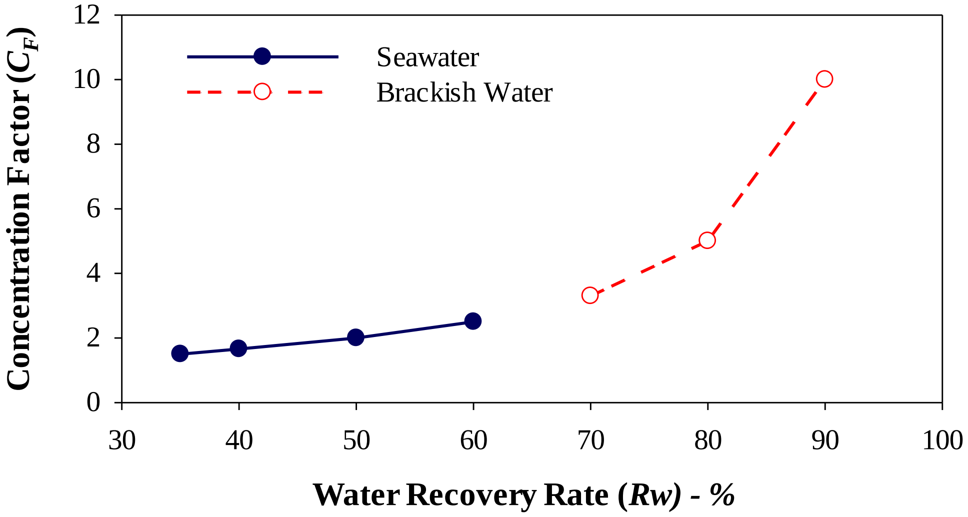


Figure 1.2 The effect of increasing *Rw* on C_F

1.1.5 Pretreatment options in inland desalination

Pretreatment is essential to offset fouling and scaling in inland RO systems. Conventional pretreatment technologies that can be applied to avoid fouling/scaling issues in brackish water desalination plants are described below:

- Ultraviolet (UV) disinfection (NSW Public Works, 2011) or oxidant addition including ozone, chloramine, potassium permanganate or chlorine to deactivate any bio-organisms that could foul the membrane (Greenlee et al., 2009). Polyamide membranes are incompatible with traditional biocides like chlorine, so disinfectants can only be applied in specific circumstances and in combination with activated carbon or sodium bisulphite to remove residual chlorine (DOW, 2007)

- pH adjustment to increase the solubility of calcium carbonate (MWH, 2005)
- Coagulant addition prior to filtration to facilitate the removal of smaller particles (Amjad, 2010)
- Granular media filtration with sand, anthracite, pumice, gravel or garnet (Greenlee et al., 2009)
- Antiscalant (AS) addition to prevent scaling by species such as calcium carbonate and sulphate, barium sulphate, and silica (Ruiz-García et al., 2015; Amjad, 2010)
- An ion-exchange process (sodium softeners) could be an option to remove hardness and trace cations (Amjad, 2010). However, total hardness reduction by ion-exchange technology can be limited by water chemistry and high chemical regeneration costs (Milne et al., 2014). Currently, there are no municipal desalination plants in Australia incorporating ion-exchange technology (NSW Public Works, 2011). Therefore, this technology was disregarded in this study
- Cartridge filters to remove particles greater than 5-10 µm, which will foul membrane channels used to remove the RO concentrate (Greenlee et al., 2009)
- A more recent trend in RO pretreatment involves the use of larger pore size membranes like microfiltration, nanofiltration and ultrafiltration (UF) to pre-treat RO feed water (Greenlee et al., 2009; Qiu and Davies, 2012). The main disadvantage of this approach is that the prefiltration membranes can also be fouled (Greenlee et al., 2009).

Overall, conventional pre-treatment mainly relies on AS addition to prevent salt precipitation during brackish water desalination (Greenlee et al., 2009). Water *Rw* is then limited by AS efficacy (Rahardianto et al., 2007), and large volumes of RO concentrate are often disposed of in evaporation ponds (NSW Public Works, 2011). In summary, the exploration of more effective technologies to combat scaling related issues during inland desalination is essential.

1.1.6 Proposed technology: ‘High-pH pretreatment’

Some researchers have studied different state of the art technologies for RO concentrate minimization (Pérez-González et al., 2012; Morillo et al., 2014). The present study will evaluate the integration of a ‘High-pH pretreatment’ between consecutive RO stages for scale control, RO concentrate minimization and recovery of by-products in inland desalination systems. The process combines softening with coagulation/flocculation at elevated pH. The ‘High-pH pretreatment’ involves the addition of a suitable base to increase the process pH to a suitable range. The chemical reactions result in precipitation and flocculation, which allow the removal of undesirable species by simple physical separation processes like settling and/or filtration. Following pH readjustment and final AS addition, the use of secondary RO will allow an increase of water *Rw*. Remarkably, $CaCO_3$ and CaO recovery from precipitated sludge could be possible. To date, the evaluation of an intermediate ‘chemical precipitation treatment’ for RO concentrate minimization has only been reported in relation to waters with a calcium concentration higher than the magnesium concentration (Williams et al., 2002; Ning et al., 2006; Bond and Veerapaneni, 2007; Rahardianto et al., 2007; Mohammadesmaeili et al., 2010; Gabelich et al., 2011). It is important to emphasise that the concentrate used in most of these previous experiments was derived from desalination plants treating reclaimed water (Mohammadesmaeili et al., 2010) or brackish surface waters (Williams et al., 2002; Rahardianto et al., 2007; Gabelich et al., 2011). In contrast, the present project will enhance and extend the process to develop an integrated technology for RO concentrate minimization during the desalination of magnesium-dominated groundwater, with a focus on viable by-products recovery.

In addition, there is a clear opportunity to investigate the combination of a ‘High-pH pretreatment’ with more advanced desalination systems such as membrane distillation (MD) for high salinity RO concentrate minimization. Therefore, this research will compare two different scale control strategies: ‘High-pH pretreatment’, and AS addition for RO concentrate minimization in a lab-scale ‘air gap membrane distillation’ (AGMD) system. The literature survey found that only one paper evaluated chemical demineralization pretreatment of a RO concentrate followed by MD technology, but it used direct contact membrane distillation instead of AGMD.

Furthermore, the study was performed with low salinity RO concentrate (Qu et al., 2009).

Finally, this study will also investigate the feasibility of ‘High-pH pretreatment’ for boron removal from magnesium-dominated groundwater samples obtained from an existing inland desalination facility. A High-pH softening treatment for boron removal has been reported in only a few studies and for different kinds of waters (Parks and Edwards, 2005, 2006, 2007; Ayoub et al., 2014; Rodarte and Smith, 2014). The efficacy of using this solution in magnesium-dominated groundwater is the least explored. The mechanism for boron removal could be related to magnesium precipitation during the softening treatment. If successful, this solution could safely facilitate compliance with strict boron standards in inland desalination plants using RO or electrodialysis technology.

The overall aim of this research is to provide an insight into technical alternatives for the integration of a ‘High-pH pretreatment’ in inland desalination plants for RO concentrate minimization, by-products’ recovery and removal of specific pollutants (such as boron).

1.2 Research gaps

1. No studies have focussed on the integration of a ‘High-pH pretreatment’ between consecutive RO stages for scale control, concentrate minimization and by-products’ recovery in a municipal desalination system dealing with magnesium-dominated groundwater
2. No previous research has been conducted on the integration of a ‘High-pH pretreatment’ and AGMD for RO concentrate minimization in a municipal desalination facility treating magnesium-dominated groundwater
3. It is unclear whether ‘High-pH pretreatment’ can enhance boron removal in inland desalination systems treating magnesium-dominated groundwater.

1.3 Research questions

The main research question in this study is: Can ‘High-pH pretreatment’ be integrated in existing or future inland desalination systems to overcome AS limitations, increase freshwater *Rw*, provide salt recovery options and remove specific pollutants such as boron? This research question leads to a subset of further questions:

1. How effective is ‘High-pH pretreatment’ of RO concentrate in preventing scale build up in secondary RO and improving the overall water *Rw* of the desalination system?
2. Can ‘High-pH pretreatment’ facilitate potential recovery of by-products from precipitated sludge?
3. Can ‘High-pH pretreatment’ be combined with AGMD for RO concentrate minimization in an existing inland desalination system?
4. How effective is ‘High-pH pretreatment’ in removing boron from magnesium-dominated groundwater?

1.4 Research aim and objectives

The overall aim of the project is to investigate the integration of a ‘High-pH pretreatment’ in existing or future inland desalination systems for scale control, RO concentrate minimization, removal of specific pollutants (such as boron) and by-products’ recovery from precipitated sludge. The main objectives are as follows:

1. To elucidate the differences between inland and seawater desalination, review the existing strategies for RO concentrate minimization towards zero liquid discharge (ZLD) in inland desalination, and compare two different scale control technologies: acid/AS addition and ‘High-pH pretreatment’
2. To evaluate the removal of scale-forming precursors from primary RO concentrate including magnesium, calcium, barium, strontium and silica to increase water *Rw* in a secondary RO and to assess the recovery of by-products such as $CaCO_3$ and quicklime from precipitated sludge

3. To compare the efficacy of two different scale control technologies, AS addition and ‘High-pH pretreatment’ (followed by pH adjustment and final AS addition) in terms of RO concentrate minimization in a lab-scale AGMD unit
4. To investigate the efficacy of a ‘High-pH pretreatment’ for boron removal in inland desalination systems treating magnesium-dominated groundwater.

1.5 Organization of the thesis

This thesis has been structured in seven chapters, and this is represented schematically in Figure 1.3.

Chapter 1 identifies the rationale of the study, research gaps, research questions, research aim and objectives.

Chapter 2 presents a review of literature associated with the major aspects of this study.

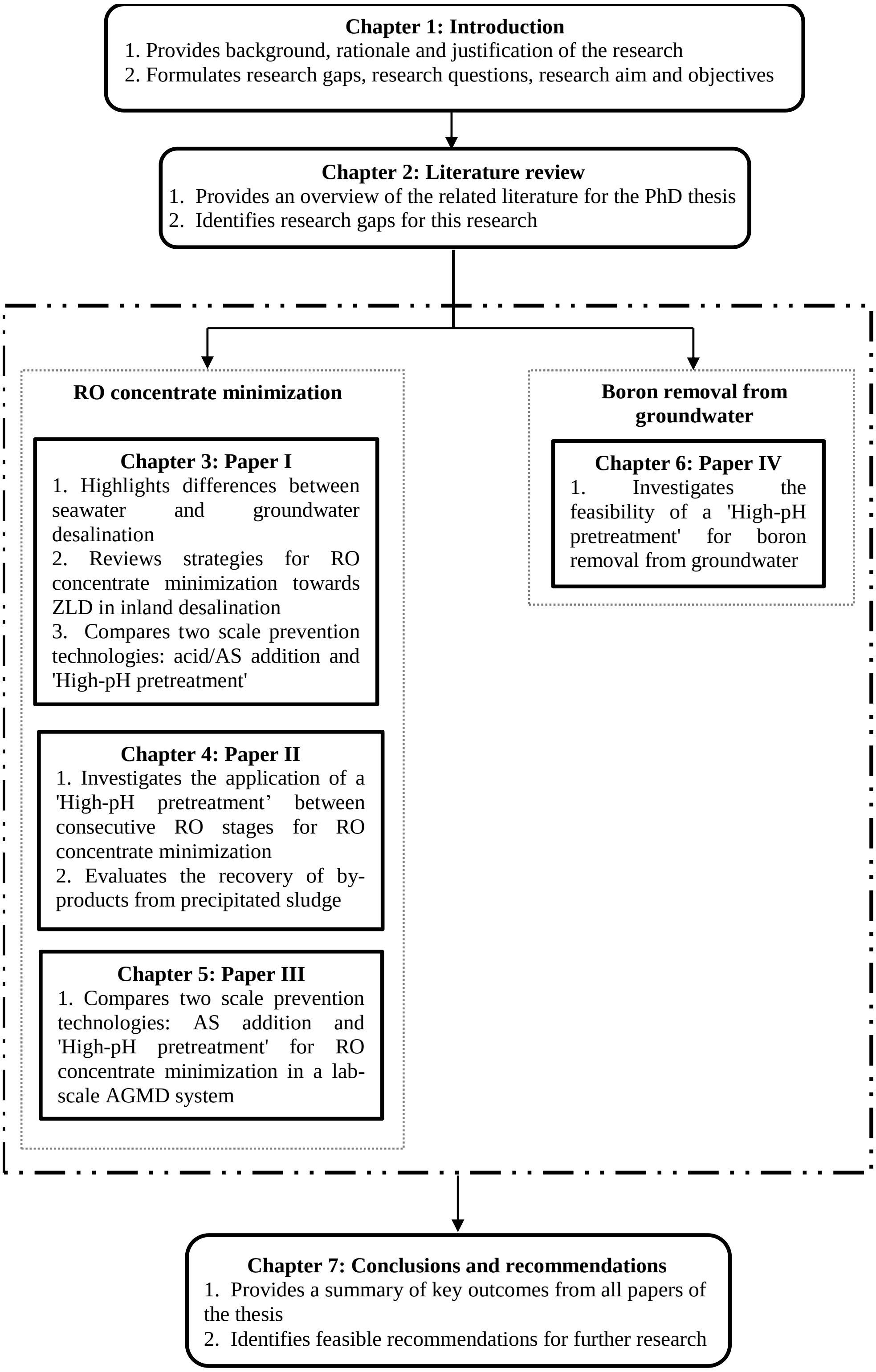
Chapter 3 provides Paper I (*A review of strategies for RO brine minimization in inland desalination plants*) that presents the main differences between inland and seawater desalination, reviews feasible strategies for RO concentrate minimization towards ZLD in inland desalination facilities, and compares two different scale prevention methods in RO desalination: acid/AS addition and ‘High-pH pretreatment’.

Chapter 4 presents Paper II (*Research on ‘High-pH precipitation treatment’ for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility*) that explores the integration of an intermediate ‘High-pH pretreatment’ between consecutive RO stages for scale control, concentrate minimization and by-products’ recovery in a municipal desalination facility treating magnesium-dominated groundwater.

Chapter 5 presents Paper III (*The effect of ‘High-pH pretreatment’ on RO concentrate minimization in a groundwater desalination facility using batch air gap membrane distillation*) that compares the efficacy of two scale prevention technologies: ‘High-pH pretreatment' and AS addition for RO concentrate minimization in a lab-scale AGMD system.

Chapter 6 presents Paper IV (*'High-pH softening pretreatment' for boron removal in inland desalination systems*) that investigates the capabilities of a 'High-pH pretreatment' for boron removal from magnesium-dominated groundwater samples collected from an existing municipal desalination plant.

Chapter 7 summarizes the main conclusions of this research and gives recommendations for practice and future research.



Chapter 1: Introduction
1. Provides background, rationale and justification of the research
2. Formulates research gaps, research questions, research aim and objectives

Chapter 2: Literature review
1. Provides an overview of the related literature for the PhD thesis
2. Identifies research gaps for this research

RO concentrate minimization

Chapter 3: Paper I
1. Highlights differences between seawater and groundwater desalination
2. Reviews strategies for RO concentrate minimization towards ZLD in inland desalination
3. Compares two scale prevention technologies: acid/AS addition and 'High-pH pretreatment'

Chapter 4: Paper II
1. Investigates the application of a 'High-pH pretreatment' between consecutive RO stages for RO concentrate minimization
2. Evaluates the recovery of by-products from precipitated sludge

Chapter 5: Paper III
1. Compares two scale prevention technologies: AS addition and 'High-pH pretreatment' for RO concentrate minimization in a lab-scale AGMD system

Boron removal from groundwater

Chapter 6: Paper IV
1. Investigates the feasibility of a 'High-pH pretreatment' for boron removal from groundwater

Chapter 7: Conclusions and recommendations
1. Provides a summary of key outcomes from all papers of the thesis
2. Identifies feasible recommendations for further research

Figure 1.3 Organization of the thesis

1.6 References

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CHAPTER 2

LITERATURE REVIEW

This chapter is organized into four sections. The first section provides an overview of Australia's groundwater resources, RO technology and brackish groundwater quality. The second section discusses the differences and similarities between brackish water and seawater desalination. The third section describes the major fouling and scaling categories in brackish water desalination and the available pretreatment technologies. It also provides the justification for the selection (in this research) of an intermediate 'High pH-pretreatment' between consecutive RO stages or between RO and AGMD for RO concentrate minimization and by-products recovery. Finally, the fourth section describes the choice of other contaminants, such as boron, that were also used to explore the efficiency of 'High-pH pretreatment' prior to RO desalination.

Chapter 3 includes the manuscript entitled 'A review of strategies for RO brine minimization in inland desalination plants' which extends and complements the information provided in this chapter.

2.1 Groundwater essentials and management

2.1.1 Australia's groundwater resources

Groundwater is a vital source of water throughout Australia and makes up about 17% of Australia's accessible water resources. Many mining operations, some indigenous communities and remote pastoral properties depend exclusively on it for their water supply (National Water Commission, 2012). Groundwater consumption in Australia is estimated to be around 5,000 GL per annum and about 70% of this resource is used for agricultural or pastoral purposes. Western Australia, Queensland and New South Wales are the highest users of groundwater. In Western Australia about 38% of the extracted groundwater is used in mining activities (Harrington and Cook, 2014). Figure 2.1 shows a map of Australia's groundwater resources.

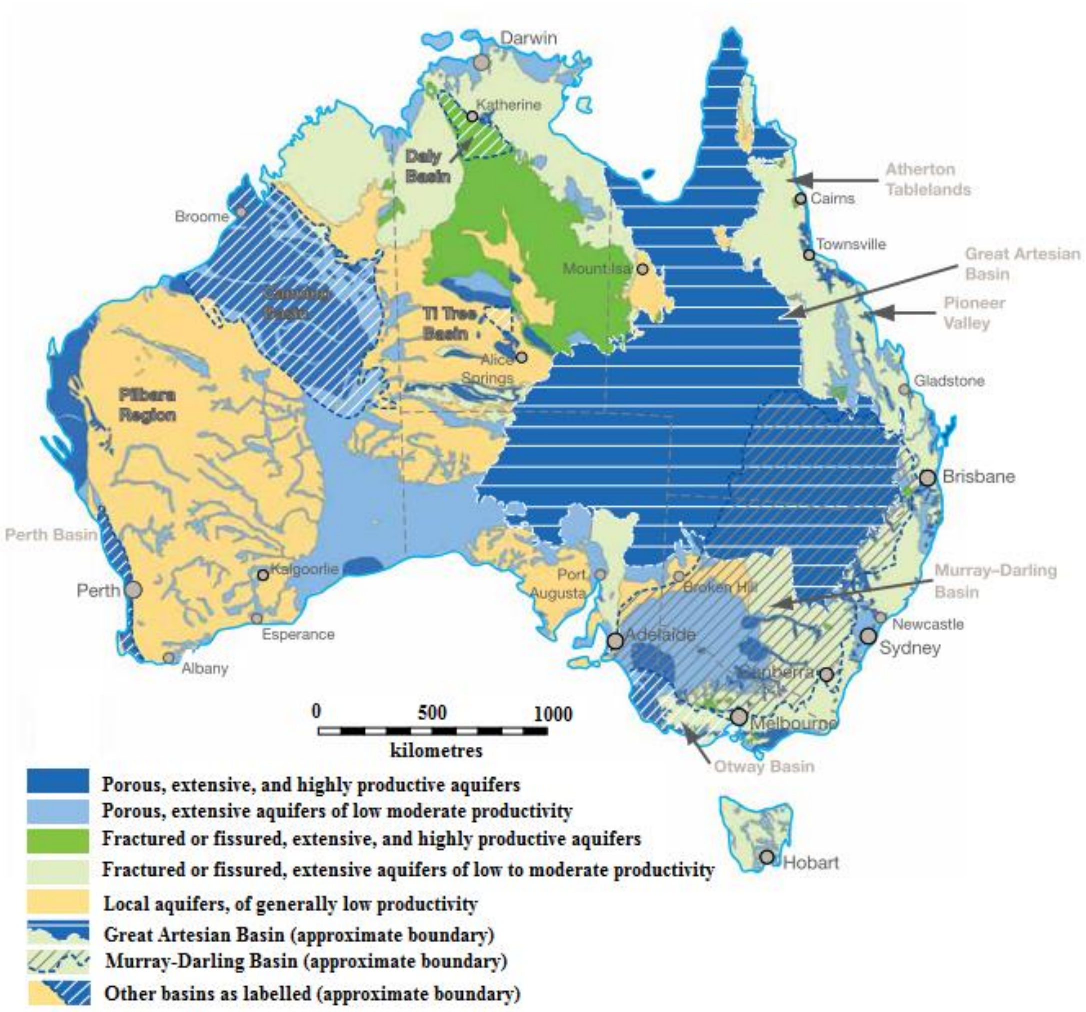

Figure 2.1 Australia's groundwater resources (Harrington and Cook, 2014)

2.1.2 RO technology in groundwater desalination

In many cases, the concentration of salts is so high that the groundwater is unsuitable for drinking or agricultural purposes without prior treatment to remove dissolved salts (NSW Public Works, 2011; Harrington and Cook, 2014). Membrane desalination using RO or nanofiltration membranes has been the dominant technology applied in municipal inland desalination (NSW Public Works, 2011). Table 2.1 shows a list of Australia's inland desalination facilities using RO technology. In the USA about 96% of the more than 300 desalination municipal desalination facilities are located inland and 77% of them use RO technology (Mickley, 2011). A design including a single RO stage system with an additional module connected to minimize the RO concentrate has been considered as the best option both economically and environmentally

(Alghoul et al., 2009). Water *Rw* can be increased up to 80% using this configuration (DOW, 2007).

Table 2.1

Brackish water desalination plants in Australia (NSW Public Works, 2011).

Brackish water desalination plants	Operation and Maintenance	Capacity (KL/day)
Yalata, SA	Council - Osmoflo	160
North Star, NSW	Council	265
Dalby, QLD	Council	4,000
Coober Pedy, SA	Council	1,500

However, RO concentrate management and disposal remains a major challenge especially for inland areas that have very limited management and disposal options (Brady et al., 2005; Bond and Veerapaneni, 2007; NSW Public Works, 2011; Fell, 2014). Evaporation ponds, surface water discharge, discharge to wastewater treatment, subsurface injection and land application are common RO concentrate disposal methods used in brackish water desalination (Mickley, 2008).

2.1.3 Brackish groundwater quality

Groundwater varies in quality, quantity and depth depending on factors like the host-rock type, nature of overlying soils, and rainfall. Salts from surrounding strata can dissolve ions in the groundwater, increasing the salt concentration (NSW Public Works, 2011). Brackish groundwater has a TDS level ranging from 1,000 to 10,000 mg/L (National Groundwater Association, 2010). The most abundant ions in brackish groundwater are calcium and magnesium carbonates, chlorides and sulphates. Sodium chloride is also present, although in a lower proportion than in seawater (NSW Public Works, 2011). The ratios of calcium/TDS, carbonate/TDS or sulphate/TDS are higher in brackish water than in seawater (Greenlee et al., 2009). Other elements that can be present in brackish groundwater are barium, iron, manganese, and silica, causing scaling/fouling issues in membranes (NSW Public Works, 2011). Precipitation of $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, CaF_2, $Mg(OH)_2$ or SiO_2 can become the limiting factor during the RO desalination process if the concentration product of the salt forming constituents exceeds the solubility product (*Ksp*) (Sutzkover-Gutman and Hasson, 2010). Boron can also be present in groundwater from natural or anthropogenic sources (Cengeloglu et al., 2008; Xu and Jiang, 2008). In addition, other pollutants found in brackish waters include arsenic, fluoride, nitrates and pesticides. In general, brackish water has a low organic carbon content and low particulate or colloidal pollutant levels (Greenlee et al., 2009). Table 2.2 compares the chemical composition of Dalby (Australia) well water with examples of brackish inland waters worldwide. The mass ratio Ca/Mg in Dalby groundwater was only 0.64, while the same ratio in other brackish waters ranged from 1.35 to 14. In contrast to previous studies, this research was performed with magnesium-dominant groundwater and RO concentrate collected in a municipal desalination plant located in Dalby. It was hypothesized that freshwater *Rw* and by-products recovery could be enhanced in inland desalination facilities treating magnesium-dominated waters as magnesium-bearing minerals precipitating at high-pH could concurrently remove other scale-forming precursors and pollutants through precipitation and adsorption/enmeshment.

Table 2.2

Chemical composition of brackish groundwaters (Brady et al., 2005; DOW, 2007; Greenlee et al., 2009).

Parameter	Groundwater Las Vegas (USA)	Tularosa Basin (USA)	Martin County (USA)	Well water (Germany)	Dalby well water (Australia)*
TDS (mg/L)	5,270	2,630	3,664	478	1,928
HCO_3 (mg/L)	210	270	146	265	434
Na (mg/L)	755	114	905	36	551
K (mg/L)	72	2	--	3.3	3.1
Ca (mg/L)	576	420	179	84	50
Mg (mg/L)	296	163	132	6	78
SiO_2 (mg/L)	77	22	--	9	33
Cl^- (mg/L)	954	170	1,867	45	863
NO_3^-	31	10	--	4.3	2
SO_4^{2-} (mg/L)	2,290	1,370	384	24	143
PO_4^{3-} (mg/L)	--	0	--	<0.05	0.3

(*) Note: Dalby groundwater average concentrations were extracted from data supplied by the Western Downs Regional Council related to the period November 2010 to October 2014. Sampling point: Bore 12.

2.2 Differences between seawater and brackish water desalination

The main differences between seawater and brackish groundwater desalination are described below.

- Seawater salinity ranges from 35,000 to 45,000 mg/L TDS, while brackish water salinity ranges from 1,000 to 10,000 mg/L TDS (Greenlee et al., 2009). The Australian Drinking Water Guidelines recommend that for good palatability, TDS in drinking water should not exceed 600 mg/L (NHMRC and NRMMC, 2011). Overall, most RO desalination facilities are designed to produce drinking water with TDS concentration below 500 mg/L (Greenlee et al., 2009)
- Seawater desalination plants are located in big cities and are designed to produce large volumes of drinking water, while inland desalination plants are often located in small towns and villages like Dalby (Queensland) and Coober Pedy (South Australia) with low treatment volumes (NSW Public Works, 2011). Consequently, inland desalination plants have cost disadvantages related to economies of scale (Brady et al., 2005)
- Mass transfer in RO desalination involves a diffusive process, where separation depends on solute concentration, water flux rate and pressure (MWH, 2005). Osmotic pressure can be defined as the minimum pressure which needs to be applied to a solution to prevent the inward flow of water across a semipermeable membrane. RO desalination requires a hydrostatic pressure higher than the osmotic pressure to create permeate flow through the membrane against the natural direction of osmosis. The osmotic pressure depends on the solution concentration and the temperature (Greenlee et al., 2009). The following equation relates osmotic pressure (π), temperature (T) and concentration (ΔC) (Degrémont and Lyonnaise des eaux-dumez, 1991):

  $$\pi = \Delta C * R * T \tag{1}$$

  with ΔC difference in concentration (mol/m^3) and R ideal gas constant. The osmotic pressure of seawater is in the range of 2,300 and 2,600 kPa while the osmotic pressure of brackish water is in the range of 100 and 300 kPa. To produce drinking water, the osmotic pressure has to be exceeded therefore, feed pressures in RO systems vary from 6,000 to 8,000 kPa in seawater desalination, and from 600 to 3,000 kPa in brackish water desalination. Consequently, brackish water treatment demands less power than seawater desalination due to the lower feed salinity (Greenlee et al., 2009). In seawater desalination plants, power recovery devices are common and average overall efficiencies up to 65% have been reported (Farooque et al., 2008)

- *Rw* is defined as the relation between permeate volumetric flow (*Qp*) and feed volumetric flow rate (*Qf*) (Rahardianto et al., 2007). An increase in *Rw* requires higher feed pressure and higher permeate flux (Greenlee et al., 2009). Water *Rw* in brackish water desalination plants can be up to 90% while in seawater desalination facilities, typical water *Rw* ranges from 35 to 45% (Greenlee et al., 2009). Overall, the water *Rw* limit in brackish desalination plants is determined by the osmotic pressure of the concentrated solution at the membrane surface and the tendency of other constituents to precipitate sooner than sodium chloride (Fell, 2014):

$$Rw = \frac{Qp}{Qf} \tag{2}$$

- In brackish water desalination salt passage through the membrane is an important phenomenon that increases with the salt concentration and the temperature. In seawater desalination, in the common feed salinity range, the effect of salinity on the salt passage is less significant and it is usually neglected in permeate salinity calculations (Wilf, 2007)
- Membrane salt rejection (*Rej*) is a measure of RO membrane performance and it can be given for crossflow operation systems as:

$$\mathrm{Re}\,j = 1 - {}^{Cp}\!/_{Cf} \tag{3}$$

where *Cp* = concentration in permeate, mole/L and *Cf* = concentration in feed water, mole/L (MWH, 2005). Brackish water membranes provide lower salt rejection than seawater membranes. Both water and salt permeability increase with temperature (Greenlee et al., 2009)

- Seawater desalination facilities are often designed with one or more passes depending on different factors, such as boron initial concentration, water *Rw*, energy costs, and product water standards (Greenlee et al., 2009). On the other hand, a design including a single stage with an additional module connected to treat the RO concentrate is recommended in brackish water desalination systems (Alghoul et al., 2009)
- Membrane replacement in seawater desalination plants may be required after 5 to 7 years of operation (Wilf, 2007), whereas brackish RO systems require membrane replacement after 3 to 5 years of operation (NSW Public Works, 2011)
- Concentrated brine in seawater desalination plants is discharged back into the ocean, whereas RO concentrate in brackish desalination plants is often discharged to the sewerage network, surface waters, land application or evaporation ponds (Brady et al., 2005).

2.3 Fouling, biofouling and scaling in brackish water desalination

2.3.1 Guidelines for RO feed water quality

Brackish waters show a wide variation in feed water composition. This has a big influence on process design and the level and cost of water *Rw* (Brady et al., 2005; Greenlee et al., 2009). Table 2.3 shows general feed water quality guidelines adopted in RO desalination to guarantee successful operation of the RO membranes.

Table 2.3

Feed water quality guidelines.

	Parameter	Measure	Guideline 1 (Amjad, 2010)	Guideline 2 (DOW, 2007)
Species causing fouling	Turbidity	NTU	<1	---
	Colloids	SDI	<5	<5
	Microbes	dip slides	<1,000	---
	Organics (TOC)	mg/L	< 3	< 3
	COD	mg/L	---	< 10
	Oil and grease	mg/L	---	< 0.1
	Colour	APHA	<3	---
	Free chlorine	mg/L	---	< 0.1
	Metals (Fe, Mn, Al)	mg/L	<0.05	---
	Ferrous iron	mg/L	---	< 4
	Ferric iron	mg/L	---	< 0.05
	Manganese	mg/L	---	< 0.05
	Aluminium	mg/L	---	< 0.05
	Hydrogen sulphide	mg/L	< 0.10	---
Species causing scaling	Calcium carbonate	LSI	<0[a]	---
	Sulphate-based compounds	mg/L	<0.05[b]	---
	Silica	mg/L	<200[c]	---

Notes: a) Can be up to 1.5 with AS, b) for barium and strontium, and c) measured in the RO concentrate stream, varies with temperature and pH.

2.3.2 Pretreatment technologies in inland desalination plants in Australia

Generally speaking, brackish water desalination plants are mainly fouled by dissolved inorganic salts and precipitation, although fouling can be aggravated by particulate and organic material (Greenlee et al., 2009). In addition, disinfection may be required in some circumstances (Qiu and Davies, 2012). Overall, pretreatment and AS addition are essential to avoid fouling/scaling problems on RO membranes. Table 2.4 shows common pretreatment technologies applied in groundwater desalination facilities in Australia (NSW Public Works, 2011). As AS is added at all existing facilities during RO pretreatment, membrane scaling is considered to be a common problem limiting freshwater *Rw* in all cases.

Table 2.4

Pretreatment technologies in brackish desalination plants in Australia (NSW Public Works, 2011).

Pretreatment	Yalata, SA	North Star, NSW	Dalby, QLD	Coober Pedy, SA
UV radiation			***	
Aeration tank		***		
Birm filters[1]		***		
Chlorine disinfection				***
Sodium metabisulphite				***
Green sand filters				***
Media filters	***		***	
Cartridge filters	***	***	***	***
AS addition	***	***	***	***

(1) Birm filters are used to remove oxidized iron particles.

The operating costs of a 250 m^3/day desalination plant in Australia dosing AS during RO pretreatment have been estimated to be US$102,254. As shown in Figure 2.2, AS and other chemical additions during RO pretreatment represent 3.4% of the total operating costs. However, this cost has to be assessed individually for any desalination project. RO concentrate management and disposal also represent 3.4% of the total operating costs. On the other hand, the cost of power use rises to 8.5 %, though this depends on groundwater quality. Finally, membrane replacement cost becomes significant, accounting for 30 % of the total operating costs. Membrane replacement is typically performed every 3 to 5 years although the level of pretreatment and groundwater quality has a great impact on the operating life of RO membranes (NSW Public Works, 2011).

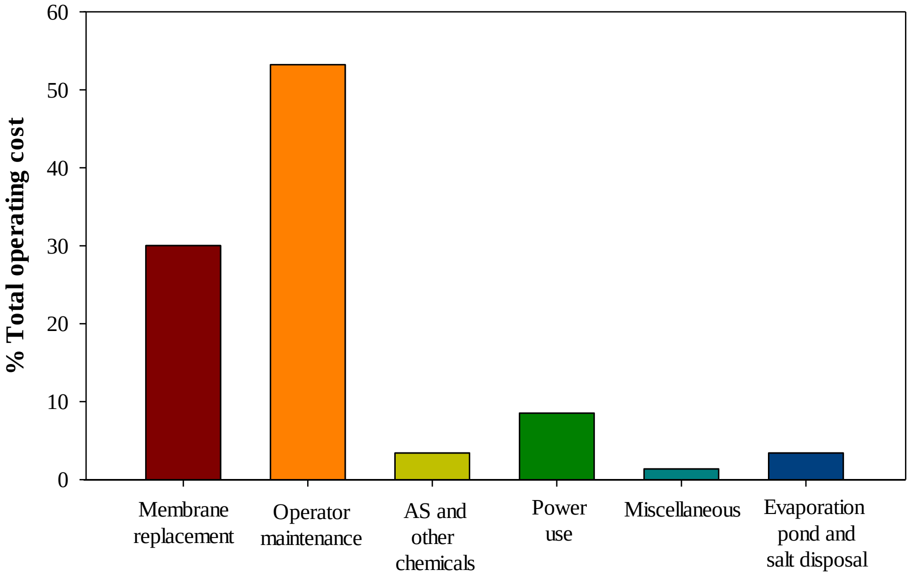

Figure 2.2 % of the total operating cost in a typical 250 m^3/day RO desalination plant in inland Australia

2.3.3 Major fouling and scaling categories in brackish water desalination

2.3.3.1 Biofouling

Biofouling is due to biofilm attachment and growth on the surface of the RO membrane or in the membrane's feed channels (MWH, 2005). In drinking water distribution networks, biofouling depends on the presence of nutrients (Vrouwenvelder et al., 2010). It also depends on other factors such as pH, dissolved oxygen content and temperature (Abd El Aleem et al., 1998). As a consequence of the biofilm, RO membrane resistance is increased and a gel is formed between the water and membrane surface (Flemming, 1997). Biofouling may originate loss of flux, reduced solute rejection, and increased head loss through membrane modules, membrane degradation, poor permeate quality and reduced membrane life (MWH, 2005).

Biofouling is often prevented in inland desalination facilities in Australia by UV radiation or chlorine disinfection (NSW Public Works, 2011). Ultrafiltration technology (UF) can also be incorporated for water disinfection (DOW, 2011). If disinfection is performed by chlorine addition, de-chlorination is essential because polyamide membranes cannot be exposed to free chlorine. Sodium bisulphite is frequently used to eliminate free chlorine in RO desalination systems (Wilf, 2007). Rather than using biocides, it might be more efficient to limit the nutrient content of the water to minimize potential biomass (Flemming, 1997).

2.3.3.2 Fouling due to particulate matter

Particulate fouling is a major concern in RO systems as RO technology does not include a back-washing step to remove foulants. Both inorganic and organic foulants may cause plugging and cake formation. Plugging refers to the accumulation of particles in the feed channels and piping. Cake formation occurs on the membrane surface, adding resistance to the flow and reducing system performance (MWH, 2005).

Plugging can be avoided with the use of cartridge filters. Cake formation can be avoided by coagulation and filtration pretreatment using sand, carbon or other media filters (MWH, 2005). Ferric chloride is considered a common coagulant in RO desalination. The use of aluminium salts is risky as precipitation of aluminium silicates can damage the membranes (Greenlee et al., 2009). Most inland desalination plants in Australia currently use a combination of media filters followed by cartridge filters (NSW Public Works, 2011). Fouled membranes exhibit higher operation pressure and increased pressure drop. In addition, the foulants layer and the presence of foulants on the feed channel spacer increase resistance to the cross flow of feed water across the membrane (Amjad, 2010).

The Silt Density Index (SDI) and turbidity are used to measure the potential for fouling with colloids and suspended solids (Amjad, 2010). The SDI test involves measuring the rate of plugging of a 0.45-micron filter by feed water at standard conditions (ASTM, 2014). The lower the SDI, the lower the potential for fouling (GE Power & Water. Water & Process Technologies, 2010; Amjad, 2010).

2.3.3.3 Fouling due to organic matter

Total organic carbon (TOC) levels under 3 mg/L have little effect on membrane permeability. However, high concentrations can result in flux decline due to adsorption of organic matter on the membrane surface (Wilf, 2007). Organic matter can also provide nutrients that sustain microbial colonies (Amjad, 2010). The removal of oil and grease before they reach the RO membrane is essential, and air flotation or media filtration with flocculation can be used for this purpose (Wilf, 2007).

2.3.3.4 Scaling

Some constituents present in brackish groundwater can precipitate if the concentration product of salt forming exceeds its solubility product (Wilf, 2007). Mineral salt scaling can be defined as the precipitation and deposition of sparingly soluble salts such as calcium carbonate, barium sulphate, calcium sulphate, strontium sulphate and calcium fluoride (DOW, 2007). Silica is also a common scale in groundwater desalination. Scaling on RO membranes is due to a concentration phenomenon, and chiefly occurs at the last stage of multistage RO systems where salt concentration is at its highest (Amjad, 2010).

Concentration polarization is a key issue in RO desalination, since precipitation occurs in the more concentrated area near the membrane surface (MWH, 2005). It could be defined as the ratio of salt concentration at the RO membrane surface and salt concentration in the bulk solution (Greenlee et al., 2009). Without pretreatment, scaling can be minimized by reducing concentration polarization, limiting salt rejection (undesirable when producing drinking water), or limiting water *Rw* (MWH, 2005). Scaled membranes require higher than normal operating pressure and the system presents lower salt rejection as a consequence of concentration polarization (Amjad, 2010).

Calcium carbonate is the most common scale in brackish desalination systems (Amjad, 2010). Calcium carbonate scale can be minimized by adjusting the process pH to 5.5-6.0 to convert carbonate to bicarbonate and CO_2. The formed carbon dioxide gas passes through the membrane (MWH, 2005). However, it is important to note that sulphuric acid addition to decrease pH can enhance the formation of scales of calcium, barium and strontium (Amjad, 2010).

The *LSI* is a measure of a solution's ability to dissolve or deposit calcium carbonate. *LSI* is defined as the difference between actual pH (measured) and calculated pH at which water is saturated with calcium carbonate (pHs) (DOW, 2007).

$$LSI = (\mathrm{pH} - \mathrm{pH_s}) \tag{4}$$

RO concentrate with *LSI* > 0 means that there is a potential for $CaCO_3$ scaling on the RO membrane (ASTM, 2010a). For high salinity brackish waters, with TDS levels in the RO concentrate above 10,000 mg/L, the Stiff & Davis Stability Index (*S&DSI*) is applied instead of the *LSI* (ASTM, 2010b).

Gypsum (calcium sulphate) scale produces progressive axial development of surface gypsum crystals along the membrane surface. A sufficiently high antiscalant addition can result in the complete reduction of surface crystals. Process pH has no influence on the precipitation of calcium or barium sulphate (Shih et al., 2005).

Conversely, different studies have autopsied membranes, concluding that silica is one of the most notorious foulants in RO membranes (Higgin et al., 2010). Silica scale is very difficult to remove with commercially available cleaners (Koo et al., 2001). Silica is frequently found in well water and its concentration usually ranges from 20 to 60 mg/L as SiO_2 (Al-Mutaz and Al-Anezi, 2004). Silica solubility is about 120 mg/L when present in the amorphous form (Hsu et al., 2008). The amorphous form can be present as dissolved, colloidal and particulate silica. Both the colloidal and the dissolved form may cause scaling issues in RO membranes (Latour et al., 2014b). The presence of silica in water is due to the dissolution of silica to become silicic acid or silicate. According to the chemistry of amorphous silica, when pH is less than 9.5, silicic acid is dominant, while when pH is above 9.5, $H_3SiO_4^-$ is predominant (Cheng et al., 2009). Then, in the presence of metals such as calcium, magnesium, iron, manganese or aluminium and coupled with the high pH, silica can form insoluble silicates (DOW, 2007). Silica solubility depends on factors such as process pH, temperature or the presence of inorganic or organic matter (Latour et al., 2013). Overall, silica and/or magnesium silicate are poorly studied scalants often present in waters with high magnesium levels and limit freshwater recoveries in water treatment systems (Amjad, 2010).

The use of AS, typically polyphosphates, phosphates and polymers enable the supersaturation of salts without precipitation. Its required dosage is determined by the limiting salt solubility product (Letterman and American Water Works Association, 1999). AS work by surface modification of crystals or by crystal inhibition (Amjad, 2010). AS are often not effective in preventing silica precipitation since silica is often present as an amorphous solid rather than a crystalline solid (Higgin et al., 2010). One disadvantage of AS utilization is that coagulants and AS (negatively charged) can form complexes and foul the membrane (Greenlee et al., 2009). Moreover, an excessive dose of AS can increase the potential of biofouling (Rahardianto et al., 2007).

Sometimes AS are ineffective, thus a ‘High-pH pretreatment’, with lime and soda ash, could be required for total hardness and silica reduction. Two main mechanisms for silica removal could be involved during a ‘High-pH pretreatment’: a) precipitation as calcium and/or magnesium silicate; and/or b) adsorption/enmeshment in precipitated $Mg(OH)_2$ and/or $CaCO_3$ (Latour et al., 2014a, 2016). Alternatively, ion-exchange technology can be applied for total hardness reduction (DOW, 2007). However, ion exchange technology is rarely used because it is expensive due to high regeneration frequencies (MWH, 2005). Most inland desalination plants in Australia are currently dosing AS to the feed water to prevent salt precipitation (NSW Public Works, 2011).

The integration of a ‘High-pH pretreatment’ between consecutive RO stages for scale suppression and RO concentrate minimization for different kinds of brackish water has been broadly reported in the literature. In all cases, the RO concentrate used for these experiments had a calcium concentration higher than the magnesium concentration. Precipitation was induced by addition of alkaline chemicals such as NaOH, $NaHCO_3$, $Ca(OH)_2$ and Na_2CO_3 (Williams et al., 2002; Ning et al., 2006; Bond and Veerapaneni, 2007; Mohammadesmaeili et al., 2010; Gabelich et al., 2011). A newer version of this technology, named accelerated precipitation softening (APS), involves alkaline pH adjustment and calcite crystal seeding of the first stage RO concentrate, followed by microfiltration and pH reduction to avoid calcite scaling in the second stage of the RO plant. This technology is more effective than AS utilization alone, and reduced calcium, barium, strontium, magnesium and silica concentrations. However, APS softening technology at pH 10.5 has achieved a moderate reduction (10-20%) of SiO_2 and magnesium (Rahardianto et al., 2007).

Overall, there are no publications assessing the integration of a 'High-pH pretreatment' between consecutive RO stages for scale control, concentrate minimization and by-products recovery in municipal desalination systems dealing with magnesium-dominated groundwater. This study targets maximum magnesium removal through a 'High-pH pretreatment' of the primary RO concentrate. It has been hypothesized that *Rw* could be enhanced in inland facilities dealing with magnesium-dominated waters since magnesium-bearing minerals that precipitate at high-pH could simultaneously remove scale forming precursors, such as silica, through precipitation and adsorption/enmeshment mechanisms. Then, following pH readjustment and final AS addition, the softened concentrate could be further concentrated in secondary RO. In addition, $CaCO_3$ recovery from precipitated sludge could be possible though CO_2 injection to selectively dissolve magnesium. Recovered $CaCO_3$ could then be re-calcined as a quicklime. This technology for by-products recovery has already been tested in conventional water treatment plants in the USA during the 1970s (Black and Thomson, 1971, 1975; Sanks, 1978).

Research gap 1: *No studies have focussed on the integration of a 'High-pH pretreatment' between consecutive RO stages for scale control, concentrate minimization and by-products recovery in municipal desalination systems dealing with magnesium-dominated groundwater.*

Electrodialysis (ED) or electrodialysis reversal (EDR), forward osmosis (FO) and MD are also membrane desalination processes. Such technologies can also be affected by salt scaling. Among them, MD technology has been proposed in some studies for minimization of RO concentrates (Drioli et al., 1999; Ji et al., 2010; Duong et al., 2015). MD is a thermally driven technology which involves the transport of vapour molecules through a microporous hydrophobic membrane (Boubakri et al., 2014). MD technology is available in different configurations: (a) direct contact membrane distillation (DCMD); (b) AGMD; (c) sweeping gas membrane distillation; and (d) vacuum membrane distillation (Alkhudhiri et al., 2012). In AGMD configuration, the vapour crosses a stagnant air gap and condenses over a cold surface (Alkhudhiri et al., 2012). In this case, the driving force is the temperature difference over the membrane and the gap (Eykens et al., 2017) .

Mineral salt scaling can occur on MD membranes, as reported in the literature (Tijing et al., 2015; Warsinger et al., 2015). Temperature is considered to be a key factor related to scaling (Warsinger et al., 2015). AS can be added to minimize the scaling problem (Duong et al., 2016). However, AS addition presents several drawbacks and limitations (Tijing et al., 2015). To date, the integration of a chemical demineralization treatment (using APS technology) between RO and MD for scale control and RO concentrate minimization has only been reported in one paper. That study was performed with low conductivity RO concentrate and utilized a DCMD set up (Qu et al., 2009). Salt precipitation and scaling might have a different effect on other configurations such as AGMD (Tijing et al., 2015). Therefore, the implementation of 'High-pH treatment' of RO concentrate followed by AGMD for RO concentrate minimization requires investigation. In addition, it would be beneficial to compare the efficacy of AS addition and 'High pH pretreatment' (followed by pH readjustment and final AS addition) for scale prevention and RO concentrate minimization in a batch AGMD unit.

Research gap 2: *No previous research has evaluated the combined effect of 'High-pH pretreatment' and AGMD technology for RO concentrate minimization in a municipal desalination facility treating magnesium-dominated groundwater.*

2.4 Efficiency of a 'High-pH pretreatment' for boron removal from groundwater

Boron can be present in water from either natural or anthropogenic sources (Cengeloglu et al., 2008; Xu and Jiang, 2008). The average boron concentration in groundwater varies from 0.3 to 100 mg/L (Hilal et al., 2011; Wang et al., 2014; Guan et al., 2016). Mostly, boron levels in groundwater are very low (<0.1 mg/L) (Bundschuh et al., 1993a). However, there are exceptions reported in the literature. In groundwater samples collected in the USA, Turkey, Italy, Cyprus and Greece, boron concentration ranged between 5 and 24.8 mg/L (Hudak, 2004; Bouguerra et al., 2008; Cengeloglu et al., 2008).

Different industrial manufacturing processes use boric acid or boron salts (Bouguerra et al., 2008), thus water contamination is possible (Wang et al., 2014; Bodzek, 2016). At present, more than 50% of the production of boron compounds worldwide is used in the glass industry (Wang et al., 2014; Guan et al., 2016). Boron levels up to 2 mg/L can also be found in domestic wastewater (Bouguerra et al., 2008). Finally, boron concentration can be high in geothermal waters (Bundschuh and Tomaszewska, 2017).

Depending on both the frequency and extent of exposure, boron can be toxic to human health (Hossain and Maraqa, 2014). In 1998, the revised European Union (EU) Drinking Water Directive included a new standard for boron concentration in drinking water of < 1 mg/L (Parks and Edwards, 2005; Weinthal et al., 2005).

For concentrations below 250 mg/L, boron is present in water as boric acid or hydroxyborate ion (Bundschuh et al., 1993b). At low pH levels, boron is present in water as un-dissociated boric acid (Bundschuh and Tomaszewska, 2017). On the other hand, hydroxyborate ion becomes the predominant species at high pH levels (Rodarte and Smith, 2014; Bundschuh and Tomaszewska, 2017). In addition, both species can co-exist as an equilibrium mixture at pH levels between 7.0 and 11.5.

Some researchers have studied state of the art technologies for boron removal from different kinds of waters (Parks and Edwards, 2005; Xu and Jiang, 2008; Hilal et al., 2011; Tagliabue et al., 2014; Wang et al., 2014; Güler et al., 2015; Bundschuh and Tomaszewska, 2017). The use of boron-selective ion-exchange resins seems to be the most effective technology (Bundschuh and Tomaszewska, 2017). In seawater desalination, boron concentration can be reduced by combining multi-pass RO with pH adjustment. The first RO pass is operated at a lower pH for salt removal while the second RO pass is operated at higher pH for effective boron removal (Greenlee et al., 2009). Alternatively, RO technology can be combined with ion exchange technology (Jacob, 2007). In brackish water desalination, a second pass at higher pH is not considered a feasible solution due to the required higher water *Rw*, the lower boron rejection of brackish RO membranes, and the presence of scale-forming ions (Greenlee et al., 2009). Moreover, it is not economically viable for groundwater with high boron concentrations (Glueckstern and Priel, 2007). Overall, it has been reported that boron rejection can be limited to 15-20% in real water desalination systems using brackish water membranes (Greenlee et al., 2009). Consequently, RO technology using brackish water membranes alone is not sufficient to fulfil current or future boron removal guidelines depending on initial boron concentration. That being the case, further boron removal from RO permeate could be achieved by implementing ion-exchange technology. Alternatively, the process could be optimized in certain plants by the implementation of additional RO stages using seawater membranes capable of achieving higher boron rejection followed by additional boron removal by selective ion exchange resins where required (Glueckstern and Priel, 2007).

The implementation of a high-pH softening treatment for boron removal has been reported in only a few studies and for different kinds of waters, such as seawater, groundwater, and flowback and produced waters (Parks and Edwards, 2005, 2006, 2007; Ayoub et al., 2014; Rodarte and Smith, 2014). Furthermore, the effectiveness of a ‘High-pH pretreatment’ for boron removal in groundwater, and in particular when the magnesium concentration is higher than the calcium concentration, is yet to be explored thoroughly. Overall, the mechanism of boron removal may be related to magnesium precipitation during the softening treatment. At high pH levels, hydroxyborate ion could be removed by sorption onto precipitated magnesium compounds (Parks and Edwards, 2007). The common presence of dissolved magnesium in brackish groundwater could facilitate the boron removal process. A recent study involving the treatment of seawater achieved 61% boron removal by precipitation softening at a pH of 11.0 (Ayoub et al., 2014).

In addition, boron removal by adsorption of hydroxyborate ions onto magnesium oxide may be another suitable option (Del Mar de la Fuente García-Soto and Camacho, 2006; Rodarte and Smith, 2014). Alternatively, a previous study reported that the addition of magnesium chloride before the softening treatment for boron removal required two-thirds the dose and one-sixth the cost than final MgO utilization. That study was performed with flow back, and produced water (from the oil and gas industry in the USA) containing 60 mg/L of boron (Rodarte and Smith, 2014).

Therefore, there is a clear research opportunity to investigate, on a laboratory-scale, the implementation of a ‘High-pH pretreatment’ in inland desalination plants dealing with magnesium-dominated waters with relatively high boron concentrations (5 mg/L), to meet stringent boron-specific standards (< 1 mg/L). It would also be beneficial to explore the optimization of the process by the preliminary addition of magnesium chloride before the ‘High-pH pretreatment’ or by means of a final polishing step for boron removal from softened water by adsorption of hydroxyborate ions onto magnesium oxide. Eventually, it would also be useful to assess the combined effect of these chemical treatments for boron removal with ED technology using a non-selective membrane.

Research gap 3: *It is unclear whether ‘High-pH pretreatment’ can enhance boron removal in inland desalination systems treating magnesium-dominated groundwater.*

2.5 Chapter summary

This chapter presents the literature review and identifies the research gaps addressed by this research project.

In the first section of the chapter, the review provides a general overview of Australia’s groundwater resources, RO technology and brackish groundwater quality. The second section presents the differences between seawater and brackish water desalination. The third section describes the major fouling and scaling categories in brackish water desalination and the available pretreatment options. It also provides the justification for this research project’s selection of an intermediate ‘High pH-pretreatment’ between consecutive RO stages or between RO and AGMD for scale control, RO concentrate minimization and by-products recovery. Finally, the fourth section describes the choice of other contaminants such as boron also used for exploring the capabilities of a ‘High-pH pretreatment’ prior to RO desalination.

The research gaps of this study have been identified step by step: 1) integration of a ‘High-pH pretreatment’ between consecutive RO stages for scale control, concentrate minimization and by-products recovery in municipal desalination systems treating magnesium-dominated groundwater; 2) evaluation of a ‘High-pH pretreatment’ and AGMD technology for RO concentrate minimization in inland desalination systems treating magnesium-dominated groundwater; and 3) evaluation of a ‘High-pH pretreatment’ to enhance boron removal in inland desalination systems treating magnesium-dominated groundwater. These gaps are discussed in detail in each of the manuscripts as shown in Chapters 4 to 6.

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CHAPTER 3

A review of strategies for RO brine minimization in inland desalination plants

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PAPER I

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3.1 Introduction

This review manuscript explores the differences between seawater, brackish groundwater and co-produced coal seam gas (CSG) water desalination. It also provides an in-depth review of the 'state of the art technologies' for RO concentrate minimization towards ZLD in inland desalination plants with special focus on the potential for scaling. Unlike previous review studies in the literature, this manuscript compares the efficacy of different two scale control technologies for RO concentrate minimization in inland desalination plants: a) acid/AS addition and b) 'High-pH pretreatment'. The second technology looks at the integration of a chemical demineralization treatment between consecutive RO stages, or between RO and other advanced desalination systems such as MD for scale control. Finally, more complex ZLD and volume reduction systems, such as the high efficiency RO (HERO™) and the SAL-PROC™, are evaluated.

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A review of strategies for RO brine minimization in inland desalination plants

Javier Rioyo[a,*], Vasantha Aravinthan[a], Jochen Bundschuh[a], Mark Lynch[b]

[a]*University of Southern Queensland, School of Civil Engineering and Surveying, Faculty of Health, Engineering and Sciences, West Street, Toowoomba, Queensland 4350, Australia, Tel. +61 7 4631 2100; emails: javier.rioyorumayor@usq.edu.au (J. Rioyo), vasanthadevi.aravinthan@usq.edu.au (V. Aravinthan), jochen.bundschuh@usq.edu.au (J. Bundschuh)*
[b]*University of Southern Queensland, School of Agricultural, Computational and Environmental Sciences, Faculty of Health, Engineering and Sciences, West Street, Toowoomba, Queensland 4350, Australia, Tel. +61 7 4631 2100; email: mark.lynch@usq.edu.au*

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ABSTRACT

Water scarcity in many inland areas is increasing the demand for new groundwater desalination plants. Co-produced coal seam gas (CSG) water (or coal bed methane as known in the USA), which is mostly brackish, is extracted in huge quantities during CSG production and requires advanced treatment. Reverse osmosis (RO) is the leading technology applied in municipal desalination and for treating CSG water in Australia and in some locations in the USA. Antiscalants are often dosed during RO pretreatment to prevent membrane scaling. Recovery rates are limited by antiscalant efficacy and large volumes of brine are frequently disposed of in evaporation ponds. The search for environmentally friendly methods for RO brine minimization is considered as a key global issue. In this paper, differences between inland and seawater desalination are highlighted. The existing technologies for RO brine minimization and zero liquid discharge (ZLD) for inland desalination are reviewed. The efficacy and application of two scaling reduction technologies for RO brine minimization: (i) acid/antiscalant addition and (ii) 'high pH precipitation treatment' are compared. Finally, more complex ZLD and volume reduction systems, such as the high efficiency RO (HERO™) and the SAL-PROC™, are analyzed as well.

Keywords: Reverse osmosis in inland areas; Brackish groundwater; Coal seam gas water; Brine minimization; Zero liquid discharge

1. Introduction

As freshwater supplies diminish, desalination of brackish groundwater resources is becoming an increasingly viable option for inland communities in countries that have limited access to fresh surface water supplies or desalinated seawater to meet increasing demand [1,2]. Reverse osmosis (RO) is the dominant, widely adopted, affordable technology in municipal desalination in comparison with thermal desalination. However, brine disposal is one of the biggest drawbacks of this technology especially for inland areas that have very limited options [1–3].

Conversely, coal seam gas (CSG) or coalbed methane is an important energy resource in many countries like United States, Australia, China, Canada and India [4–6]. Large amounts of brackish groundwater are co-produced during gas production [7,8]. It is estimated that about 300 GL/year of CSG water could be produced over the next two decades in Australia alone [4,9]. This large-scale extraction of typically brackish groundwater associated with CSG exploitation has created concerns over potential adverse effects on groundwater resources and arable land. In Australia, the simple storage of co-produced CSG water is no longer permitted [6,10], and advanced treatment by RO is considered the best available technology [6,11]. In the USA, deep well reinjection is very common [10] although ion-exchange technology has been also applied for reducing the concentrations of sodium and bicarbonate [12]. In China, CSG water is mainly managed by surface impoundments and evaporation [13].

Overall, RO brine management remains as a significant challenge in co-produced CSG water desalination when the

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* Corresponding author.

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huge quantities involved and environmental risks of storage are considered [4,8,11,14,15].

Since both inland municipal and CSG water treatment facilities cannot dispose of RO brine into a large body of water, such as the ocean, they operate at high recovery rates (R_w) to minimize the volume of brine to be discharged. Previous studies have reviewed the state of the art technologies for RO brine minimization [16,17]. Among these technologies was the use of two or more RO stages to further increase the R_w [2,18].

Considering that RO is a membrane separation process, the consequences of high R_w on the membranes are increased energy demand due to the increased osmotic pressure required corresponding to the increase in total dissolved solids (TDS), reduced permeate quality, and increased scaling. Increased concentration also leads to increased scaling. Some constituents present in brackish groundwater will precipitate if the concentration product of the salt formed exceeds its solubility product (K_{sp}). Sparingly soluble salts that can scale the RO membrane are $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, CaF_2 and SiO_2 (silica) [19]. Scaled membranes require higher than normal operating pressure, and chemical cleaning is required to minimize the risk of irreversible scaling [20], which leads to reduced membrane lifetime.

Different technologies, such as adsorption, precipitation or ion-exchange, can be applied between consecutive RO stages to prevent scale formation and increase R_w. However, further research is needed to improve the efficiency [2]. Among other technologies, an intermediate 'high pH precipitation treatment' allows the removal of undesirable precipitated species from primary RO brine by physical separation processes.

However, not all the brine can be concentrated by applying multistage RO systems. Once the risk of membrane scaling is overcome, practical restrictions to the osmotic pressure become the limiting factor. RO technologies allow brine concentration to reach 65,000–75,000 mg/L TDS. After this limit is reached, more advanced and expensive concentration technologies are required [21].

High recovery systems can achieve recoveries above 92% depending on the feed water composition [21]. However, even if brine is concentrated and reduced in volume, the final disposal of this reduced volume remains very difficult for inland plants with the focus on avoiding contamination to inland aquifers and other environments. This has led several researchers to investigate the development of zero liquid discharge (ZLD) applications where brine discharge is not possible. In this case, reject brine is no longer considered as a waste but as a resource from which useful dry salts, metals and desalinated water can be recovered so there is no discharge of liquid waste from the treatment facility. The technologies available aiming at ZLD are expensive and the most common approach in municipal desalination involves the following steps: primary RO system, intermediate treatment of RO concentrate to reduce its precipitation potential, secondary RO system, thermal desalination and evaporation ponds [2]. Other conventional processing technologies include thermal crystallizers, spray dryers and landfills [21].

Overall, RO brine minimization, including possible salt recovery, aiming for ZLD is a significant economic challenge for inland desalination facilities. Further research is needed to minimize capital (Capex) and operating (Opex) expenditure in ZLD processes [2,8,21,22]. This paper aims to (a) review the differences between seawater, brackish and CSG water desalination and the challenges faced; (b) critically review the existing technologies for minimizing the brine volume and ZLD in inland desalination; (c) highlight the scaling potential in these technologies; (d) provide insights into strategies integrating an intermediate 'high pH precipitation treatment' with another concentration system for RO brine minimization for groundwater supplies; and (e) analyze more complex ZLD and volume reduction systems like the high efficiency RO (HERO™) and the SAL-PROC™.

2. Differences between seawater, brackish groundwater (municipal desalination plants) and co-produced CSG water desalination

2.1. Comparison of the quality of the source waters

As shown in Figs. 1 and 2, seawater has a similar composition worldwide [23]. Chloride is the predominant ion followed by sodium, sulphate, magnesium, calcium and potassium. The standard TDS concentration in seawater is 35,000 mg/L [23]. In general, desalination costs are influenced by ocean salinity and temperature [24]. Boron removal is complex [25]. Its concentration in seawater is about 4.8 mg/L. Boron content can be reduced below 0.5 mg/L by combining RO and ion-exchange technology [26] or applying multipass RO with pH adjustment [27]. The R_w in seawater desalination is limited by osmotic pressure, energy consumption and allowable salinity/boron concentration in the RO permeate [23]. On the other hand, RO concentrate disposal is not a problem, as brine can be discharged back into the ocean with the pumping system and length of piping key factors in the design process [25]. Seawater desalination plants are often configured with one or more RO passes depending on different factors, such as boron concentration, R_w, energy costs, and product water standards [25]. Scaling is not considered as a limiting factor [23] although seawater membranes can be fouled by organic and particulate material [28]. Seawater desalination plants working with open intakes are also prone to biofouling [23]. About one-third of feed seawater

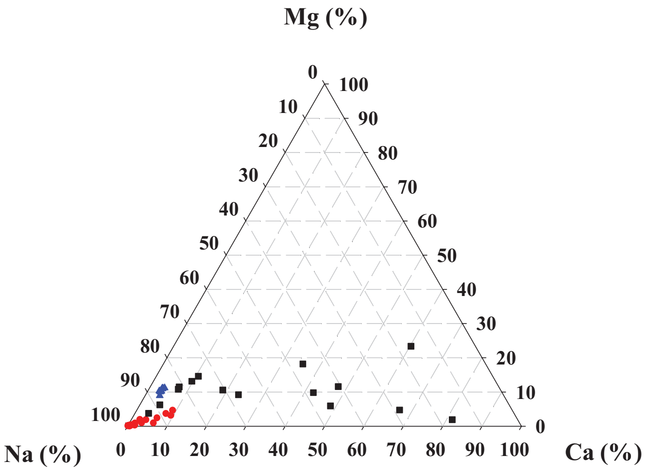

Fig. 1. Relationship (%) between significant cations present in seawater (blue colour), brackish groundwater (black colour) and co-produced CSG water (red colour).

is recovered as permeate while two-thirds is discharged as RO brine with a TDS level of about 52,000 mg/L. The costs of desalinating seawater in Australia and the USA are estimated at US\$1.5–2.3/m^3 [11] and US\$1.54–2.43/m^3 [29], respectively. The use of energy recovery devices in seawater desalination is common for reducing overall operating expenses. Efficiencies up to 65% were previously reported [30]. (Note: Quality data to complete Figs. 1 and 2 represent worldwide characteristics and was collected from different books/technical papers [3,9,11,23,31–44] and analytical records supplied by the Western Downs Regional Council (Australia) from different municipal groundwater wells.)

In contrast, brackish groundwater has a lower TDS level ranging from 1,000 to 10,000 mg/L [45]. Its chemical composition varies widely depending on different factors like the host-rock type, the nature of overlying soils and rainfall [1]. It typically has low particulate or colloidal contaminants and low organic carbon content while silica and boron concentrations can vary significantly. Therefore, and in contrast to seawater, precipitation of carbonates, sulphates and silicates, and hence membrane scaling can be problematic. Precipitates of $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$ and silicates can become limiting factors for desalination. R_w levels in municipal facilities vary from 75% to 90%, and the ratios of calcium/TDS, carbonate/TDS or sulphate/TDS are higher than in seawater desalination [25]. Further RO brine minimization is required. Brine management costs are also higher in inland desalination compared with seawater desalination [16]. A design including a single stage system with an additional module connected to treat RO brine is considered the best option both economically and environmentally by some researchers as shown in Fig. 3. This configuration increases recovery and minimizes operating costs [46]. Depending on feed water salinity, single stage RO systems are typically sufficient for recovery of around 40%–60% freshwater, while two stage RO systems can increase R_w up to 80% [23]. Due to lower salinity (<10,000 mg/L) and osmotic pressure of the brackish feed water, the first stage in a two stage system commonly operates at high flux but low pressure (up to 4.1 MPa) [47]. In this case, brackish water membranes are selected during the design process [23,46]. Brine generated is then treated in an additional RO stage at higher pressures (up to 6.9 MPa) [47], due to the higher osmotic pressure required when the TDS concentration and salinity are higher. Seawater membranes are often selected for the second RO stage [46] due to their potential to provide higher salt rejection (R_s) while treating high salinity feed water of up to 50,000 mg/L TDS [23].

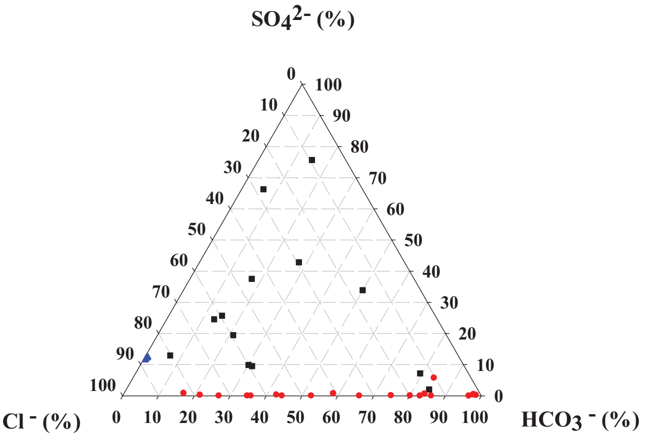

Fig. 2. Relationship (%) between significant anions present in seawater (blue colour), brackish groundwater (black colour) and co-produced CSG water (red colour).

Co-produced CGS water in Australia generally has TDS levels that range from 300 to 10,000 mg/L [48]. In the Rocky Mountains region of USA, the TDS content varies from 150 to 39,260 mg/L [38]. Overall, CSG water quality can vary significantly even between wells in close proximity [6,39]. As shown in Fig. 2, co-produced CSG water primarily contains NaCl and $NaHCO_3$ [7,8,14]. Sulphate concentration is low. CSG water composition is a result of different biological and geological processes that have taken part in the formation of CSG [37].The pH level and sodium adsorption rate can be high. In the Rocky Mountains, values of 9.26 and 452.8 mg/L have been recorded [38]. In Australia values of 9.1 and 567 mg/L have been observed [9]. Co-produced CSG water may also contain hydrocarbons or saturated gases depending on the well source [49]. Variable amounts of aluminium, silica, barium, calcium, magnesium and fluoride can also be present. Boron concentrations up to 4.7 and 3.1 mg/L were recorded in the USA and Australia, respectively [9,38]. In general, modular RO plants for co-produced CSG water treatment are designed in a multistage configuration [11,39] and R_w levels around 75%–80% can be easily achieved [6,14,39,49,50]. In the USA, generated RO brine is frequently managed by deep-well injection [12]. In Australia, RO brine is often placed in evaporation ponds while alternative options for beneficial uses are explored [6,8,14,48,49]. Layers of clay and synthetic membranes are required in pond construction to prevent contamination of groundwater aquifers [10]. The design of

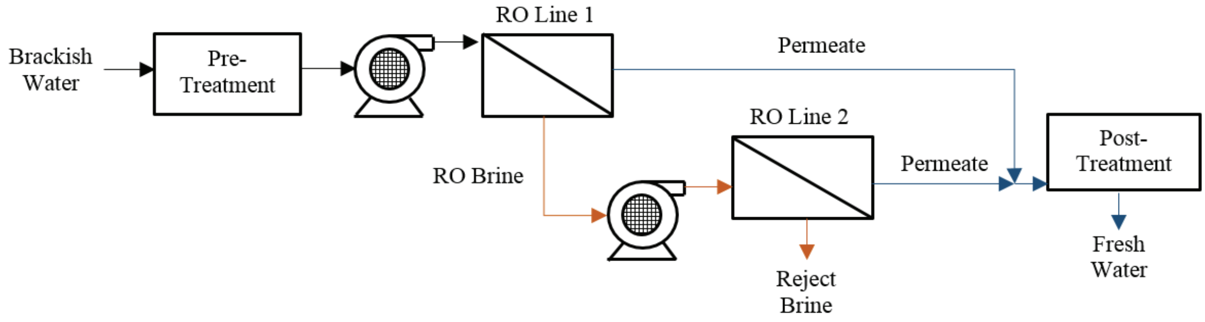

Fig. 3. Multistage RO system with intermediate pumps.

Table 1
Differences between seawater, brackish groundwater (municipal facilities) and co-produced CSG water

	Seawater desalination	Brackish groundwater desalination	Co-produced CSG water desalination
Water quality	Chloride is the predominant ion TDS = 35,000 mg/L [24]	Chemical composition is variable TDS = 1,000 to 10,000 mg/L [45]	Bicarbonate is often the dominant anion species [9,14] TDS = 300 to 10,000 mg/L [9,48]
Rw during RO desalination	35%–50% [25]	75%–90% [25] 65%–85% [21]	75%–80% [6,14,39,49]
RO brine disposal methods	Discharged back into the ocean [25]	Evaporation ponds, surface water discharge, discharge to wastewater treatment, subsurface injection and land application [21]	In Australia RO brine is temporally disposed of in evaporation ponds while other options are studied [6,8,14,48–50]. In the USA, deep well injection is common [8,12]

a CSG brine pond generally includes two separate lining layers and a monitoring system [14]. Table 1 summarizes the general quality characteristics, achievable R_w and existing RO brine disposal methods for seawater, municipal brackish groundwater and co-produced CSG water desalination.

2.2. Pretreatment options in RO desalination

Seawater pumped from the ocean needs to be pretreated to remove suspended solids and other matter in order to avoid membrane fouling. Worldwide, conventional pretreatment in RO plants often includes the addition of coagulant, pH adjustment, media filtration, cartridge filters, disinfection and final antiscalant addition [24,51]. Although $CaCO_3$ precipitation is possible, it is not likely to occur due to the low R_w expected in most seawater desalination plants [25].

Brackish groundwater sources for drinking purposes in municipal systems have less fouling propensity than surface water with consequently less extensive pretreatment needed prior to RO. Depending on the microorganism content, disinfection may be necessary [52]. Total hardness reduction by ion-exchange technology can be limited by water chemistry and chemical regeneration costs [53]. Conventional pretreatment in municipal facilities often combines media filtration with acid or antiscalant addition to prevent scaling. Antiscalants retard the precipitation of sparingly soluble salts and promote supersaturation [19]. Commercially available antiscalants are relatively cheap [54] and work by inhibiting crystal formation or by surface modification of the crystals [20]. However, it is important to mention that antiscalant addition during RO pretreatment can have adverse effects in a later brine treatment that uses precipitation to remove potential scale forming minerals. In fact, $CaCO_3$ precipitation from RO brine can be reduced and filtration performance decreased [55]. Moreover, an excessive dose of antiscalants during RO pretreatment can increase the risk of biofouling [56,57].

Co-produced CSG water can vary in quantity and composition, and so requires a reliable and flexible pretreatment process. Since the wells are not cased, co-produced water with high suspended solids is discharged into the pond from where the water is sourced for RO pretreatment. Algae formed in the feed pond and dissolved organic compounds from the fracking process or the coal seam also need to be removed before the desalination process [11]. Reduction of total suspended solids is essential since a silt density index lower than 3 is required for the desalination process. The use of suitable coagulants and flocculants for solid–liquid separation (clarification process) requires screening work and later sludge management [49]. Particle separation technologies frequently used during CSG water pretreatment are dissolved air flotation and microsand ballasted flocculation [7]. Lime softening or weak acid cation resins can also be used for CSG water softening before RO desalination [4]. Variable levels of fluoride, silica, barium, sulphate and calcium render the treatment process difficult and may require the use of specific antiscalants [49]. Disinfection can be achieved by chlorination/dechlorination [49] or ozone addition [4]. Recently, the use of containerized treatment plants combining microfiltration for suspended solids removal with spiral wound RO membranes has shown to be a cost-effective and reliable solution for CSG water treatment. These mobile treatment plants can be automatically controlled via a programmable logic controller [58].

3. ZLD and RO brine minimization technologies in inland desalination plants

3.1. ZLD concepts, brine minimization technologies, and challenges in municipal desalination

High recovery systems aimed at brine minimization have been defined in municipal desalination as those systems achieving recoveries higher than 92% [21]. ZLD is defined as a high recovery system allowing that no effluent leaves the ground-level plant boundary. In a ZLD approach, all the brine is either recovered by a combination of technologies to produce desalinated water or dry salts. Technologies commonly recommended in ZLD processing systems include: RO, vacuum evaporators, crystallizers, evaporation ponds and spray dryers. Salinity and composition of the brine to be processed in the ZLD system has a substantial influence on capital and operating costs. Sequential and selective removal/recovery of salts from concentrated brine should follow the sequence shown in Table 2, from low to high solubility levels. Although technically feasible, high recovery and ZLD systems are currently not economically viable in municipal desalination [21].

Table 2
Sequence for salt recovery/removal in a ZLD process

Salt solubility level	Salt	
Sparingly	$CaCO_3$ $CaSO_4$ $Mg(OH)_2$	↓ Salt removal/recovery Sequence
Moderately	$Na_2(CO)_3$ $Na_2(SO)_4$	
Soluble	NaCl	
Highly	$CaCl_2$ $MgCl_2$	

As previously stated, membrane desalination is considered to be the predominant technology to be used in municipal desalination [2] and ZLD systems. Operating costs are reduced by applying a system including consecutive RO stages for brine minimization. Fig. 3 shows a 'two-stage RO system' with modules connected to reject brine with booster pumps. By implementing 'seawater membranes' in the second stage, R_w increases and additional permeate output can be achieved [52]. The osmotic pressure depends on the concentration of dissolved salts in solution [31]. Due to the lower salinity of the brackish feed water, 'RO line 1' operates at a lower pressure. The brine generated in 'RO line 1' is then fed into 'RO line 2', where the salinity becomes higher. Overall, tandem RO processes for maximum water recovery and RO brine minimization are considered to be promising alternatives in brackish water desalination. However, particular process conditions need to be analyzed carefully on a site-by-site basis [18].

Electrodialysis (ED) or electrodialysis reversal (EDR), forward osmosis (FO) and membrane distillation (MD) are also membrane separation processes. ED is another desalination technology that employs electrical potential difference to move ions through ion-exchange membranes. As shown in Table 3, ED is considered as an alternative to RO but it is often only recommended for treating brackish water with TDS level below 10,000 mg/L [23]. For higher salinities, RO is more competitive since ED cost is proportional to the amount of salts carried through the membrane [59]. Further research is required to avoid scaling in ED units and to improve selectivity and permeability of membranes [17].

FO is another technology for brine concentration with low energy consumption [17]. In contrast to RO, the osmotic pressure is the driving force for mass transport [60]. The main drawbacks of FO technology are the risk of salt precipitation on the membrane, the need to develop more robust membranes and a suitable draw solute to improve the separation process [17,60]. Finally, MD is a promising alternative for treating highly concentrated water. The vapour pressure difference induced by the temperature difference across a hydrophobic membrane acts as the driving force [8,14,50]. Still MD is not a mature technology and most of the research work thus far published has focussed on laboratory scale studies to investigate the influence of operating conditions [61].

Although RO is the leading technology in inland desalination and ZLD systems, not all of the RO brine can be concentrated using additional RO stages [2]. The configuration shown in Fig. 3 increases R_w but is far from achieving ZLD [17]. Once the brine is highly concentrated (TDS > 50,000 mg/L) and thus limited by the osmotic pressure, RO technology is not effective [23]. In this situation another downstream process, such as vacuum evaporation, has to be applied in municipal desalination facilities [18]. In this approach, vacuum evaporation follows RO when sufficient treatment has been performed to remove potential scalants. This approach minimizes costs and reduces the volume of brine that eventually has to be concentrated by the evaporator, as shown in Fig. 4 [2,21]. Finally, concentrated brine can be disposed of in an evaporation pond. Alternatively, it is technically possible to obtain salts in a solid, dry and crystalline form by applying a later crystallization process [62]. Such a ZLD solution is environmentally friendly with consequent nil discharges into the environment. However, further research is required to reduce energy requirements and to develop new systems recovering residual heat or steam [17]. Table 3 summarizes the main features of significant concentration technologies applicable in municipal desalination depending on feed water salinity.

As shown in Table 3, RO is by far the most cost-effective solution in terms of energy consumption, capital and operating costs.

MD, FO and ED technologies have been tested on a pilot plant scale for RO brine minimization in inland desalination, although it is difficult to assess their feasibility on an industrial scale. Martinetti et al. [68] tested/compared vacuum-enhanced direct contact membrane distillation (VEDCMD) and FO for RO brine minimization in two different streams with TDS levels averaging 7,500 and 15,000 mg/L. R_w levels in both technologies were limited by salt precipitation. Water recoveries up to 90% and 81% were achieved, respectively, by FO and VEDCMD. In both cases, antiscalant addition was shown to be effective at maintaining high water flux for an extended time.

Korngold et al. [69] applied ED for the treatment of RO brine saturated with $CaSO_4$ and/or SiO_2. The RO brine was generated in a brackish water desalination facility in Mashabei-Sadeh. The ED treatment was undertaken under reverse polarity in a non-continuous operation. The brine, circulating through the ED system, also passed through a separate $CaSO_4$ precipitator. Mineral precipitation was enhanced by the addition of gypsum seeds. RO brine concentration was successfully increased from 1.5% to 10%. Eventually, further RO brine minimization was limited by SiO_2 precipitation in the ED brine.

Oren et al. [70] also applied ED for RO brine minimization. The feed to the ED unit corresponded to RO brine generated during the desalination of brackish water from the Negev Highlands (Israel). Water recoveries around 97%–98% were achieved by combining RO with ED. Brackish feed water was concentrated from 3,000 to 100,000 mg/L TDS. Chloride levels around 200 mg/L or less were measured in treated water. The ED system was run in a batch mode. Scaling during the ED treatment was prevented by acidification, operating the ED module in a reversal mode (EDR) and by incorporating a side loop crystallizer/settler module. Eventually, concentrated brine from the ED treatment was further concentrated by Wind Aided Intensified eVaporation (WAIV) that brought final brine concentration to over 300,000 mg/L TDS.

Closed circuit desalination is another alternative for brine minimization based on a batch-like operation. Generated RO brine is recirculated to the same RO membrane. A previous study conducted with brackish water achieved 97% water recovery in a single stage operation system and was

Table 3
Recommended operating range, maximum concentration capabilities, energy requirements and production costs for different concentration technologies applicable in brackish water desalination

Technology	System	Operating range	Concentration capacity	Energy requirements	Production costs (US\$/m^3)
RO membranes	Membrane separation process	Brackish water RO membranes: TDS, 50–12,000 mg/L [23]	–	Brackish water (0.54 kWh/m^3)[a]	Municipal brackish water desalination (US\$0.28 to 0.63/m^3)[c] CSG water (US\$1.54/m^3)[d]
		Seawater RO membranes: TDS, 8,000–50,000 mg/L [23]	TDS: 65,000–75,000 mg/L [21]	Seawater (4–6 kWh/m^3)[b]	US\$1.5–2.3/m^3 (seawater)[e]
Electrodialysis (ED/EDR)	Membrane separation process	TDS: 300–10,000 mg/L [23]	TDS: up to 100,000 mg/L[f]	Up to 15 kWh/m^3[g] 6.6–8.7 kWh/m^3 (TDS = 0.45 g/L) [59] (seawater)	US\$0.38–6.38/m^3 (brackish water)[h]
Mechanical vapour recompression (MVR) evaporators	Thermal separation process	Following RO desalination	TDS: above 160,000 mg/L[i]	36 kWh/m^3[j] 30–50 kWh/ton of distillate [67]	(US\$2.1–4.7/m^3)[K]
Crystallizers	Thermal separation process	Following vacuum evaporation[l]	Solid Most of remaining water is recovered as distillate [21]	Vapour compression crystallizers: 52.8–66 kWh/m^3 of feed water [21]	MVR crystallizer: (US\$7.4–10.5/m^3)[k] Mechanical forced circulation crystallizer: (US\$14.8–25.4/m^3)[k]

[a] Brackish water RO treatment plant. Feed water TDS = 4,000 mg/L. R_w = 80% [52].
[b] Sydney seawater desalination plant: 4.2 kWh/m^3. Kwinana (Perth) desalination plant: 4–6 kWh/m^3 [24].
[c] Cost of brackish groundwater desalination in Texas [63].
[d] CSG water desalination in Australia. TDS content in CSG feed water = 6,000 mg/L [11].
[e] Cost of seawater desalination in Australia [11].
[f] EDR technology. Brackish water was concentrated from 3,000 to 100,000 mg/L [64].
[g] Typical values of operational parameters for ED units [65].
[h] EDR treatment costs for treating brackish waters. Production costs depends on R_w and brine disposal costs [66].
[i] Concentration capacity depends on feed water salinity. 160,000 mg/L for a feed water salinity of 60,000 mg/L [21].
[j] Falling film vacuum evaporator. 4,000 L/h capacity [62].
[k] Data provided by Condorchem Envitech. Environmental engineering firm specialized in evaporation techniques.
[l] Concentration and precipitation of salt or sludge from liquid brines.

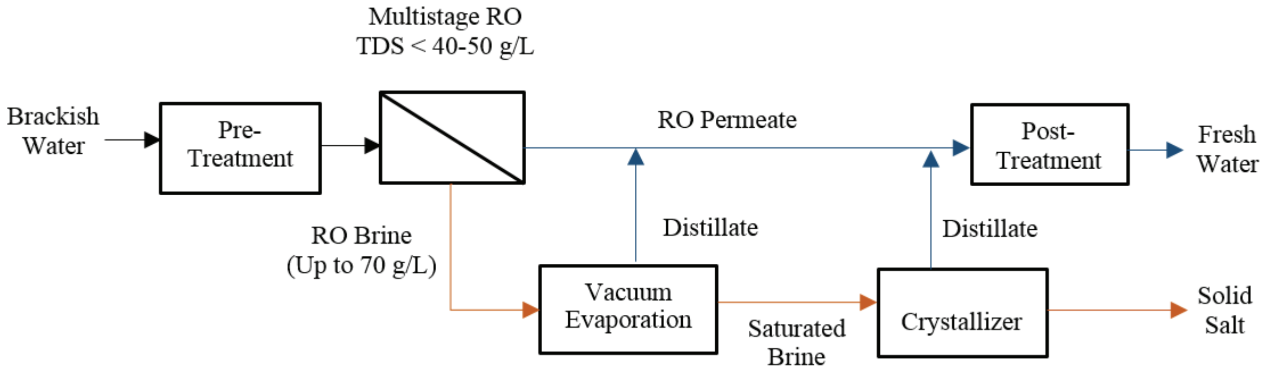

Fig. 4. Traditional ZLD 'lay-out' (municipal desalination).

only limited by salt scaling. This process required less feed pressure and energy when compared with a three stage RO system. In addition, this alternative improved membrane performance and eliminated the use of energy recovery devices [17,71].

WAIV technology was also proposed and compared with traditional evaporation ponds for RO brine minimization. This technology uses wind energy to increase the evaporation rate of brine. This technology, influenced by weather conditions, incorporates a support structure with fabric sheets. During the process, the brine is initially distributed across the sheets. Then, it is concentrated as it flows down the sheets assisted by the evaporation effect of the wind passing across the surfaces. Collected brine at the bottom of the unit can be recycled and further concentrated again in the WAIV plant [72]. Katzir et al. [73] used bench pilot WAIV units to further concentrate ED and RO brines generated during desalination of brackish groundwater. This study also aimed at salt recovery. ED brine was concentrated by WAIV up to 230,000 mg/L TDS. During the experiments, $CaSO_4$ precipitation on the feed basin and the evaporation surfaces was reported. This circumstance led to an enrichment of magnesium relative to sodium in the resulting super-concentrated brine [73]. Overall, one of the main drawbacks of WAIV technology is that it can also pollute groundwater. More experiments at industrial scale are required for process optimization [17].

3.2. ZLD and RO brine minimization technologies in CSG water desalination

The 'CSG Water Management Policy 2012' states the position of the Queensland Government in relation to CSG water management and use. This Policy prioritizes the recovery of useable products from CSG brine wherever feasible [6,8,14,74].

Different studies have been carried out in Australia aiming at RO brine minimization and ZLD in CSG facilities [6,8,14,75]. In this regard, Simon et al. [75] investigated the feasibility of producing NaOH from CSG brine by membrane electrolysis (ME). $NaHCO_3$, Na_2CO_3 and NaCl are the dominant sources of sodium available in CSG brines. In this research, synthetic solutions of these salts were prepared and used as feedstock for the experiments. ME was shown to be more effective for desalting $NaHCO_3$ solutions followed by NaCl and then Na_2CO_3 solutions of equivalent concentration. Moreover, water recovery rates increased as the brine concentration decreased. Finally, it was also reported that the use of 100 g/L $NaHCO_3$ solutions resulted in NaOH production with lower strength (about 12% w/w) than that produced from NaCl solutions with the same concentration. This issue was attributed to the lower electrical conductivity and osmotic pressure of the $NaHCO_3$ solutions.

Duong et al. [8] researched a process for CSG brine (TDS = 14,100 mg/L) minimization including a pilot MD plant equipped with a novel spiral-wound air gap MD module. Water recoveries around 95% were reported by a process combining UF/RO and MD. Membrane scaling was not observed in these experiments. This phenomenon could be attributed to the addition of antiscalant during RO pretreatment and the small temperature gradient applied in the MD step. However, SiO_2 and calcium scales could be present in long-term operation and further research was recommended.

Nghiem et al. [6] investigated a process for the treatment of slightly brackish CSG water (TDS = 2,510 mg/L) generated in the Gloucester Basin (Australia). The process combined UF, RO and multieffect distillation (MED). Water recoveries around 95% were achieved. Generated super-concentrated brine was predominant in $NaHCO_3$ (TDS = 48,000 mg/L). It was reported that antiscalant addition to the RO brine prevented scaling on the evaporative tubes during MED operation. However, mineral deposition on the sight glass of the MED evaporative chamber was observed. The issue was addressed by chemical cleaning with sulphamic acid and NaOH at the end of the experiments.

Duong et al. [14] successfully investigated NaOH production from CSG RO brine by a combination of MD and ME. The feasibility of ME technology for NaOH production using brine generated in seawater or CSG water desalination facilities had been reported in previous studies [75,76]. CSG brine concentration to near saturation was initially required for NaOH production by ME. For this research, synthetic solutions mixing NaCl and $NaHCO_3$ were prepared simulating CSG brine. The MD plant was operated at 90% water recovery and no membrane scaling was observed during the tests. Higher R_w levels resulted in precipitation of NaCl, $NaHCO_3$ and Na_2CO_3 on the membrane and a decrease in distillate quality and water flux. This study concluded that ME combined with MD for NaOH production can achieve energy savings for both processes [14].

Duong et al. [50] also focussed their research on membrane scaling control during RO brine (TDS = 17,100 mg/L) minimization using MD. Generally, prevention of membrane scaling should always be considered as the first option regardless of the efficacy of chemical cleaning. MD experiments showed that water recoveries above 70% resulted in salt precipitation and water flux decline. In this regard, later membrane cleaning was not able to completely remove scale deposits from the membrane. As a consequence, concentration polarization and membrane scaling increased while MD performance decreased. It was also reported that water recoveries around 80% were achievable without membrane scaling by reducing concentration polarization phenomenon by way of limiting feed brine temperature and water flux.

WAIV technology was also tested for CSG RO brine minimization. Initial experiments by a CSG operator were conducted in Roma (Australia) with a demonstration unit. This study concluded that WAIV is able to evaporate 24 times more water than a conventional evaporation pond of equivalent footprint area [72].

Overall, RO brine management remains as a significant technological challenge in CSG desalination and only a limited number of studies on a pilot plant scale have been undertaken in Australia and worldwide [75,77]. Feasible alternatives need to consider RO brine composition and the huge volumes involved. NaOH production from CSG RO brine by ME seems to be a promising option. This alternative has been reported in different technical papers [14,75]. However, the total volume of impurities present in CSG brine could be a limitation for this ZLD approach [76]. Moreover, no matter which technology is initially selected for RO brine minimization/concentration, further research is required to reduce/avoid scaling problems.

3.3. Scaling potential in ZLD and brine minimization technologies

The concentration factor (C_F) in RO desalination can be defined by the following equation where C_c and C_f are the brine and feed water concentrations, respectively, and R_s is the nominal salt rejection [25,56]:

$$C_F = \left(\frac{C_c}{C_f}\right) = \left(\frac{1}{1-R_w}\right)\times\left[1-R_w\times(1-R_s)\right] \qquad (1)$$

According to Eq. (1), when R_w is increased above 70%, C_F increases dramatically enhancing the precipitation of sparingly soluble salts on the RO membrane. Maximum achievable R_w during brackish water desalination can be limited by antiscalant efficacy and salt precipitation on the RO membrane.

In thermal desalination, scaling of heat transfer surfaces is also of great concern having a substantial influence on the overall performance of the desalination process [78]. The scaling risk also has to be reduced when applying other desalination technologies including FO, MD or ED. Table 4 shows references found in the literature of common sparingly soluble salts that might limit overall R_w and scale different concentration technologies.

3.4. Scale minimization technologies: 'high pH precipitation treatment' vs. acid/antiscalant addition

Two opposite and contradictory solutions can be considered to avoid scaling while increasing recoveries in existing inland desalination plants. The first one, involving acid/antiscalant addition to the RO brine, allows salt supersaturation to a certain extent. Then, R_w can be increased by implementing an additional RO stage. In this case, achievable R_w is limited by antiscalant efficacy.

The second option looks at the integration of an intermediate 'high pH precipitation treatment' for RO brine minimization between consecutive RO stages or between RO and another brine concentration system. In contrast to the use of antiscalants, this solution involves mineral precipitation and removal of sparingly soluble salts from the RO concentrate. Following pH adjustment and possible antiscalant addition, the softened brine can be further concentrated by an additional RO stage or another advanced concentration technology. Higher R_w is achievable by applying this second strategy [56,85] with salt recovery options available.

The integration of an intermediate 'high pH precipitation treatment' during municipal brackish water desalination was broadly investigated by different researchers. Most of the work was undertaken on laboratory scale and, using pilot plants, aimed at increasing R_w during inland desalination.

Ning et al. [88] investigated an intermediate lime softening treatment for the concentrates (TDS = 7,465 mg/L) generated in a primary RO system operated at 85%–90% water recovery. That precipitation treatment successfully removed SiO_2 and $BaSO_4$ from primary RO brine. In addition, an extra 70% brine concentration was achieved in a secondary RO unit.

Williams et al. [89] examined the removal of calcium, barium, strontium, magnesium and silica from primary RO concentrate generated from desalting Colorado River water (TDS = 585 mg/L) to allow further concentration in a secondary RO step. A chemical precipitation treatment including coagulation, sedimentation and filtration was applied before further concentrating the brine in a secondary RO stage. R_w of 98% was possible by following this path.

Table 4
Potential scaling salts affecting different desalination technologies

Technology	Reverse osmosis (RO)	Forward osmosis (FO)[a]	Membrane distillation (MD)[b]	Electrodialysis (ED/EDR)[c]	Thermal desalination systems[d]
Scalant	RO membrane	FO membrane	MD membrane	Ion-exchange membrane	Tubing and process surfaces
$CaCO_3$	Yes [20,23]		Yes [50,79,80] (at relatively high saturation indexes)	Yes [81]	Yes [20,82]
$CaSO_4$	Yes [20,23]	Yes [83,84]	Yes [50,79,80,85]	Yes [69]	Yes [20,82]
$BaSO_4$	Yes [20,23]				
$SrSO_4$	Yes [20,23]				
SiO_2	Yes [20,23]	Yes [84]	Yes [8,50,79,80]	Yes [69]	
$Ca_3(PO_4)_2$	Yes[e]		Not found in MD literature [79]		
CaF_2	Yes [23]				
Magnesium scales			Yes[f]		Yes [20,82]

[a] Following chemical cleaning, FO shows better flux recovery than RO in the event of silica scale. Chemical cleaning is also more effective in FO than in RO in the event of $CaSO_4$ scale [84].

[b] Calcium sulphate scale was found to be a common problem in MD [50]. Overall, MD is more fouling resistant than RO [79,86].

[c] Electrodialysis reversal (EDR) has the advantage of descaling membrane surfaces by utilizing a flow and polarity reversal [4,87].

[d] Thermal brine minimization is often limited by precipitation of sodium sulphate, sodium carbonate and sodium chloride [21].

[e] Calcium phosphate scaling can be common when RO is applied to municipal wastewater [23].

[f] Feed solutions with high levels of Mg^{2+} may cause problems in MD [50,79].

Rahardianto et al. [56] looked into the application of accelerated precipitation softening (APS) for the treatment of primary RO from desalting mildly brackish surface water (TDS = 941 mg/L) to allow further concentration in a secondary RO process. The treatment involved alkaline pH adjustment, calcite crystal seeding, microfiltration and pH adjustment to avoid scaling issues during secondary RO. It was demonstrated that high R_w in brackish desalination was achievable by using this technology.

Qu et al. [85] conducted a similar study combining APS with direct contact membrane distillation for the treatment of primary RO brine, increasing overall R_w from 50% to 98.8%. The process included pH adjustment with NaOH, followed by calcite seeding and final microfiltration.

Gabelich et al. [90] explored an intermediate chemical demineralization treatment for primary RO brine (TDS = 4,995 mg/L) generated from desalting Colorado River water. The process included NaOH and $NaHCO_3$ addition for salt precipitation followed by pH neutralization with H_2SO_4, and achieved an increase of the R_w from 85% to 95%.

Sanciolo et al. [91] studied the application of APS technology for the treatment of primary RO brine generated in inland municipal wastewater treatment plants. The removal of 'calcium scale precursor ions' was tested with three different seed materials: (a) $CaCO_3$, (b) $CaSO_4$, and (c) $Ca_3(PO_4)_2$. The first two were not effective. Best results were achieved after addition of $Ca_3(PO_4)_2$ seed particles at 20 g/L or PO_4^{3-} ion in stoichiometric excess of the Ca concentration. Although effective, this treatment resulted in high chemical and energy costs.

Mohammadesmaeili et al. [92] studied the removal of different potential scalants from reclaimed water RO brine by selective precipitation. Products with resale value were recovered during the precipitation process. Three different softening processes were tested including: (a) the traditional lime-soda ash treatment; (b) a modified process with preacidification to eliminate carbonate, and (c) another one including a gypsum crystallization step in combination with the modified process to be applied with high sulphate brines. Overall, good quality calcite and gypsum were recovered in the precipitation process while high efficiency in foulant removal was achieved.

Bond et al. [2] carried out bench scaling tests with RO concentrates of different characteristics in order to remove different insoluble salts affecting R_w during RO desalination. This intermediate process was considered critical since it has a direct impact on following treatment steps like secondary RO or possible thermal desalination. Different technologies were evaluated either individually or in combination including chemical precipitation, fluidized bed crystallization, adsorption with activated alumina and ion-exchange.

In summary, most previous work was aimed at maximizing recovery of water in municipal desalination by removing the potential scale forming offenders from primary RO by using "high pH treatment" aided by NaOH, $Ca(OH)_2$, $NaH(CO)_3$, Na_2CO_3 and also by inducing the crystal formation by adding seed crystals such as $CaCO_3$ and $CaSO_4$. The nature of the chemicals added essentially depends on the RO brine characteristics, cost and salts recovery options from generated sludge. Overall, NaOH is easier to store and manipulate than other chemicals and could be more effective for treating both low and high alkalinity waters [93].

There is an existing groundwater treatment facility in Southern California incorporating an intermediate softening process. This installation includes a high-rate pellet softening and solids clarifier system to treat primary RO brine. Softened and filtered brine is eventually fed to a secondary RO stage. This plant produces $CaCO_3$ pellets that can be used in different applications [94].

Since the initial RO pretreatment in inland desalination plants is usually aided with antiscalant addition, other researchers have investigated antiscalant scavenge/removal when applying an intermediate 'high pH precipitation treatment' between consecutive RO stages.

Greenlee et al. [55] investigated the impact of antiscalants added during RO pretreatment on a later brine treatment, including salt precipitation and solid/liquid separation processes. It was shown that antiscalant addition during RO pretreatment reduced calcium precipitation from RO brine and negatively affected the following solid/liquid separation process. Overall and for higher antiscalant doses, a greater decrease in calcium precipitation was observed during RO brine treatment. In another report, Greenlee et al. [95] also investigated an intermediate RO brine treatment between consecutive RO stages including the following steps: optional oxidation of antiscalants with ozone and H_2O_2, 'high pH precipitation', and solid–liquid separation. The oxidation step was shown to increase calcium precipitation, while the antiscalants solubilizing capabilities were reduced. The R_w increased from 80% to 90% for the non-ozonated brine and from 80% to 94% for the ozonated brine.

Rahardianto et al. [96] also studied a two-step chemically enhanced seeded precipitation (CESP) process performed between consecutive RO stages for the treatment of primary RO brine. The process combined lime treatment to allow $CaCO_3$ precipitation and antiscalant (polycarboxylic acid) scavenge followed by $CaSO_4$-induced precipitation with gypsum seeding. This process could be less chemically intensive than conventional softening while increasing overall R_w from 63% to 87% by applying a secondary RO stage.

McCool et al. [97] investigated antiscalant removal from an RO concentrate with high gypsum scaling potential by lime treatment prior to seeded gypsum precipitation (CESP process). Adequate antiscalant removal (up to 90%) was achieved after the lime treatment process facilitating later seeded gypsum precipitation. Then, R_w can be further increased by implementing a secondary RO stage [97].

Overall, previous research has shown that the application of an intermediate 'high pH precipitation treatment' was able to decrease the adverse impacts of residual antiscalant added during RO pretreatment in municipal desalination. Lime treatment or direct contact with $CaCO_3$ is potential solutions to mitigate negative effects of antiscalants on later salt precipitation and solid/liquid separation processes. This can be a significant issue when considering feasible strategies for RO brine minimization and salt recovery in municipal desalination. Further research is needed to find economical chemical treatments.

Conversely, high bicarbonate concentration in the CSG RO brine remains as a major constraint for the integration of an intermediate 'high pH precipitation treatment' for scale control and RO brine minimization during CSG water desalination. This issue could be addressed to some extent when an acid is initially added to the RO brine to covert HCO_3^- into CO_2, which may be off-gassed. This alternative reduces the quantity of solids generated in the downstream 'high pH precipitation treatment' and the alkaline reagent demand associated with increasing the pH level, though the neutralization of the initially added acid needs to be factored in.

3.5. Other ZLD and volume reduction systems (commercially available or patent protected)

Other existing 'volume reduction technologies' are the ARROW™, HEEPM™, HERO™, and VSEP™ systems. With the exception of HERO™ the rest of the systems is considered as emerging technologies [21]. The HERO™ system, patented by Mukhopadhyay [98], is a process conceived for treatment of water in membrane separation processes. The integration of the HERO™ system in a two stage RO system has already been considered by different authors [17,21]. The hardness/alkalinity ratio in feed water is most often initially adjusted by alkali addition. Then, hardness is removed quantitatively from the primary RO brine in a weak acid cation exchange resin given the adequate hardness/alkalinity ratio. Following that, CO_2 is removed in a degasification process. Eventually, the pH is increased up to 10.5 or higher enhancing the rejection of various species such as silica in the secondary RO membrane system. This technology minimizes the risk of salt precipitation on the RO membrane and water recovery above 90% is achievable when treating brackish water [17]. The application of HERO™ minimizes Capex relative to the brine concentration system. However, although energy costs are also reduced, chemical and solids disposal costs are increased [21].

SAL-PROC™ is a ZLD system that allows the sequential extraction and recovery of different salts like gypsum, NaCl, $Mg(OH)_2$, $CaCl_2$, $CaCO_3$ and Na_2SO_4 from RO brines [16]. This system is particularly recommended for brackish inland brines and for brines with high concentrations of sulphate, potassium and magnesium [17]. SAL-PROC™ combines multiple evaporations and/or cooling stages, supplemented by mineral and chemical treatments. When RO technology is combined with SAL-PROC™ the system is referred as Reverse Osmosis SAL-PROC (ROSP) [15]. Recovered products are high quality. Ahmed et al. [99] have suggested some potential applications for recovered salts. SAL-PROC™ technology was tested by Arakel et al. [15] for the treatment of brackish water from Lake Tutchewop. This solution allowed the recovery of saleable products and achieved ZLD.

SAL-PROC™ was also tested for the treatment of RO brine generated during CSG water treatment in Queensland (Australia). The volumes of saline water were huge. ROSP technology produced fresh or irrigation quality water, chemicals and minerals products as shown in Fig. 5. Overall, SAL-PROC™ technology allows sustainable management and could facilitate a cost-effective solution for large volumes of saline effluent [15].

There is an existing patent for the manufacture of sodium hydroxide and sodium chloride products from CSG RO brine containing NaCl and at least $NaHCO_3$ or Na_2CO_3. This solution combines different processes including lime addition, chemical precipitation for RO brine purification, concentration by evaporation and cooling [100]. In addition, the 'Optimised Salt Recovery' process has also been presented as an alternative to traditional costly selective salt recovery processes. This process works through modification of the CSG brine chemistry to avoid co-precipitation of major salts, while trace impurities are removed from the RO brine [101].

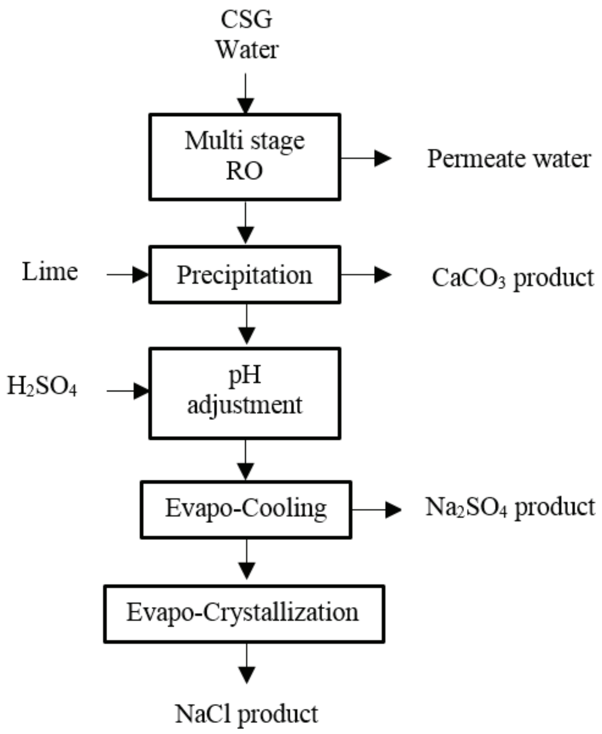

Fig. 5. Application of SAL-PROC™ technology to CSG produced water [15].

Finally, the optimized pretreatment and unique separation (OPUS) process developed by Veolia is recommended for desalination of hard water with high concentrations of silica, organics, heavy metals, boron and particulates. It involves a combination of different processes, such as degasification, precipitation softening, media filtration, ion-exchange, cartridge filtration and RO operated at high pH. The OPUS system has been tested in the oil and gas, and mining industries. The application of this system provides high R_w levels, reduced waste volume, low energy consumption and facilitates an effective control of scaling. OPUS II is a new version of this system specifically focussed on the oil and gas industry. OPUS II simplifies the pretreatment by using ceramic membranes that improve oil removal and facilitate a more compact design [102].

4. Advantages and shortcomings of ZLD, RO brine minimization, and scale control technologies: further research opportunities

The advantages and disadvantages, and research needs/opportunities of the most relevant technologies and systems for RO brine minimization, ZLD and scale control in inland desalination plants have been summarized in Table 5.

Table 5
Summary of characteristics of relevant technologies and systems described in this review paper for RO brine minimization, scale control and ZLD in inland desalination

RO brine concentration technologies

Technology/system	Maturity	Technical	Economic aspects
Evaporation ponds	Industrial scale	Risk of groundwater contamination Discouraged or banned for CSG water management in Queensland (Australia)	Requires large areas of land
WAIV technology	Pilot plant scale	Risk of groundwater contamination Influenced by weather conditions Risk of scaling and fouling Further research required for process optimization	Higher evaporation rates than evaporation ponds
Multistage RO	Industrial scale	Leading technology R_w limited by the risk of scaling and the practical limits to provide the osmotic pressure	Cost-effective solution in terms of energy consumption, Capex and Opex
Evaporators and crystallizers	Industrial scale	R_w in evaporators limited by scaling Further research required to develop new systems recovering residual heat or steam	ZLD approach for RO brine High Capex and Opex
ED	Pilot plant scale	Cost-effective only for treating waters with TDS level below 10,000 mg/L Further research required to avoid scaling and to improve selectivity and permeability of membranes	NaOH production from CSG RO brine can be feasible by ME technology High Capex and Opex
FO	Pilot plant scale	High concentration capacity R_w limited by the risk of scaling Need to develop more robust membranes and a suitable draw solution	Simplicity Moderate energy consumption
MD	Pilot plant scale	Promising alternative Further research required to avoid scaling	High Capex Lower energy requirements than evaporators and crystallizers
Closed circuit desalination	Industrial scale [17]	R_w limited by the risk of scaling	High Capex

Scale control technologies

Technology/system	Maturity	Technical	Economic aspects
Acid/antiscalant addition	Industrial scale	Limited efficacy An excessive dose can cause biofouling	Simplicity Low Capex High Opex
'High pH precipitation treatment'	Industrial scale	Feasible alternative when antiscalants are not further effective Further research required to find economical chemical treatments Its application for CSG brine minimization can be limited by bicarbonate concentration	Salt recovery options Chemically intensive High Capex Later acid/antiscalant addition can be required

Other ZLD and volume reduction systems

Technology/system	Maturity	Technical	Economic aspects
HERO™	Industrial scale for non-municipal applications	Interstage system Minimizes risk of salt precipitation	Minimizes Capex relative to the brine concentration system
SAL-PROC™	Patented Tested for the treatment of CSG brines	Combines multiple technologies Reduction of environmental and operational footprints	Allows selective recovery of salts from RO brine High Capex and Opex
OPUS/OPUS II	Tested in the oil and gas and mining industry	Combines multiple technologies. Reduces scaling risk	Reduced brine volume Low energy consumption High Capex and Opex

5. Conclusions

RO is the dominant technology applied in inland municipal desalination and for treating CSG water in Australia. However, RO brine disposal is considered to be an environmental challenge and one of the main handicaps of this technology. Antiscalants are often dosed during RO pretreatment to prevent membrane scaling. Water recoveries are then limited by antiscalant efficacy and large volumes of brine are mainly disposed of in evaporation ponds while alternative options for RO brine minimization and ZLD are researched. Overall, high recovery and ZLD systems could only be applied in specific cases considering the high Capex and Opex involved. In addition, no matter which concentration technology is selected for RO brine minimization, it becomes necessary to cope with the scaling potential problem.

The traditional ZLD approach recommended in municipal desalination combines sequential RO stages with vacuum evaporation/crystallization when sufficient treatment has been performed to remove potential scalants. This solution requires further research to reduce energy requirements and to develop new systems recovering residual heat or steam. Alternatively, MD, FO or ED technologies have also been proposed for RO brine minimization. However, those technologies were tested at a laboratory level or at a pilot plant scale making it difficult to assess their feasibility on an industrial scale.

Conversely, the Queensland Government Policy, in regard to ‘CSG water management and reuse’, has prioritized the recovery of useable products from CSG brine when feasible. Initial studies performed in Australia have revealed the possibility of producing NaOH from CSG brine by ME. In addition, CSG RO brine minimization has also been achieved on a pilot plant scale by the application of processes combining UF/RO and MED or UF/RO and MD. Overall, economic aspects of these promising alternatives require further investigation, including identifying areas where cost reduction might be possible.

The integration of an intermediate ‘high pH precipitation treatment’ in municipal brackish water desalination was broadly investigated on a laboratory scale, and using pilot plants in the USA. The application of this treatment between consecutive RO stages or between RO and another concentration system is chemically intensive and expensive. However, this approach could overcome antiscalant limitations and increase R_w levels, while salt recovery options are enhanced. But options that can be used to increase the water recovery and to facilitate a ZLD solution require rigorous laboratory investigation due to groundwater and RO brine site specific characteristics. Additionally, the application of this precipitation treatment for scale control and brine minimization in the CSG industry can be limited by high bicarbonate concentration in the CSG RO brine.

Finally, more complex systems for ZLD and RO brine minimization like the SAL-PROC™ have been successfully tested for the treatment of brackish water and CSG brine increasing water recoveries while producing saleable products. SAL-PROC™ involves high Capex making its implementation on an industrial scale difficult. However, recovery of saleable products can help to reduce costs, thus making this technology more attractive.

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Conflicts of Interest

The authors declare no conflict of interest.

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3.3 Concluding remarks

Freshwater *Rw* in inland desalination systems using RO technology is often limited by AS efficacy, and large volumes of concentrate are mainly disposed of in evaporation ponds. Alternative options for RO concentrate minimization and ZLD were researched. Overall, no matter which concentration technology is selected for RO concentrate minimization, coping with scaling is necessary. This Chapter shows that the integration of an intermediate ‘High-pH pretreatment’ in municipal brackish water desalination was broadly investigated on laboratory scale, and using pilot plants in the USA. This approach could overcome AS limitations and increase water *Rw* levels, while salt recovery options could be enhanced. However, options that can be used to increase the water *Rw* and facilitate by-products recovery, require rigorous laboratory investigation due to groundwater and RO concentrate site-specific quality. In this regard and in contrast to the previous studies, the brackish groundwater used for this research program had a magnesium concentration higher than the calcium concentration.

Generally speaking, high recovery and ZLD systems could only be applied in specific cases considering the high Capex and Opex involved. However, the final objective of this study was to encourage the beneficial use of the RO concentrate in a way that protects the environment and maximises its productive use as a valuable resource.

CHAPTER 4

Research on 'High-pH precipitation treatment' for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility

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PAPER II

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4.1 Introduction

This paper explores 'High-pH pretreatment' of RO concentrate followed by secondary RO treatment to increase overall water *Rw* in a municipal desalination facility. In contrast with previous studies that used calcium dominated waters, this study deals with RO concentrate with a magnesium concentration higher than the calcium concentration. This approach is shown to be promising for overcoming AS limitations and membrane scaling during RO desalination. Scale-forming precursors including magnesium, calcium, strontium, barium and SiO_2 are removed from the primary RO concentrate by precipitation and adsorption/enmeshment mechanisms. The study also evaluates $CaCO_3$ and CaO recovery from the precipitated sludge through CO_2 gas injection to selectively dissolve magnesium.

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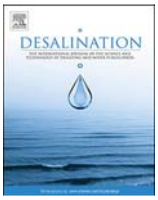


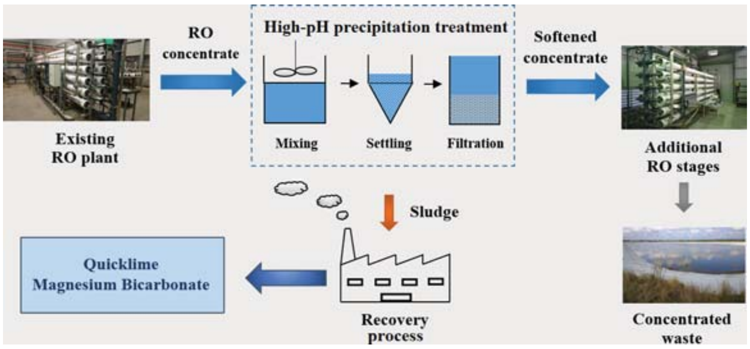
Research on ‘high-pH precipitation treatment’ for RO concentrate minimization and salt recovery in a municipal groundwater desalination facility

Javier Rioyo[a,*], Vasantha Aravinthan[a], Jochen Bundschuh[a], Mark Lynch[b]

[a] University of Southern Queensland, School of Civil Engineering and Surveying, Faculty of Health, Engineering and Sciences, West St, Toowoomba, Queensland 4350, Australia

[b] University of Southern Queensland, School of Agricultural, Computational and Environmental Sciences, Faculty of Health, Engineering and Sciences, West St, Toowoomba, Queensland 4350, Australia

GRAPHICAL ABSTRACT



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ABSTRACT

This study evaluated ‘high-pH precipitation treatment’ of a reverse osmosis (RO) concentrate followed by secondary RO treatment to increase overall water recovery in an existing inland desalination system. In contrast with previous studies that used calcium dominated surface waters, this study dealt with magnesium dominated groundwater. The high-pH process removed scale-forming precursors including magnesium, calcium, strontium, barium and SiO_2 from primary RO concentrate by precipitation and adsorption/enmeshment. Lime and soda ash were determined to be the superior caustic agents when compared to sodium hydroxide for the high pH demineralization process. Following ‘high-pH precipitation treatment’, pH readjustment and antiscalant addition, the use of secondary RO enabled the overall water recovery to be increased from 80 to 97%. In addition, this study evaluated $CaCO_3$ and CaO recovery from the precipitated sludge through CO_2 gas injection to selectively dissolve magnesium.

1. Introduction

On a global scale, membrane desalination using reverse osmosis (RO) or nanofiltration membranes has been the leading technology applied in inland desalination [1]. However, concentrate management remains as one of the main limitations of this technology considering

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* Corresponding author.
E-mail address: Javier.RioyoRumayor@usq.edu.au (J. Rioyo).

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the limited disposal options available [2]. In order to minimize the volume of RO concentrate to be disposed of, brackish water desalination systems tend to operate at high water recovery rates (*Rw*), typically from 65 to 85% [3]. However, fresh water recovery in RO desalination of brackish waters is limited by salt scaling. Different salts, such as $CaCO_3$, $BaSO_4$, CaF_2, $CaSO_4$, $Mg(OH)_2$ or SiO_2, can precipitate on the RO membrane if the concentration product of the salt forming constituents present exceeds the solubility product (K_{sp}) [4]. Salt scaling on the RO membrane can lead to permeate flux decline and reduced membrane life [5]. In addition, operating pressures are higher in scaled membranes while salt rejection is lower [6]. In order to mitigate this problem, antiscalants are often injected during RO pre-treatment to prevent salt precipitation [4,7,8]. Antiscalants retard the precipitation of sparingly soluble salts by inhibiting crystal formation or by surface modification of new crystals [6]. Eventually, *Rw* in the desalination system becomes limited by antiscalant efficacy, and this is an impediment to achieving high product water recovery in inland plants [5].

Another concurrent strategy to enhance both fresh water recoveries and concentrate minimization during the desalination process is to remove scale-forming precursors by the application of an intermediate ‘chemical precipitation treatment’ to the RO concentrate between primary and secondary RO stages [1,9–12]. In contrast with previous RO concentrate demineralization studies performed in the USA with brackish surface waters, groundwater and RO concentrate collected at a municipal desalination facility located in the Western Downs Regional Council (Australia) had a relatively higher magnesium concentration and a lower calcium concentration. The mass ratio Ca/Mg in the RO concentrate was only 0.74, while the same ratio in the studies carried out in the USA ranged from 1.77 to 2.98 [5,9–11,13].

In studies carried out in the USA with calcium dominated concentrate, the presence of inorganic scalants, such as $CaSO_4$, $BaSO_4$, and SiO_2, limited overall *Rw* in the desalination system when conventional scale-control strategies based on pH adjustment and antiscalant addition were applied. In all cases, an intermediate precipitation strategy was tested for scale-forming precursor removal [5,10,11].

Silica and/or magnesium silicate are poorly studied scalants that are often present in waters with high magnesium levels, limiting fresh water recoveries in water treatment systems [6]. In this regard, no studies have been conducted in order to find out the effect of magnesium dominated RO concentrate in salt precipitation and salt recovery following a ‘high-pH precipitation treatment’. It was hypothesized that *Rw* could be enhanced in facilities treating magnesium dominated waters since magnesium-bearing minerals that precipitate at high pH treatment could concurrently remove other scale forming precursors including silica through precipitation and adsorption/enmeshment [14]. In addition, calcite and quick lime recovery from precipitated sludge could be possible through CO_2 gas injection to selectively dissolve magnesium.

Therefore, the aim of this research was to generate knowledge about the integration of a ‘high-pH precipitation treatment’ between consecutive RO stages for the treatment of magnesium dominated concentrates. As a case-study, an existing groundwater desalination facility in Australia was used. Fig. 1 shows a proposed plant layout aiming at RO concentrate minimization and salt recovery. The specific objectives of this research were a) removal of scale-forming precursors from primary RO concentrate, which included magnesium, calcium, barium, strontium and silica, to increase *Rw* in a secondary RO; and b) recovery of by-products, such as $CaCO_3$ and quicklime, from precipitated sludge for later utilization.

2. Background

Some researchers have extensively studied state of the art technologies for RO concentrate minimization [15–17]. A design including consecutive RO stages was suggested as a feasible method to maximize water recovery [3,8,17–19]. This solution could be applied to some extent in existing plants, though further membrane stages cannot be applied for concentrate minimization without first treating the existing RO concentrate to decrease its membrane scaling potential [1]. This could be achieved by applying an intermediate chemical precipitation treatment between consecutive RO stages, allowing for the addition of new RO stages to an existing facility. This intermediate step removes undesirable precipitated species from the primary RO, thus permitting both further concentrate minimization and higher water recovery [1,9–12].

The application of an intermediate ‘chemical precipitation treatment’ between consecutive RO stages has been broadly reported in relation to calcium dominated waters. Most of the research, which was carried out using pilot plants, was aimed at maximizing recoveries by precipitating potential scale-forming salts from primary RO concentrates. Precipitation was induced by the addition of different alkaline reagents such as NaOH, $NaHCO_3$, $Ca(OH)_2$ and Na_2CO_3 [1,5,9–12]. In some cases, a preferential surface area for heterogeneous nucleation and crystal growth was also facilitated by adding seed crystals, such as calcite or gypsum [5]. Previous research has also described the impact of antiscalants added during RO pre-treatment on a later precipitation treatment for RO concentrate minimization. It has been demonstrated that antiscalants inhibit $CaCO_3$ precipitation and precipitated particles were smaller than those formed in the absence of antiscalant [20]. Research was also performed on antiscalant scavenging and removal by different methods. Different strategies, like adding ferric chloride to remove phosphonate inhibitors by way of co-precipitation with ferric hydroxide [13] or advanced oxidation processes with ozone and hydrogen peroxide [21], were successfully tested. Finally, it was also reported that effective antiscalant scavenging could be achieved by an initial RO concentrate treatment with lime and direct contact with precipitated $CaCO_3$ particles. $CaSO_4$ de-supersaturation in the RO concentrate could then be achieved by seeded gypsum precipitation [22,23].

The concentrate used in most of these previous experiments was derived from desalination plants treating brackish surface waters [5,10,12] or reclaimed water [9] in the USA, rather than groundwater. The groundwater may have specific characteristics depending on the aquifer [24].

Brackish surface waters tend to be rich in calcium and low in sodium compared with seawater, while sulphate tends to be the predominant anion as opposed to chloride [25]. In these studies that dealt with Colorado River water in the USA, the concentration of inorganic scalants such as $BaSO_4$, $CaCO_3$, $Ca(SO)_4$, $SrSO_4$, $MgSO_4$ and SiO_2 clearly increased above their solubility limits when higher fresh water recoveries were considered [5,10,12]. To cope with this problem, most tested interstage precipitation strategies afforded significant removals of scale-forming ions, such as calcium, barium and strontium, while magnesium and SiO_2 removal efficiency was variable [5,10,12]. In that regard, accelerated precipitation softening technology at pH 10.5 achieved a moderate reduction (10–20%) of SiO_2 and magnesium [5].

Conversely, this study targeted the maximum magnesium removal from the primary RO concentrate generated in a groundwater desalination facility. It was considered that silica removal could be maximized through high pH precipitation of magnesium-bearing minerals. Concurrently, calcium, barium and strontium could also be removed during the demineralization process and salt recovery options could be achieved through maximum concentrate purification.

3. Material and methods

3.1. RO concentrate generation and desalination plant description

This study was carried out with RO concentrate collected at an inland desalination facility located in the Darling Downs region of Queensland (QLD), Australia. The plant was able to treat up to 3700 m^3/day of brackish groundwater, depending on household water

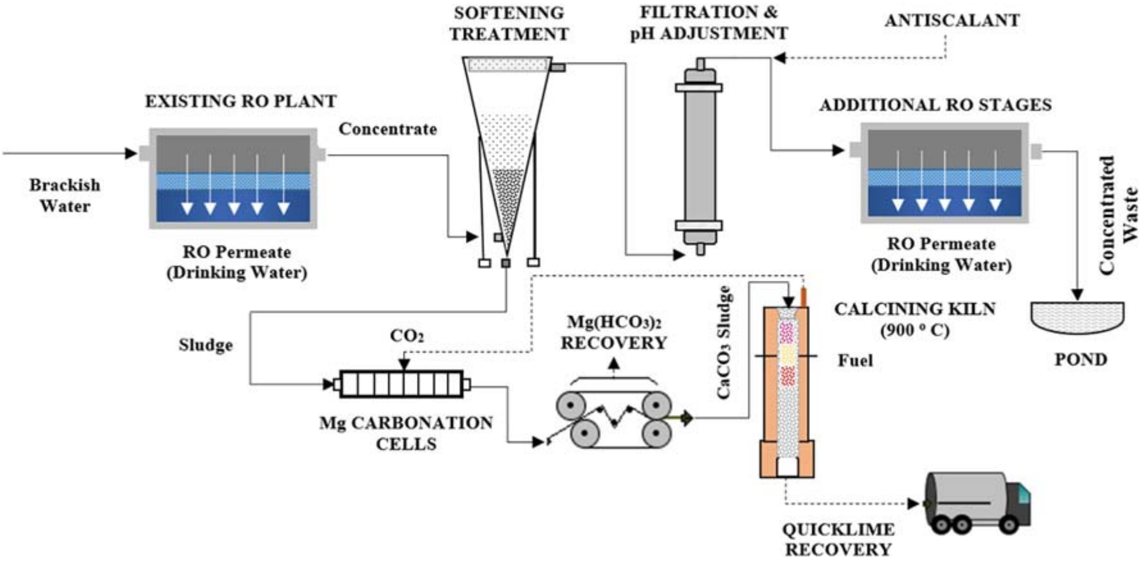

Fig. 1. Proposed plant layout for RO concentrate minimization.

demand. According to the plant management, water recoveries of up to 80% were achievable. This facility generated an average of 300 m^3/day of RO concentrate which was disposed of in four evaporation ponds.

Fig. 2 shows the layout of the desalination plant. RO feed water was supplied from up to 3 of the 5 different artesian wells available in the vicinity of the plant. Its pretreatment process combined media filtration (gravel, sand and anthracite), antiscalant/dispersant (SpectraGuard SC) addition, bag and cartridge filters, and UV disinfection. Pre-treated water was then pumped through a 2-stage RO filtration system. Following filtration, the produced permeate was aerated to remove CO_2 and the pH was adjusted by NaOH addition. Finally, RO permeate was blended with groundwater to increase water hardness and alkalinity.

The RO plant had two stages. Stage 1 used low-energy RO membranes (DOW FILMTEC™ XLE-440, The Dow chemical company, USA) operated at 0.95 MPa, whereas stage 2 used high-rejection brackish water membranes (DOW FILMTEC™ BW30-400, The Dow chemical company, USA) at 1.6 MPa.

RO concentrate for these experiments was taken from the RO3 discharge and preserved in a laboratory refrigerator below 5 °C. No precipitates were observed using this storage method. The main characteristics of well feed water and RO concentrate are summarized in Table 1.

3.2. *'High-pH precipitation treatment' studies*

Batch demineralization tests were carried out in the University of Southern Queensland environmental laboratory at room temperature (23–25 °C) using a VELP 'jar test' apparatus (model JLT6) containing six 1-L plastic beakers. In all experiments, a 'high-pH precipitation treatment' strategy was applied to assess the removal of scale-forming precursors including magnesium, calcium, strontium, barium and SiO_2.

RO concentrate was treated with varying amounts of NaOH (1 N) to give six different pH levels (10.0, 10.3, 10.6, 10.9, 11.2 and 11.5). Considering RO concentrate quality shown in Table 1, the addition of soda ash was not required for non-carbonate hardness (NCH) removal when softening was performed with NaOH at high-pH levels. This meant that an excess of carbonate ions were available to remove most of the calcium ions as $CaCO_3$ precipitate.

For comparison purposes, experiments were also conducted applying both the lime and the lime-soda ash softening treatments to the RO concentrate. Required lime and soda ash doses were calculated according to the methodology described in 'Introduction to

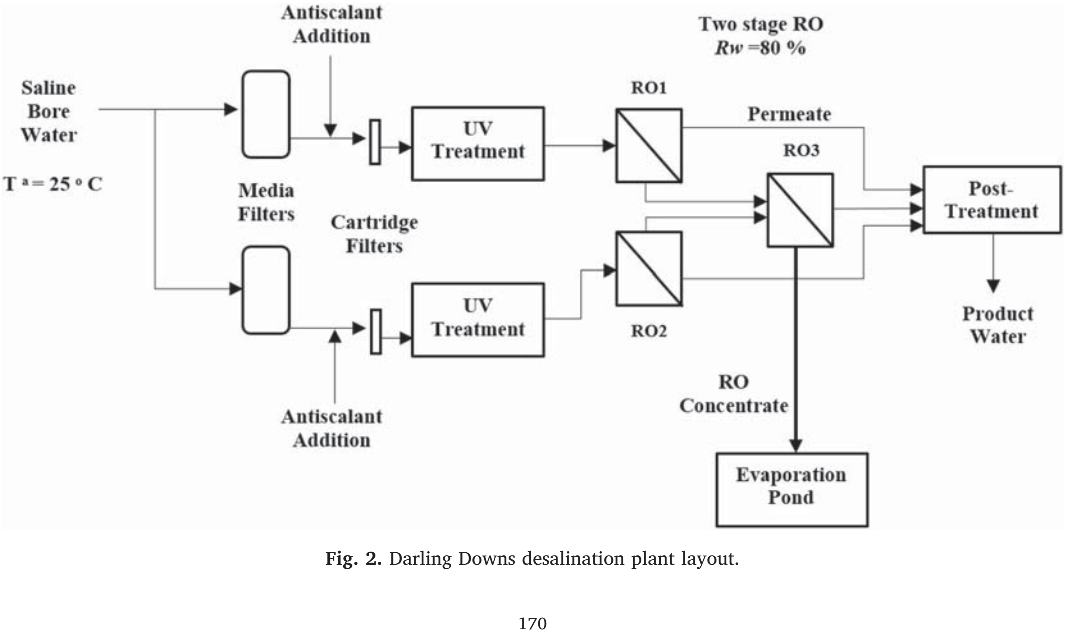

Fig. 2. Darling Downs desalination plant layout.

Table 1
Characteristics of well water (Western Downs Regional Council) and RO concentrate.

Parameter	Well water characteristics		RO concentrate characteristics
	Min.	Max.	
pH (Units)	7.5	7.85	7.9
Conductivity (mS/cm)	3.4	3.5	14.5
Turbidity (NTU)	0.1	0.6	< 1
TDS (mg/L)	1860	2050	9334
Alkalinity (mg/L $CaCO_3$)	324	370	2150
Sodium (mg/L)	526	580	3357
Potassium (mg/L)	2.8	3.2	25
Calcium (mg/L)	44	52	277
Magnesium (mg/L)	69.6	84.7	372
Strontium (mg/L)	2	2.5	13
Barium (mg/L)	0.05	0.06	0.35
Sulphate (mg/L)	130	160	788
Chloride (mg/L)	786	934	3752
Fluoride (mg/L)	–	–	2.2
Silica (mg/L SiO_2)	31	35	191

Note: Well water quality data corresponds with 'bore n-12' and was supplied by the Western Downs Regional Council. Well water characteristics were very similar in the 5 different artesian wells available in the vicinity of the plant. All wells tapped into the same aquifer so that the water from each well was essentially the same.

Environmental Engineering, Third Edition' [26].

All reagents were added at the beginning of the initial rapid-flash mixing time (2 min at 150 rpm). Thereupon, following a 30 min slow mixing time at 50 rpm, all waters were allowed to settle for one hour. Finally, supernatant samples and the dissolved fraction obtained by filtration were collected for analysis. Settled solids were also collected by vacuum filtration and dried at 50 °C before being analysed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). All jar test trials were repeated three times.

To simulate a worst-case scenario, additional experiments were carried out spiking with magnesium sulphate heptahydrate to the RO concentrate in order to increase both magnesium and sulphate concentration. The same jar test methodology described above was applied when softening the spiked concentrate with NaOH and lime. However, for samples treated by the lime-soda ash softening a two-stage process was required in order to effectively remove calcium by precipitation. In such cases, the jar test sequence was modified to include the following steps: 1) 2 min rapid mixing time at 150 rpm including lime addition; 2) 30 min slow mixing time at 50 rpm; 3) 2 min rapid mixing time at 150 rpm including soda ash addition; 4) 30 min slow mixing time at 50 rpm; and 5) 1 h settling time.

3.3. Quicklime recovery studies

The feasibility of quicklime recovery from precipitated sludge was only studied for RO concentrate treated by the lime-soda ash softening process. This option was considered less feasible for RO concentrate softened with caustic soda due to the higher residual alkalinity and expected lower presence of $CaCO_3$ in the precipitated sludge.

At completion of the jar tests and following settling time, the clear supernatant of softened concentrates was carefully syphoned and around 300 mL of decanted slurry was collected in a 1 L beaker. Agitation was then provided using a magnetic stirrer model Bibby HB502. CO_2 gas was bubbled through the slurry solution from a 50 L (food grade) cylinder supplied by BOC Australia in order to dissolve precipitated magnesium. The flow of CO_2 gas using an 'aquarium type air stone' was regulated to produce micro-fine and well dispersed bubbles. During that time, the pH was continuously monitored. CO_2 gas addition was stopped when the slurry pH level was around 7.3. Previous studies in conventional water treatment plants had reported that further CO_2 addition could result in the loss of CO_2 to the atmosphere [27].

The remaining sludge, mainly $CaCO_3$ and impurities, was dewatered and collected by vacuum filtration. Recycled $CaCO_3$ was then calcined at 900 °C for 20 min in a laboratory muffle furnace, model Labec LCF 1512, for quicklime recovery. Samples of dewatered $CaCO_3$ and produced quicklime were analysed by FTIR. Additional samples were sent to an external laboratory for XRD analysis. The chemical reaction for the calcination step is shown below [28]:

$$CaCO_3 \xrightarrow{heat} CaO + CO_2\uparrow \quad (1)$$

Finally, a magnesium bicarbonate solution was also collected from the filtrate. Possible applications of this solution were studied. This alternative, favoured by the high magnesium concentration in the RO concentrate, has never been tested in inland desalination plants aiming at RO concentrate minimization and salt recovery.

3.4. Reagents and analytical methods

All chemicals employed in the analyses were 'reagent-grade' supplied by HACH, Chem-Supply, Sigma Aldrich and Australian Chemical Reagents.

The pH was determined using a pH electrode, model Eutech PC 2700, calibrated in buffer solutions of pH 4, 7, and 10. Conductivity was measured using a conductivity meter, model Sper-Scientific. Analysis of turbidity was performed using a Lovibond turbicheck-meter.

A titration technique using H_2SO_4 was applied for total alkalinity determinations [29]. TDS concentration was determined according to the Standard Methods: 2540 C 'Total Dissolved Solids Dried at 180 °C' [30].

A Shimadzu atomic absorption spectrophotometer (AAS), model AA-7000, was used for the quantitative determination of cations. All samples were acidified using concentrated nitric acid before commencing the analysis. When the air-C_2H_2 flame was used, chemical interferences were prevented by addition of a lanthanum solution. In the case of N_2O-C_2H_2 flame utilization, potassium chloride was added instead of the lanthanum solution.

Sulphate and chloride were analysed by ion chromatography using a Dionex ICS-2000 analyser according to Thermo Scientific application note n-154 [31]. An IonPac AS15 (4 mm) column was used to perform these analyses.

Fluoride and molybdate-reactive silica were determined using a UV-VIS spectrophotometer (HACH model DR-2700), according respectively to the SPADNS (HACH 10225) and the silicomolybdate (HACH 8185) methods [32,33].

SEM-EDX determinations in precipitated solids were undertaken using a SEM-JCM6000 scanning electron microscope.

Powder XRD analysis of precipitated solids were performed using a Philips X'Pert apparatus with CuK_α = 1.542 A radiation, operating at 40 kV and 20 mA in the 10° to 80° 2-theta scanning range. The diffraction patterns were compared using the X'Pert HighScore Plus software. Powder diffraction files (PDF) from the International Centre for Diffraction Data were used as references.

FTIR spectra of precipitated solids were undertaken using a Shimadzu RF-6000 spectrophotometer incorporating the LabSolutions IR software for surface functional groups analysis. Surface functional groups play an important role in the adsorption processes. In all cases, 10 scans were taken for both the background and the samples and the FTIR spectra resolution was set at 8 cm^{-1}. All samples were prepared mixing 0.2 mg of sample and 200 mg of KBr.

Table 2
RO concentrate. *SI* levels calculation. T = 25 °C.

Parameter	*SI*
LSI	2.02
S&DSI	1.52
$CaSO_4$	0.11
$BaSO_4$	11.0
$SrSO_4$	0.22
SiO_2	1.36

Notes: There is a risk of $CaCO_3$ scale on the RO membrane for positive Langelier Saturation Index (*LSI*) or Stiff & Davies Stability Index (*S&DSI*) values [35,36]. $CaSO_4$, $BaSO_4$ and $SrSO_4$ show a precipitation tendency for *SI* levels (measured as the 'ion product' divided by Ksp) above 1. SiO_2 also shows a precipitation tendency for *SI* levels (measured as silica concentration in RO concentrate divided by calculated silica solubility) above 1. $Mg(OH)_2$ *SI* level calculated by ROSA software resulted in a value of zero.

3.5. Saturation indexes (SI) calculation

For this research, the scaling potential by SiO_2 and other salts was calculated using ASTM standards for RO applications [34–37]. The Reverse Osmosis System Analysis (ROSA) software by DOW Water & Process Solutions was also applied to estimate RO concentrate minimization capacity and membrane scaling potential following a 'high-pH precipitation treatment'. ROSA software has been frequently used in membrane modelling for detailed design in spite of being limited to applications incorporating DOW membranes [38].

4. Results and discussion

4.1. Justification of an intermediate 'high-pH precipitation treatment' for RO concentrate minimization

Table 2 shows calculations of the scaling potential by SiO_2 and different salts in the RO concentrate by ASTM standards. For this purpose, the ionic strength (*I*) of the RO concentrate was approximated by the formula [34,39]:

$$I = \frac{1}{2}\sum m_i z_i^2 \tag{2}$$

resulting in a value of 0.2 (molal), where m_i and z_i were the molal concentration and ionic charge of ion *i*, respectively.

As shown in Table 2, the performed *SI* calculations suggest that the RO concentrate was saturated with respect to $CaCO_3$, $BaSO_4$ and SiO_2. Further volumetric minimization of the RO concentrate could be achieved by implementing new RO stages. Nevertheless, as shown in Figs. 3 and 4, *SI* values for most problematic salts increased as the RO concentrate was further minimized. In no case was $Mg(OH)_2$ precipitation feasible at this pH level (7.9).

The risk of $CaCO_3$ scale could be controlled by acid addition [39,40]. $BaSO_4$ and CaF_2 precipitation could also be avoided by antiscalant utilization [39]. Commercial antiscalants like Vitec 4000, allow an increase in the $BaSO_4$ and CaF_2 *SI* levels up to 105 and 1000 respectively [41].

That being said, the rate of concentrate minimization in the new RO stages was limited by the risk of SiO_2 precipitation on the RO membrane, which has been a common issue in many inland desalination plants [25,42]. To prevent this problem, there are some specific antiscalants which target SiO_2 scale, in which SiO_2 concentration in the super concentrated waste could be increased by up to two times the saturation under certain operating conditions [41]. However, for practical applications it has been recommended to limit SiO_2 concentration to 200 mg/L [6] (currently 191 mg/L in the RO concentrate). Consequently, further minimization of the concentrate by secondary RO would require adopting a different approach.

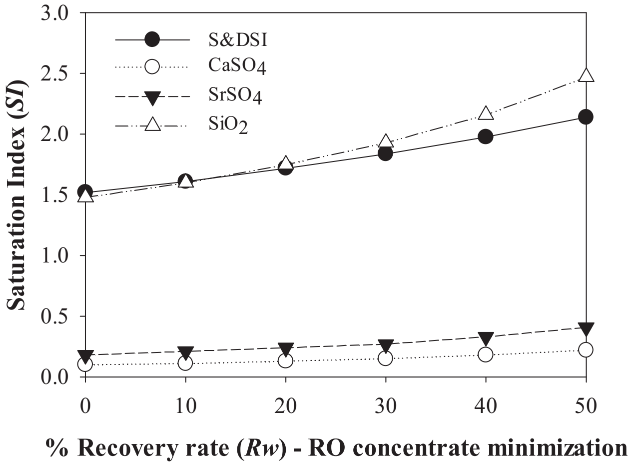

Fig. 3. RO concentrate minimization in secondary RO. S&D*SI*, $CaSO_4$, $SrSO_4$ and SiO_2 *SI* levels vs. *Rw*. ROSA simulation. Water type: Well water SDI < 3. T^a = 25 °C.

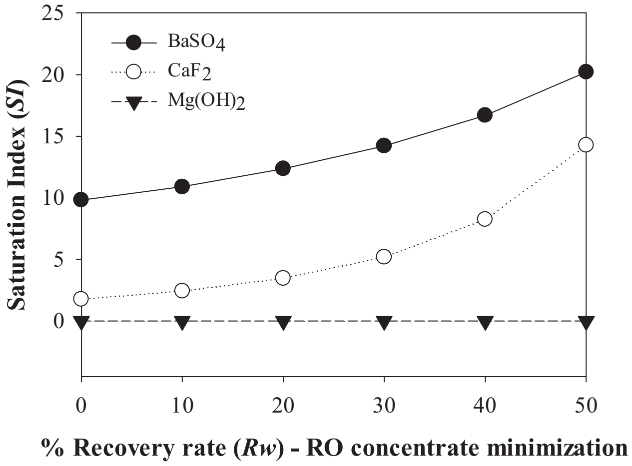

Fig. 4. RO concentrate minimization in secondary RO. $BaSO_4$, $Mg(OH)_2$ and CaF_2 *SI* levels vs. *Rw*. ROSA simulation. Water type: Well water SDI < 3. T^a = 25 °C.

Figs. 5 and 6 show calculations of the scaling potential by different inorganic salts in the RO concentrate as the pH was adjusted at different levels ranging from 4 to 11 by HCl/NaOH addition. As shown in Fig. 5, $Ca(SO)_4$, $Ba(SO)_4$, $Sr(SO)_4$ and CaF_2 *SI* levels were found to be almost pH insensitive as the pH level in the RO concentrate increased. However, $CaCO_3$, $Mg(OH)_2$ and SiO_2 solubility were pH dependent. As shown in Fig. 6, a pH level of about 9.5 was required to saturate the primary RO concentrate with $Mg(OH)_2$. Therefore, the integration of an intermediate 'high pH precipitation treatment' could facilitate magnesium and calcium removal from primary RO concentrate. Concurrently, other scale forming precursors including barium, strontium and SiO_2 could be removed during the softening treatment by precipitation and adsorption/enmeshment mechanisms.

Overall, to cope with limitations imposed by conventional scale-control strategies, an intermediate 'precipitation treatment' for divalent cation removal including magnesium, calcium, barium and strontium together with coagulated SiO_2 and colloidal matter, could be

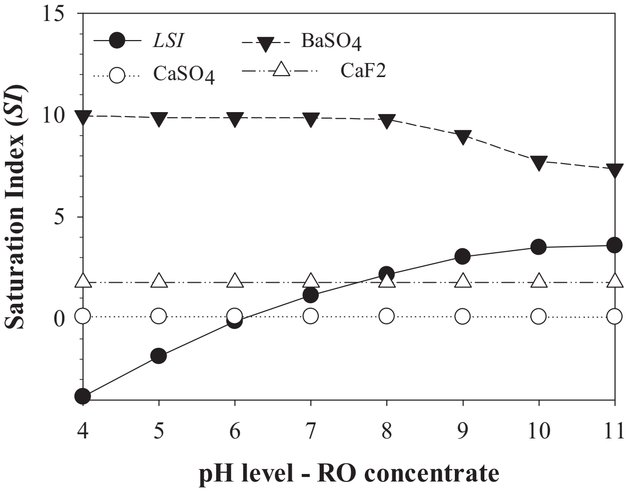

Fig. 5. RO concentrate. *LSI*, $CaSO_4$, $BaSO_4$, $BaSO_4$ and CaF_2 *SI* levels vs. pH. ROSA simulation. Water type: Well water SDI < 3. T^a = 25 °C.

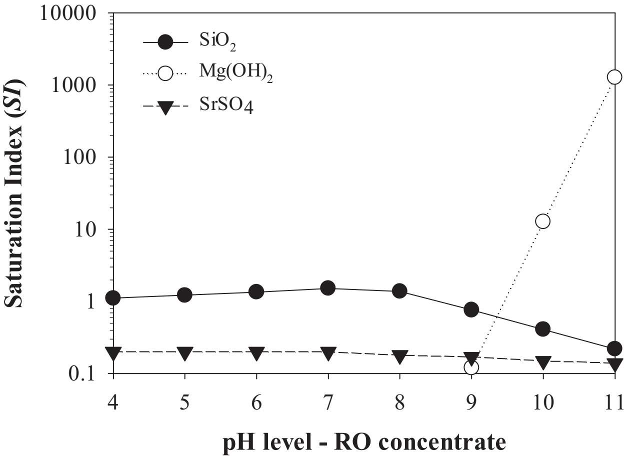

Fig. 6. RO concentrate. SiO_2, $Mg(OH)_2$ and $SrSO_4$ *SI* levels vs. *pH*. ROSA simulation. Water type: Well water SDI < 3. T^a = 25 °C.

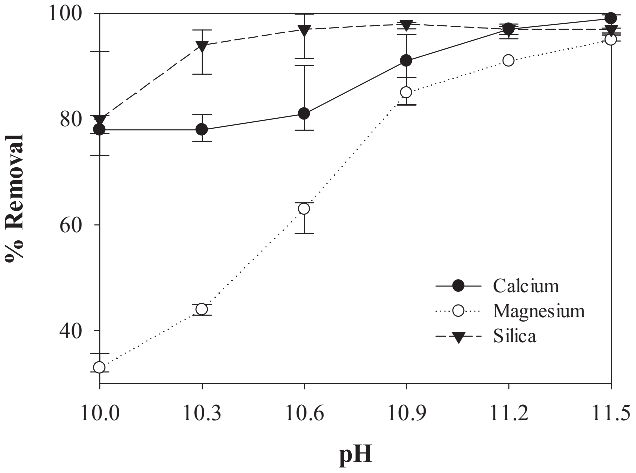

Fig. 7. Percentage removals of calcium, magnesium and SiO_2. RO concentrate softening was performed with NaOH at different pH levels.

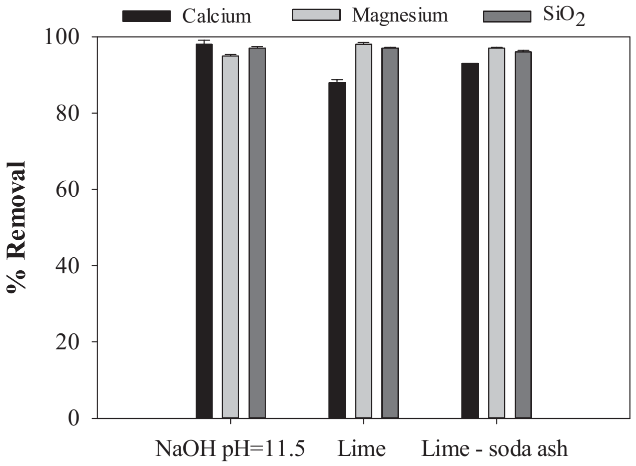

Fig. 8. Percentage removals of calcium, magnesium and SiO_2. RO concentrate softening was performed with a) NaOH (pH 11.5); b) lime (pH 11.1); and c) lime and soda ash (pH 11.1).

considered as a feasible alternative to increase fresh water recoveries [43]. Higher *Rw* levels could be achieved by lowering the silica concentration to 20–30 mg/L [25]. In addition, salt recovery options from precipitated sludge could be available. Acid/antiscalant utilization would be eventually required following an intermediate 'high-pH precipitation treatment' to guarantee maximum process optimization in the additional RO stages.

4.2. 'High-pH precipitation treatment' for RO concentrate minimization

4.2.1. Chemical demineralization efficiency

The experimental results of the NaOH softening process were illustrated in Fig. 7. In this chart, the percentage removal of calcium, magnesium and SiO_2 were plotted against the RO concentrate pH level. Optimal removal rates for calcium and magnesium were achieved at pH 11.5. In addition, SiO_2 removal rates above 95% were observed when the RO concentrate pH was above 10.6.

A comparison of the simultaneous removal of calcium, magnesium and SiO_2, following a softening treatment with a) NaOH at pH 11.5; b) lime; and c) lime and soda ash, was plotted in Fig. 8. The calculated lime dose, 2.9 g/L as $Ca(OH)_2$, was added at the beginning of the lime softening treatment for carbonate hardness removal. Addition of Na_2CO_3 (0.08 g/L) together with the same dose of lime was also required during the lime and soda ash softening treatment for non-carbonate hardness removal. The highest calcium removal rates, around 98%, were obtained in the samples treated only with NaOH at pH 11.5. As expected, Na_2CO_3 addition during the lime and soda ash treatment also facilitated a 5% increase in calcium removal with respect to the samples treated only with lime. Silica removal rates in all treatments were very similar around 96–97%. Conversely, magnesium removal rates in the RO concentrate samples treated with a) NaOH at pH 11.5; b) lime; and c) lime and soda ash were respectively 95, 98 and 97%. Overall, we could conclude that the three tested treatments were highly effective in these experimental conditions.

However, the NaOH softening treatment showed some drawbacks during jar test experiments. Firstly, a 72% increase in total alkalinity was measured in softened RO concentrate. This had a negative impact on the *LSI/S&DSI*. Secondly, conductivity increased up to 16.5 mS/cm. This higher salinity limited water recovery in the new RO stages when the practical limits to surpass the osmotic pressure were considered. Energy requirements also increased concurrently. It is important to mention that concentrates could only be concentrated by RO to a maximum of 65,000–75,000 mg/L, in NaCl dominated waters [44]. Thirdly, pH normalization using HCl or H_2SO_4, together with antiscalant addition were required before passing softened RO concentrate through the new RO stages. As a consequence of the increased alkalinity, the cost for final pH stabilization also increased for RO concentrate samples softened only with caustic soda. Finally, flocs produced during

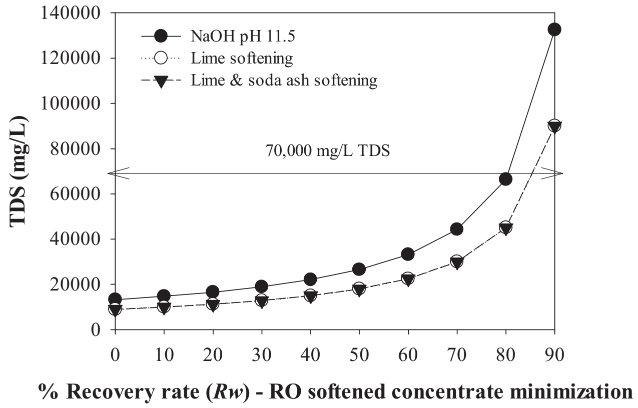

Fig. 9. *Rw* in secondary RO vs. TDS level. RO softened concentrate + antiscalant addition + pH adjustment to 6.5 by HCl addition. ROSA simulation. Water type: Well water SDI < 3. $T^a = 25\,^\circ C$. Softened RO concentrate was concentrated by secondary RO to a maximum of 70,000 mg/L TDS.

the NaOH softening treatment were smaller and more disperse. Therefore, polyelectrolyte addition was required to improve the solid/liquid separation process.

As shown in Fig. 9, the TDS level increased as the softened RO concentrate (by the three previous mentioned methods) was further concentrated by additional RO stages. RO concentrate softened with NaOH appeared to be the most unfavourable alternative since *Rw* was limited to around 80% (total *Rw* = 95%) when additional RO stages were implemented. On the other hand, softened RO concentrate treated by the lime and the lime and soda ash softening treatment could achieve fresh water recoveries of around 87% (total *Rw* = 97%) in both cases. Since the risk of salt precipitation was properly minimized through a 'high-pH precipitation treatment', *Rw* calculations were carried out on the basis that the softened RO concentrate (following pH stabilization and antiscalant addition) was further concentrated by additional RO stages to a maximum of 70,000 mg/L TDS.

This research targeted the maximum Mg removal from the existing RO concentrate. The goal of this research was to achieve maximum concentrate purification to increase *Rw* while enhancing salt recovery options. By contrast, some studies performed in the USA, limited Mg$(OH)_2$ precipitation during the intermediate demineralization treatment due to its poor settling characteristics [13] and related difficulties during the solid-liquid separation process [5].

4.2.2. Silica removal mechanism

4.2.2.1. Silica removal efficiency during 'high-pH precipitation treatment'. Two main mechanisms were considered for silica removal during a softening treatment: a) precipitation as calcium and/or magnesium silicate; and/or b) by adsorption/enmeshment in precipitated $Mg(OH)_2$ and/or $CaCO_3$ [14,45]. The first mechanism can become more predominant at pH levels above 11 [14]. As shown in Table 3 and based on the *pKs* constants, precipitation of magnesium silicates is more feasible than $Mg(OH)_2$ precipitation. Moreover, magnesium silicate precipitation is favoured against calcium silicate precipitation due to its lower solubility.

Table 3
Negative log k_{sp} values of common salts.

Name	Formula	*pKs*	Reference
Antigorite	$Mg_3Si_2O_5(OH)_4$	34.5	[45]
Forsterite	Mg_2SiO_4	26.9	[45]
Enstatite	$MgSiO_3$	16.6	[45]
Brucite	$Mg(OH)_2$	11.6	[45]
Calcite	$CaCO_3$	8.5	[39]
Aragonite	$CaCO_3$	8.2	[39]
CaH_2SiO_4	CaH_2SiO_4	8.16	[45]
Lime	$Ca(OH)_2$	5.15	[45]
Calcium sulphate	$CaSO_4$	4.3	[39]

According to the bibliography, the catalytic effects of dissolved magnesium in the silicic acid condensation reaction become visible for water pH levels above 9. In addition, experiments conducted in batch runs have demonstrated that magnesium concentration affects the silica precipitation process more than calcium concentration [6].

Overall, it is considered that silicon can be removed during softening treatment by co-precipitation of magnesium silicate when the molar ratio Si/Mg is higher than 1/6 [46,47]. For silica precipitates, such as enstatite ($MgSiO_3$), a molar ratio Si/Mg = 1/1 is required. This ratio would be lower if silica precipitates as Mg_2SiO_4 (forsterite) or $Mg_3Si_2O_5(OH)_4$ (antigorite) [45]. Previous studies have also reported that a molar ratio Si/Mg of 1/22 was required for adsorption of SiO_2 on $Mg(OH)_2$ [47]. Considering the data provided in Table 1, sufficient magnesium ions were present in the RO concentrate to remove most of the silica as magnesium silicate. In this regard, the molar ratio Si/Mg in the RO concentrate was 1/5 resulting in a mass ratio Si/Mg of about 1/4.

Fig. 10 shows SEM images of precipitated solids obtained after softening the RO concentrate with a) NaOH at pH 11.5; b) lime; and c) lime and soda ash. In all cases, the formed solids showed some crystalline phases within amorphous precipitates. Semi-quantitative chemical analysis of precipitated solids shown in Fig. 10 were also provided in Table 4. Results were obtained from the EDX analyser. This technique analysed the solid surface with 1–2 μm penetration depth. The most interesting finding was that the measured atomic Si/Mg ratios were about 1/4 in all cases. Therefore, and considering the high-pH levels, precipitation as silicate appeared to be the main mechanism for silica removal.

Powder XRD and FTIR analysis were also performed on the precipitated solids. XRD analysis identified the calcite pattern in all samples. However, since precipitated magnesium silicate can show an amorphous structure in these experimental conditions, no match was found using the XRD technique. The crystalline solids as seen in Fig. 10 could therefore be related to calcite. Secondly, the presence calcium carbonate was also confirmed by FTIR analysis. FTIR spectra also showed in all cases a band between 1100 and 900 cm^{-1} that could be attributed to silicate ions [48]. Fig. 11 shows a comparison between the FTIR absorption spectra of precipitated solids obtained after softening the RO concentrate with lime and soda ash and the FTIR absorption spectra of calcium carbonate.

We conclude that maximum silica reduction, apparently through magnesium silicate polymerization, was favoured by the high-pH of the softening treatment and the existing Si/Mg and Ca/Mg ratios present in the RO concentrate.

4.2.2.2. Effect of increased magnesium and sulphate concentration on silica removal efficiency during 'high-pH precipitation treatment'. In order to simulate a worst-case scenario, magnesium sulphate heptahydrate was added to the RO concentrate to increase magnesium and sulphate concentration up to 574 and 1586 mg/L, respectively. This also resulted in an increase in the non-carbonate hardness of the RO concentrate. Overall, an increase in dissolved magnesium concentration can enhance the silica removal process when insufficient hardness is present in raw water [14]. The higher magnesium concentration also resulted in higher $Mg(OH)_2$ *SI* levels as the RO concentrate pH level was increased. Required doses of NaOH (1 N), lime and soda ash were recalculated according to these new conditions resulting respectively in 81 mL/L, 3.5 g $Ca(OH)_2$/L and 0.9 g Na_2CO_3/L.

Experiments softening the RO concentrate with a) NaOH at pH 11.5; and b) lime, were repeated in triplicate following the same jar test methodology described in Section 3.2. In this regard, NaOH addition provided average calcium, magnesium and SiO_2 removal rates of 96, 93 and 97%, respectively. Conversely, softening experiments with lime

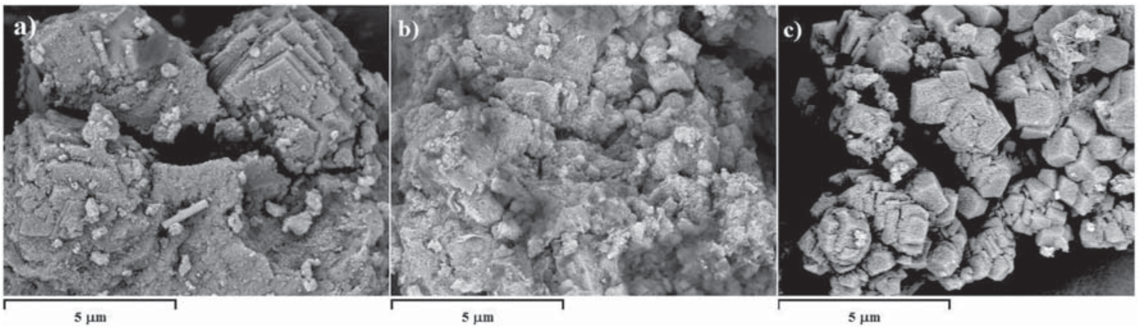

Fig. 10. SEM images of precipitated solids following RO concentrate softening with a) NaOH at pH 11.5; b) lime; and c) lime and soda ash.

achieved average magnesium and SiO_2 removal rates of 98 and 95%, respectively. In contrast, calcium concentration increased due to the higher required lime dose to remove spiked magnesium.

The jar test methodology had to be modified for RO concentrate samples softened by the traditional lime and soda ash treatment. Process kinetics were altered and more reaction time was required for effective calcium removal. As described in Section 3.2, a two-stage process was applied where the lime was added in the first stage and the soda ash during the second stage. Recorded average removals of calcium, magnesium and SiO_2 were respectively 95, 98 and 92%.

Overall, no sulphate reduction was observed in any case, and high silica removal rates were achieved. However, the lower Si/Mg molar ratio of about 1/7.5 in the spiked sample could have altered the silica removal mechanism. In a such a case, adsorption/enmeshment of silica in precipitated $Mg(OH)_2$ and/or $CaCO_3$ could have occurred.

4.2.3. Barium, strontium and fluoride removal efficiency

Barium removal rates above 71% were measured in the RO concentrate softened respectively with a) NaOH at pH 11.5; b) lime; and c) lime and soda ash. While performing this study, barium analytical determinations were conditioned by the achievable detection limit in the AAS unit. Conversely, recorded strontium removal rates following the same softening treatments described above were 97, 92 and 94% respectively. No sulphate reduction was observed in any of these softening experiments. Sulphate removal can be possible by precipitation with lime as $CaSO_4$, however the latter is limited by its solubility [29].

Achieved barium and strontium removal rates could be seen to be in agreement with the bibliography. A previous study treating reclaimed water RO concentrates by a modified lime-soda ash softening also reported barium removal rates from 72 to 77% and strontium removal rates above 95% [9]. In addition, another study applying a 3-step intermediate chemical demineralization treatment to nanofiltration concentrate enhanced barium removal rates above 90% using homoepitaxial templating employing barite itself as a seed crystal during the last step [13].

Barium and strontium can be removed during a softening treatment by co-precipitation with $CaCO_3$ [10,49]. The removal of both cations during the precipitation treatment can be correlated with the main operational factors affecting calcium removal: a) calcium and carbonate

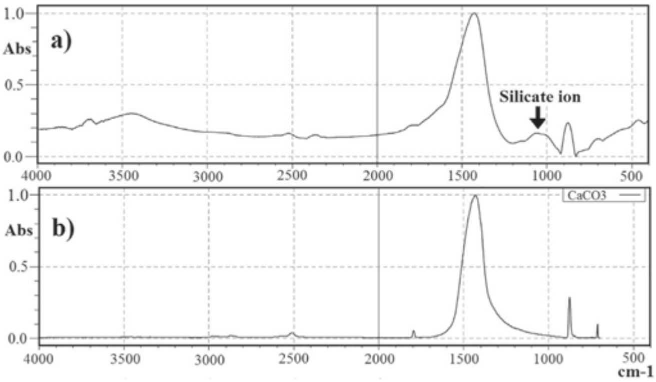

Fig. 11. Comparison between a) FTIR absorption spectra of precipitated solids obtained after softening the RO concentrate with lime and soda ash and b) FTIR absorption spectra of pure $CaCO_3$.

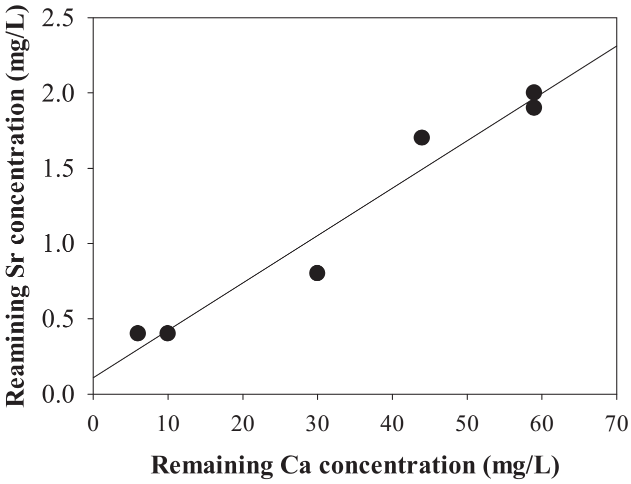

Fig. 12. Correlation between Sr and Ca 'remaining concentrations' in the softened RO concentrate. Softening was conducted with caustic soda at different pH levels ranging from 10.0 to 11.5.

Table 4
Average composition of precipitated solids (EDX analysis) shown in Fig. 10.

Precipitated solid	Softening treatment	C	O	Na	Mg	Si	Cl	Ca	Au	Si/Mg
		(Atomic %)								
Fig. 10a)	NaOH pH 11.5	17.95	56.86	1.33	11.14	2.77	0.85	6.10	3	1/4
Fig. 10b)	Lime softening	18.98	56.44	0.60	9.42	2.41	0.80	9.51	1.88	1/4
Fig. 10c)	Lime-soda ash softening	44.71	38.91	–	1.22	0.31	–	11.54	3.32	1/4

Note: Detected chloride and sodium in precipitated solids could be related to trapped concentrate collected in the precipitate. Detected Au in all samples corresponded to the sputter coating process applied to the specimens before undertaking SEM analysis.

Table 5

K_{sp} values of different salts [50].

Name	Formula	K_{sp}
Barium sulphate	$BaSO_4$	1.1×10^{-10}
Barium carbonate	$BaCO_3$	$5.1 \times 10–^{9}$
Barium hydroxide	$Ba(OH)_2$	5.0×10^{-3}
Strontium sulphate	$SrSO_4$	3.2×10^{-7}
Strontium carbonate	$SrCO_3$	1.1×10^{-10}
Strontium hydroxide	$Sr(OH)_2$	Slightly soluble
Magnesium hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Calcium carbonate	$CaCO_3$	2.8×10^{-9}

concentrations; and b) effluent pH level [10]. The former hypothesis was demonstrated in Fig. 12. There was a clear correlation ($R^2 = 0.967$) between calcium and strontium 'remaining concentrations' in the RO concentrate softened with NaOH. As the pH increased, both calcium and strontium removal rates increased. Conversely, the lime and soda ash softening achieved a slight improvement in strontium removal with respect to the RO concentrate treated only with lime, due to the extra calcium removed.

Table 5 shows the solubility product constants of different barium and strontium salts. If carbonate alkalinity is present in the raw water or added as soda ash, barium removal by precipitation as barium carbonate is possible due to its low solubility. In contrast, barium precipitation as barium hydroxide during a softening treatment is difficult considering that its solubility is much higher than that of the magnesium hydroxide. Finally, extra barium or strontium removal is also possible by sorption to other solids formed during the softening treatment [50].

Some investigators have shown that the presence of magnesium ions in solution can inhibit the precipitation of $CaCO_3$ [51,52]. Previous research has also provided power law kinetic models to understand the simultaneous precipitation of $Mg(OH)_2$ and $CaCO_3$ in the water softening process [51]. The crystallization of $CaCO_3$ and $Mg(OH)_2$ appeared to be independent [51,53]. During the lime and soda ash softening treatment, the kinetics of the $Mg(OH)_2$ crystallization process are a sensitive function of pH [53].

In summary, barium and strontium removal from the RO concentrate should have occurred by substitution of calcium in the calcite crystal lattice structure. The efficacy of the treatment could be limited by the available calcium and alkalinity concentration in the RO concentrate. However, extra barium and strontium removal could also have happened by sorption to other precipitated compounds coupled with the high-pH of the softening treatments.

Conversely, fluoride concentration was reduced by > 50% in the RO concentrate softened respectively with a) NaOH at pH 11.5; b) lime; and c) lime and soda ash. Fluoride analytical determinations in this study were also conditioned by the achievable detection limit in the UV spectrophotometer. According to the bibliography, fluoride in groundwater can be precipitated using lime as calcium fluoride leaving about 8 mg/L F^- in the water [54]. In this study and considering the low fluoride concentration in the RO concentrate (2.2 mg/L), fluoride removal could have occurred by adsorption onto magnesium precipitates. In that regard, the existing Ca/Mg ratio in the RO concentrate could have facilitated the fluoride removal process.

4.3. *Quicklime recovery studies*

Sludge generated after the lime and soda softening treatment was selected for recovery tests in order to maximize $CaCO_3$ recovery. For this purpose, around 300 mL of decanted slurry was collected in a 1 L beaker and carbonated by bubbling pure CO_2 until the pH level was adjusted to around 7.2 in the different trials. During this step, CO_2 gas dissolved magnesium from precipitated sludge. Carbonated sludge, mainly $CaCO_3$ was then filtered and a magnesium bicarbonate solution was collected from the filtrate.

Table 6

Characteristics of recycled magnesium bicarbonate solution.

Parameter	Magnesium bicarbonate solution	
	Average (mean)	Standard deviation
pH (Units)	8.4	0.12
Conductivity (mS/cm)	15.8	0.5
Alkalinity (mg/L $CaCO_3$)	3999	490
Calcium (mg/L)	33.2	23
Magnesium (mg/L)	681	79
Silica (mg/L SiO_2)	165	33

Notes: Carbonation trials were undertaken in triplicate. Following filtration an increase in the pH solution was observed. The carbonation process redissolved magnesium, but SiO_2 as well.

A saturated solution of calcium bicarbonate has a lower pH than a saturated solution of magnesium bicarbonate, therefore as CO_2 is injected, the solution is buffered at a pH of around 7.5 (due to the magnesium bicarbonate). This circumstance guarantees that little calcium will dissolve [55].

Table 6 shows the composition of this magnesium bicarbonate solution. Although limited by its high electrical conductivity and silica content, this currently non-commercially valued solution could be used as a coagulant in industrial water treatment. Alternatively, it could be disposed of in evaporations ponds or further concentrated by another technology for possible magnesium recovery. Overall, the high TDS content of this non-saturated magnesium solution could preclude its direct discharge to the sewer [56]. Eventually, about 55% magnesium recovery was achieved by following this methodology.

Figs. 13 and 14 show the powder XRD pattern and the FTIR transmission spectra of samples of carbonated sludge. X'Pert HighScore Plus (XRD) and LabSolutions IR (FTIR) software packages for data analysis revealed that following the carbonation step, the sludge contained $CaCO_3$ with a density of 2.7 g/cm^3. Fig. 13 matched the XRD pattern of rhombohedral calcite (PDF 01-072-1937 - 74% similarity) with peaks at 23.0°, 29.4°, 35.9°, 39.4°, 43.1°, 47.4°, 48.5° and 57.3°. The strongest diffraction intensity was indexed to the calcite (104) 2-theta = 29.4°.

$CaCO_3$ identification was also confirmed with the bibliography, since carbonate ions in the FTIR spectra should appear in the following group frequencies: 1490–1410/880–860 cm^{-1}. As shown in Fig. 14, the first absorption was intense and broad, and the second had medium intensity and was narrow [48]. The FTIR spectra also showed a wide band at 3448 cm^{-1}, which was due to O—H vibration [48], and that could be attributed to water and hydroxide groups. In addition, the peaks at 1103 and 462 cm^{-1} could be associated with the bands of

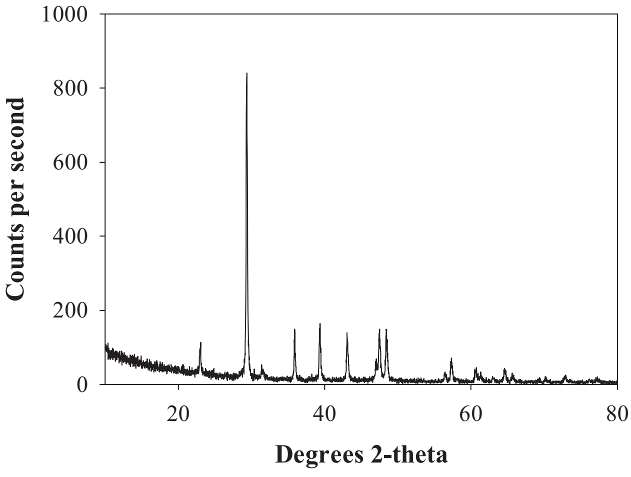

Fig. 13. XRD pattern of recycled $CaCO_3$.

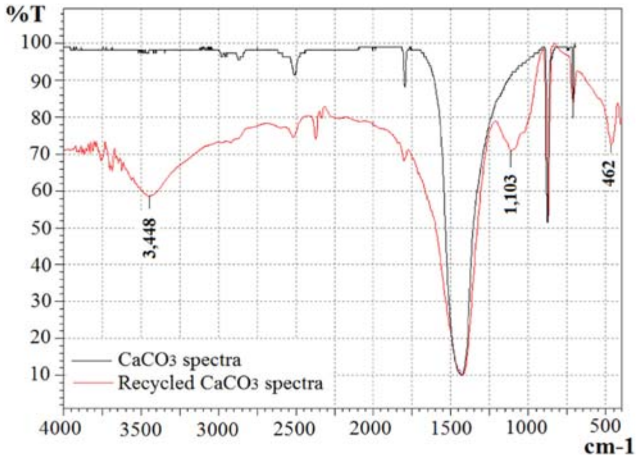

Fig. 14. Comparison of FTIR (transmission) spectra between recycled $CaCO_3$ and pure $CaCO_3$.

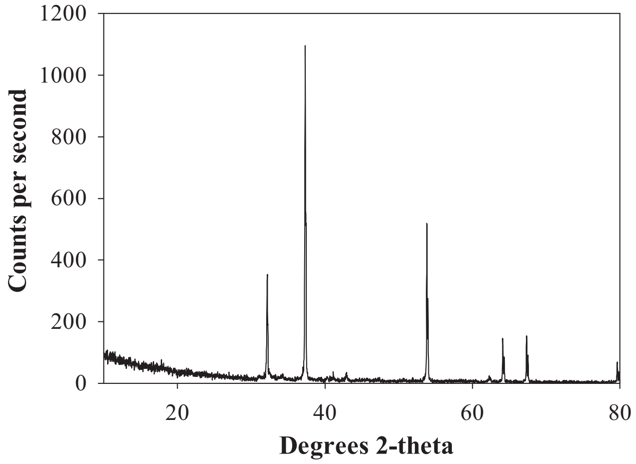

Fig. 15. XRD pattern of produced CaO.

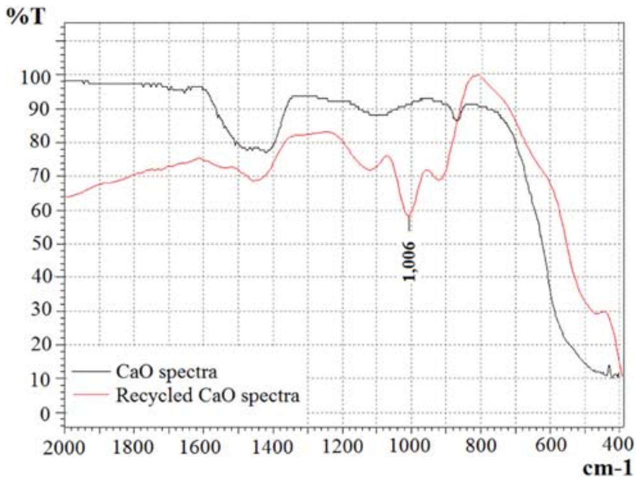

Fig. 16. Comparison of FTIR (transmission) spectra (from 2000 to 400 cm^{-1}) between produced CaO and pure CaO.

characteristic frequency of residual magnesium silicate. According to the bibliography, silicate ions are related to group frequencies ranging from 1100 to 900 cm^{-1} [48] while the peak around 460 cm^{-1} could be attributed to Mg—O vibrations [47].

The $CaCO_3$ recovery process could be optimized on an industrial scale by applying a flotation process to remove impurities [57,58]. In addition, if the quicklime recovery process by calcination was not shown to be useful, the application of the $CaCO_3$ cake in agriculture as a pH stabilizer for soil could be a feasible alternative to be tested. Ahmed et al. also suggested other possible applications for recovered $CaCO_3$ from RO concentrate in inland desalination plants such as a) paper coating pigment; and b) filler in plastics paint, ink and sealant production [59].

Figs. 15 and 16 show powder XRD analysis and FTIR transmission spectra (from 2000 to 400 cm^{-1}) of recycled $CaCO_3$ following calcination at 900 °C. The data analysis confirmed the production of a quicklime with a density of 3.35 g/cm^3. Fig. 15 matched the XRD pattern of cubic calcium oxide (PDF 01-077-2010) with peaks detected at 32.2°, 37.3°, 53.8°, 64.1°, and 67.3°.

As shown in Fig. 16, the strong IR absorption band around 400 cm^{-1} could be related to the lattice vibrations of calcium oxide. The FTIR spectra also showed a peak at 1006 cm^{-1} that could be attributed to the presence of a silicate ion group [48] in the calcined product. Produced CaO could be applied for water treatment or soil stabilization in construction projects.

5. Conclusions

The integration of an intermediate 'high-pH precipitation treatment' between consecutive RO stages for concentrate minimization and salt recovery in inland desalination plants was studied for the first time with magnesium dominated waters. RO concentrate from an existing groundwater desalination plant in Australia was treated with different alkaline reagents, such as NaOH, $Ca(OH)_2$, and Na_2CO_3, resulting in significant removal of scale-forming precursors including magnesium, calcium, strontium, barium, and SiO_2 by precipitation and adsorption/enmeshment mechanisms. SEM-EDX and FTIR determinations performed on the generated solids showed that precipitation as silicates appeared as the main mechanism for SiO_2 removal. Considering feasible salt recovery options and performance, the lime soda and ash softening treatment showed more advantages than the caustic soda treatment for the high-pH precipitation process. In that regard, the NaOH softening treatment increased RO concentrate alkalinity and conductivity with consequent negative impact on the *LSI/S&DSI*, achievable fresh water recoveries and energy requirements during the desalination process. In addition, the process resulted in smaller and more disperse flocs.

Software simulations suggested that following RO concentrate softening with lime and soda ash, pH re-adjustment and antiscalant addition, overall *Rw* could be further increased from 80% to 97% by using secondary RO. Conversely, $CaCO_3$ recovery from precipitated sludge during the lime and soda ash treatment was shown to be feasible through CO_2 injection to selectively dissolve magnesium. Recovered $CaCO_3$ was then re-calcined as quicklime. This intermediate 'high-pH precipitation treatment' for RO concentrate minimization coupled with the quicklime recovery process could be easily retrofitted in an existing desalination plant dealing with magnesium dominated waters.

Acknowledgements

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Additional note regarding economic considerations for the implementation of a 'High-pH pretreatment' for RO concentrate minimization

An experienced engineering company (Condorchem Envitech) estimated the capital cost of a modular 'High-pH pretreatment' plant for RO brine softening (500 m^3/day) to be US$ 844,186.00. The price included the supply of raw water tanks, pumping and dehydration systems with press filter, coagulation-flocculation and lamellar settling equipment, chemicals dosing systems and clarified storage tanks. Civil works, assembly and interconnections of equipment on site and government approval for the installation were not included in this preliminary budget.

Table 7 shows the cost of chemicals for 'High-pH pretreatment' of the RO concentrate with a) NaOH at pH 11.5; b) lime; and, c) lime and soda ash. It also shows the current cost of AS utilization in the desalination plant. Regardless of an increase in the chemical cost, 'High-pH pretreatment' could increase freshwater *Rw* from 80 to 97 % and reduce the cost of RO concentrate management and disposal. Generally speaking, waste and by-products management represents an important factor that has to be carefully studied considering the high volumes involved in these kind of projects.

Table 7

Comparison of current pretreatment cost and 'High-pH pretreatment' cost for scale control

Scale control technology	Freshwater *Rw* (%)	Price (US$/$m^3$ raw water)
Current pretreatment (AS addition)	80	0.02
NaOH pH 11.5	95	0.93
Lime softening	97	0.43
Lime and soda ash softening	97	0.46

Notes: Concentrated AS price used for this calculation was US$48.597/L and was provided by the Western Downs Regional Council. The plant is currently dosing 3 ppm AS of a diluted batch (10:1) in the first RO stage and 6 ppm in the secondary RO stage. NaOH, $Ca(OH)_2$ and Na_2CO_3 prices used in the softening calculations were 310, 150 and 275 US$/ton respectively (Bevacqua et al.). The cost of acid (for final pH stabilization) and AS following 'High-pH pretreatment' are not included in Table 7.

The ‘High-pH pretreatment’ process must be complemented with additional RO stages for softened RO concentrate minimization. It is important to mention that the efficacy of the ‘High-pH pretreatment’ will have a significant impact on: a) the longevity of the new RO membranes (typically three to five years in brackish water desalination); b) RO membrane productivity; and c) RO membranes cleaning frequency. Eventually, this should lead to an optimization of the Opex costs.

BW30 membranes used in the first RO stage can only treat feed waters up to 10,000 mg/L TDS without reaching the maximum operating pressure of 4.1 MPa. Therefore, seawater membranes supplied by The DOW chemical company should be selected for secondary RO stages. Seawater membranes can be applied to feed waters up to 50,000 mg/L TDS. Table 8 shows the flow performance range of different commercially available seawater elements (DOW, 2007).

Table 8

FILMTEC element characteristics (DOW, 2007)

Element type	Diameter (cm)	Permeate flow at standard conditions (L/h)	Maximum operating pressure (MPa)
SW30	6.3, 10.1	24-300	6.9
SW30HR	20.3	950	8.4
SW30HRLE	20.3	1200	8.4
SW30XLE	20.3	1400	6.9

The flux limit to be used in the design of the secondary RO system depends on the fouling tendency of the feed water. Since data of other RO membrane systems operating in similar feed water conditions are not available, the flux limit could be collected from information available in the RO Design Guideliness (DOW, 2007). According to the FILMTEC^{TM} technical manual, the average system flux ranges from 13 to 20 L/m^2.h for 8 inch FILMTEC elements in seawater applications. Therefore, this average system flux could be aplicable to this project. However, selection of the right membrane element type with its respective membrane surface area, calculation of the average membrane flux, number of elements, pressure vessels and stages needed for this project should be accomplished by an experienced design engineering company as well as the required Capex for the upgrade of the desalination plant.

The total cost of desalination depends on key factors such as: a) energy requirements; b) feed water salinity and water quality; c) economies of scale; and d) operating and maintenance costs (NSW Public Works, 2011). The operating costs could also be affected by environmental regulations. Eventually, a comprehensive study on a pilot plant scale would be required to assess whether 'High-pH pretreatment' of the RO concetrate is cost-effective for this single project, but this is beyond the scope of this PhD project work. The increase in Capex, energy, operator/maintenance, membrane replacement, and chemical costs should be compensated by the reduction of the cost of RO concentrate management.

Regardless of the environmental benefits, high capital cost and operating expenditure could be a limitation for the application of this chemically intensive solution in municipal desalination. However, this alternative can increase freshwater *Rw* in municipal desalination plants, salt recovery options are available and the volume of super-concentrated concentrate requiring final disposal into evaporation ponds is minimized.

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Additional note regarding Fig. 2. Darling Downs desalination plant layout

To make clearer the flow of permeate and RO concentrate in the Darling Downs desalination plant, an improved version of Fig.2 (Paper II) has been presented below.

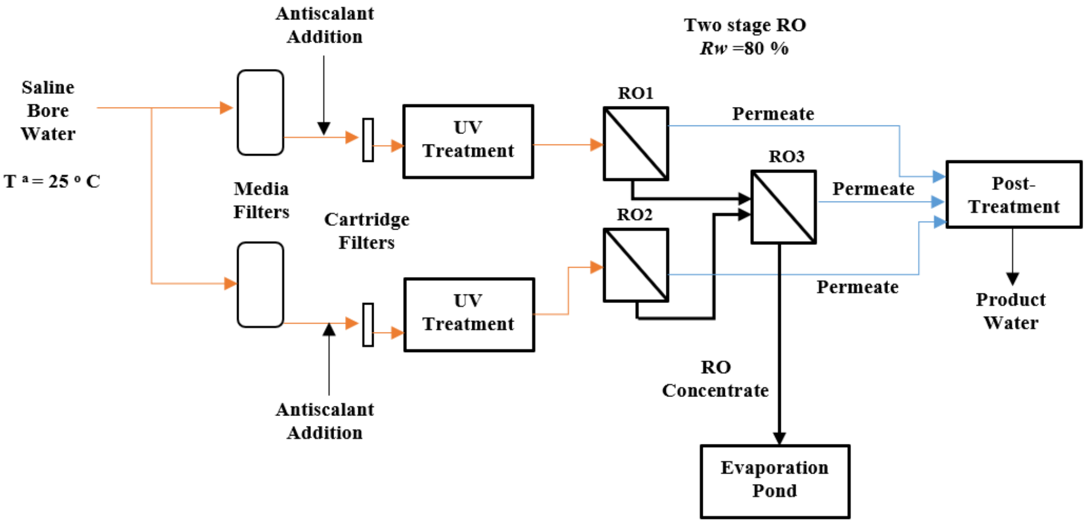

Fig. 2. Darling Downs desalination plant layout (updated)

Additional note regarding a minor error in the published paper.

A minor error was recently discovered in the published paper. The FTIR spectrophotomer used for these experiments was a Shimadzu model IRAffinity-1S.

4.3 Concluding remarks

The integration of an intermediate ‘High-pH pretreatment’ between consecutive RO stages for concentrate minimization and salt recovery, has been studied for the first time with magnesium-dominated groundwater. In contrast to previous studies, this study targeted maximum magnesium removal from the primary RO concentrate. The outcomes of this research show that precipitation with lime and soda ash gives greater efficiency than caustic soda utilization. The chemical demineralization process resulted in significant removal of scale-forming constituents including magnesium, calcium, strontium, barium, and SiO_2 through precipitation and adsorption/enmeshment mechanisms. SEM-EDX and FTIR determinations performed on the precipitated solids demonstrated that precipitation as silicates appears to be the main mechanism for SiO_2 removal.

Following ‘High-pH pretreatment’, pH re-adjustment and AS addition, overall water *Rw* was shown to be further increased from 80% to 97% using secondary RO. In addition, $CaCO_3$ recovery from the precipitated sludge was possible through CO_2

injection to selectively dissolve magnesium. Recovered $CaCO_3$ was then re-calcined as quicklime. These findings show that this intermediate 'High-pH pretreatment', for RO concentrate minimization and by-products recovery, could be retrofitted in an existing desalination facility in Australia.

CHAPTER 5

The effect of 'High-pH pretreatment' on RO concentrate minimization in a groundwater desalination facility using batch air gap membrane distillation

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PAPER III

Rioyo, J., Aravinthan, V., & Bundschuh. 2018. The effect of 'High-pH pretreatment' on RO concentrate minimization in a groundwater desalination facility using batch air gap membrane distillation. (Under Review, Submitted on 4 February 2019, reference number: SEPPUR_2019_448).

5.1 Introduction

Chapter 3 showed that the integration of an intermediate 'High-pH pretreatment' in municipal brackish water desalination was broadly investigated on a laboratory scale and using pilot plants in the USA. However, options that can be used to increase the water *Rw* and facilitate by-products recovery require rigorous laboratory investigation due to the quality of site-specific groundwater and RO concentrate. Thus, Chapter 4 investigated the integration of an intermediate 'High-pH pretreatment' between consecutive RO stages for concentrate minimization and salt recovery in an inland desalination plant in Australia dealing with magnesium-dominated groundwater. Now, for the first time, Chapter 5 investigates the implementation of an intermediate 'High-pH pretreatment' between RO technology and batch AGMD for scale control and RO concentrate minimization in the same municipal desalination facility.

This manuscript compares the efficacy of a) 'High-pH pretreatment' and b) AS only addition to high salinity RO concentrate for scale control and RO concentrate minimization in a lab-scale AGMD unit. The paper hypothesizes that the High-pH demineralization treatment (followed by pH readjustment and final AS addition) will permit operation of the batch AGMD system at a higher temperature, thus increasing permeate flux.

The effect of 'High-pH pretreatment' on RO concentrate minimization in a groundwater desalination facility using batch air gap membrane distillation

Javier Rioyo *, Vasantha Aravinthan, Jochen Bundschuh

University of Southern Queensland, School of Civil Engineering and Surveying, Faculty of Health, Engineering and Sciences, West St, Toowoomba, Queensland 4350, Australia

* Corresponding author. *Tel.: +61 7 4631 2100. E-mail: Javier.RioyoRumayor@usq.edu.au*

ABSTRACT

This study compared the efficacy of two different scale control strategies: (i) 'High-pH pretreatment'; and (ii) antiscalant (AS) addition for reverse osmosis (RO) concentrate minimization in a lab-scale air gap membrane distillation (AGMD) unit. In contrast with previous studies that investigated the demineralization of low conductivity RO concentrate and ulterior minimization using direct contact membrane distillation (DCMD), we systematically investigated the performance of batch AGMD configuration with and without the preliminary reduction of scale-forming constituents from high salinity RO concentrate. The results indicated that 'High-pH pretreatment' was more productive than sole AS addition to the RO concentrate which resulted in significant salt precipitation once the concentration factor (*CF*) in the AGMD system increased above 1.3. Following 'High-pH pretreatment', pH re-adjustment, and final AS addition, the use of AGMD enabled us to minimize the existing RO concentrate with an initial total dissolved solids (TDS) level of 10.8 g/L by a *CF* of 3.2. This approach controlled the formation of mineral scales in crucial components of the unit such as the AGMD membrane, feed water tank, and heating element. In addition, this chemical demineralization process allowed the operation of the AGMD unit at a higher temperature, and thus permeate flux also increased.

Keywords: reverse osmosis; inland desalination; brackish groundwater; air gap membrane distillation; concentrate minimization;

1. Introduction

In the USA, more that 96 % of the municipal desalination systems are located inland, making reverse osmosis (RO) technology the preferred option for drinking water production [1]. In Australia, most inland desalination systems also employ RO technology to supply high quality freshwater from brackish groundwater [2]. Concentrate management and high cost prevail as major limitations of this membrane technology, restricting the construction of new facilities [1]. The operation of these municipal systems at high water recoveries (*Rw*) can reduce the amount of RO concentrate that eventually needs to be disposed of. However, *Rw* is limited by the precipitation of sparingly soluble inorganic salts on the RO membranes. This occurs when the concentration product of the salt-forming precursors goes beyond its solubility product (*Ksp*). Even if scale inhibitors are injected during RO pretreatment, *Rw* becomes limited by the scale suppression capacity of the selected antiscalant (AS) [3, 4].

Some researchers have proposed membrane distillation (MD) technology for minimization of RO concentrate and high salinity streams volume [5-13]. MD is a thermally driven technology which involves the transport of vapour molecules though a microporous hydrophobic membrane [14]. In such a context, temperature is considered a key factor related to scaling [15]. Salt precipitation and deposition can occur on different elements of the MD system such as the membrane, pipes, feed water tank or heating element. Overall, scaling of the MD membrane has remained as a challenging problem, as reported in the literature [15, 16]. The use of AS can minimize the membrane scaling problem [15, 17]. This solution is always preferable to membrane cleaning [17]. However, the drawbacks of using AS include the following: (a) an excessive dose of AS can foul the membranes by promoting biofouling; (b) AS can react with other chemicals added during RO pretreatment, promoting adverse effects on the membranes; (c) AS can react with metal ions enhancing scales on the membranes [16]; and (d) many AS molecules can also decrease the surface tension of the feed water solution, causing membrane pore wetting as well as reduced lifetime in MD membranes [18].

Overall, the need to explore alternative techniques to alleviate the scaling problem is predicated on the understanding of the scale formation mechanisms specifically occurring in MD systems. We previously investigated the incorporation of a ‘High-pH pretreatment’ between serial RO stages for membrane scaling control, concentrate reduction and by-products recovery [4]. In order to conduct this research project, an existing groundwater desalination plant in inland Queensland (Australia), was used. In contrast to previous studies performed in the USA, well water and RO concentrate collected at the municipal desalination plant had a relatively lower calcium concentration and a higher magnesium concentration. The ‘High-pH pretreatment’ reduced the concentration of scale forming constituents including calcium, magnesium, strontium, barium and silica [4]. However, the inorganic precipitation process in MD plants may be different from those of pressure driven membrane technologies such as RO, due to variation in operating conditions such as temperature. The literature survey found that only one paper evaluated chemical demineralization pretreatment of a RO concentrate followed by MD technology [19]. The aim of the research was to decrease the scaling potential of RO concentrate when using direct contact membrane distillation (DCMD) technology. The case-study, conducted by Qu et al., used low conductivity (960 µS/cm) RO concentrate generated in a drinking water preparation system in Beijing (China) [19]. Most studies reported in the research papers have utilized a DCMD configuration when evaluating MD technology for different applications. In that regard, salt precipitation might have a different effect on other configurations such as AGMD [16, 17]. To date, none of the previous studies has investigated the treatment of RO concentrate from groundwater sources and assessed the performance of batch AGMD configuration with and without the preliminary removal of scale-forming precursors. Therefore, this study focused on the integration of AGMD technology with a ‘High-pH pretreatment’ for RO concentrate reduction in an inland desalination facility treating magnesium-dominated groundwater. Fig.1 illustrates a proposed lay-out. The main objectives of this study were to compare the efficacy of two different technologies, AS addition and ‘High-pH pretreatment’ (followed by pH adjustment and final AS addition), in terms of RO concentrate minimization in a batch AGMD unit and scale prevention on different elements of the desalination system.

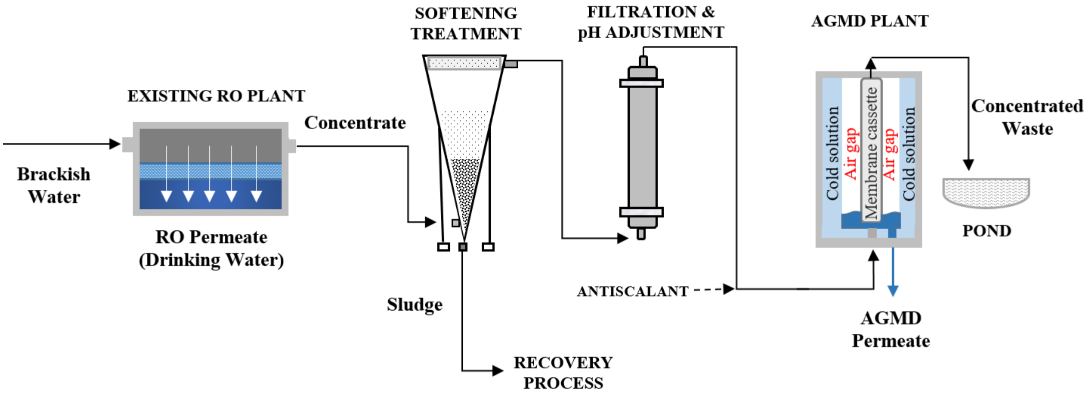


Fig.1. Proposed lay-out for RO concentrate reduction using AGMD technology.

2. Background

MD is a promising technology still in the premature stages of development and commercial deployment [15, 20-22]. In MD systems, the vaporization process takes place at the membrane’s hot surface [20]. MD involves the transport of vapour thorough a non-wetted, porous and hydrophobic membrane. This process is driven by a water vapour pressure difference across the membrane, induced by the temperature difference across the same membrane [23, 24]. The water flux (J) of the AGMD system in L/m^2.h can be calculated according to the next equation, where K_m is the system mass transfer coefficient and ΔP is the water vapour pressure difference between the feed and the coolant stream [17]:

$$J = K_m * \Delta P \quad (1)$$

MD technology is operated at lower hydrostatic pressure than RO and at a lower operating temperature than conventional evaporation technologies [14]. MD membranes have low thermal conductivity and low resistance to mass transfer, which assists in avoiding heat loss across the membrane [20]. Membrane thickness decreases mass and heat transfer through the MD membrane [18, 24]. Permeate flux is also favoured in membranes with higher porosity since they present a bigger surface area for evaporation [21]. In addition, permeate flux and mass transfer are also enhanced with the increase in pore size [13]; nonetheless, the pore size should be kept as small as possible to minimize the risk of pore wettability [21, 25].

In MD systems, both temperature and concentration polarization are key parameters affecting the process. Temperature polarization can be defined as the temperature gap between the liquid-vapour interface and the bulk solution. Temperature polarization phenomenon came to be significant at high feed water concentrations, high feed water temperatures, and low feed water velocities. Concentration polarization can be defined as the intensification of solute concentration on the membrane surface with respect to the bulk solute concentration [20].

Since MD technology is not greatly affected by feed water salinity, it could be considered as an interesting alternative for certain desalination applications [26]. Besides, it is less susceptible to fouling than RO technology. Therefore, it does not require such an intensive pretreatment in comparison to RO [17]. However, the main disadvantages of MD technology are: (a) the lower permeate flux rates when compared with RO technology; (b) temperature and concentration polarization phenomena; (c) membrane fouling and scaling issues; (d) limitations in the design of membranes and MD modules; and (e) the high thermal energy requirements [16].

Among these drawbacks, membrane scaling has remained a challenging problem which attracted growing attention, as reflected in recent literature [15-18]. This can be prevented to a certain degree by pretreatment and chemical cleaning [15]. The consequences of membrane scaling are: (a) pore wetting; (b) permeate flux reduction; (c) increased temperature and concentration polarization; and (d) membrane damage and chemical degradation. The phenomenon of permeate wetting occurs when the pressure in the feed water channels of the membrane goes beyond the liquid entry pressure (LEP) [15].

To date, the following four configurations have been investigated in MD systems: (a) DCMD; (b) AGMD; (c) sweeping gas membrane distillation (SGMD); and (d) vacuum membrane distillation (VMD) [20]. Fig. 2 illustrates these MD configurations. DCMC is considered the simplest MD configuration, though the heat loss by conduction is considered its main handicap [20]. In this set up both the feed water solution and the cold permeate are in direct contact with both sides of the membrane [27]. The vapour is moved across the membrane to the permeate side. Then, condensation occurs inside the membrane module. It has been employed in the food business for the concentration of aqueous solutions [20]. In AGMD systems the vapour crosses a stagnant air gap and condenses over a cold surface [20]. In this configuration the driving force is the temperature difference over the membrane and the gap [27]. Despite the reduction in heat loss by conduction, the existing air gap increases heat and mass transfer resistances, so permeate flux is reduced [24]. At lab scale, AGMD produced fluxes that were up to four times lower than DMCD, while at pilot scale, AGMD could produce higher fluxes than DCMD [27]. Overall, AGMD could be considered more energy efficient than other MD configurations [7]. SGMD is another variation in MD technology that applies an inert gas to sweep the water vapour at the permeate side of the membrane. Condensation then happens outside the membrane module [28]. Its main limitation is the requirement for a large condenser, since a small volume of permeate diffuses in a large sweep gas volume. Finally, VMD uses a pump to generate a vacuum in the permeate membrane side. In this case, heat loss by conduction is insignificant and condensation occurs outside the membrane module [20].

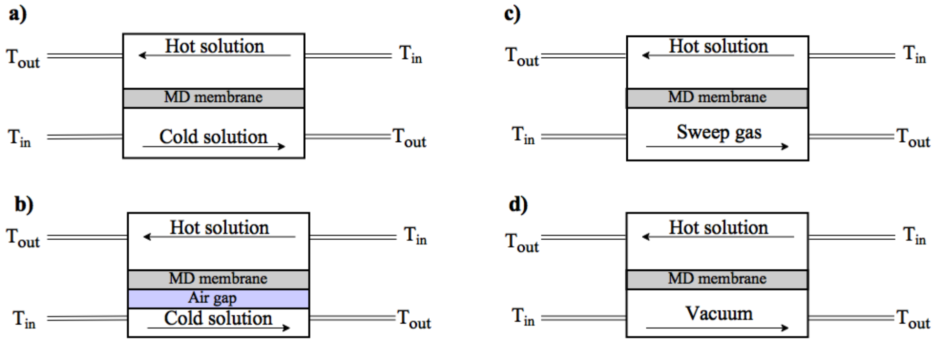


Fig.2. Common configurations in MD systems: a) DCMD; b) AGMD; c) SGMD; and d) VMD.

The influence of key operating parameters such as feed water temperature, coolant temperature, feed water flow-rate and salinity on AGMD performance have been described in different studies and with different kinds of water, including high salinity solutions and CSG produced water [7, 12, 22, 29-31]. Table 1 summarizes the main findings.

To date, none of the previous studies have focused on the treatment of high TDS RO concentrate produced during the desalination of magnesium-dominated groundwater sources or assessed the performance of batch AGMD configuration. One point specifically hypothesized in this research was that the combination of RO technology, an intermediate ‘High-pH pretreatment’ for scale control, and batch AGMD could help to solve the limitations of the single units by using their synergetic capabilities in order to enhance RO concentrate reduction and freshwater recovery of the overall desalination system.

Table 1
Effect of operating parameters on AGMD performance.

Operating parameter	Effect on permeate flux (*J*)	Reasons
Feed water temperature increases	⬆	• Water vapour pressure grows exponentially with the feed water temperature. Therefore, the driven force of the MD system is favoured [12].
Feed flow rate increases	⬆	• As a consequence of the higher mass transfer coefficient, the gap between the bulk and membrane surface temperature and the difference between the bulk and membrane surface concentration are reduced. Consequently, temperature and concentration polarization phenomena on the membrane surface are reduced [12, 31].
Feed water concentration increases	⬇	• Water vapour pressure decreases, and temperature polarization increases [29]. Energy consumption is likewise expected to rise as the feed water concentration grows [13].
Coolant temperature rises	⬇	• The vapour pressure difference across the membrane decreases [12].

3. Materials and methods

3.1 RO concentrate characteristics

The RO concentrate used for these experiments was collected in an inland desalination facility located in Dalby, Queensland, Australia. Table 2 includes the composition of the RO concentrate used for this study.

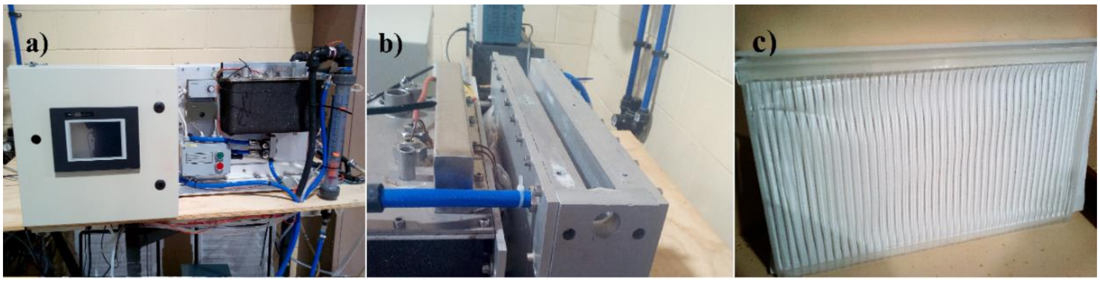
Table 2
Characteristics of the RO concentrate used for these experiments.

Parameter	RO concentrate
pH (Units)	8.1
Conductivity (mS/cm)	15.9
TDS (mg/L)	10829
Alkalinity (mg/L $CaCO_3$)	1421
Potassium (mg/L)	17
Sodium (mg/L)	3229
Magnesium (mg/L)	320
Calcium (mg/L)	148
Strontium (mg/L)	5
Barium (mg/L)	0.2
Chloride (mg/L)	4746
Fluoride (mg/L)	1.25
Sulphate (mg/L)	584
Silica (mg/L SiO_2)	115

3.2 Lab-scale AGMD system description

The AGMD unit available at University of Southern Queensland was supplied by Scarab Development AB (Sweden), as shown in Fig. 3a. This lab-scale unit incorporates an immersion heater (model Ratek TH5/TH52K) inserted in a feed water tank (25 L capacity) that can regulate the feed water temperature. The feed water flow-rate can be set to a maximum of 40 L/h by manipulating the pump speed of a submersible pump (model SEAFLO 12 v). Manufacturer recommended that higher feed water flow-rates could cause high pressure levels inside the membrane cassette, overcoming the mechanical resistance of the membrane. In addition, the feed water pump can be operated to a maximum of 60^{o}C. The cooling system (model Ratek RC1) was designed to cool the condensation plates inside the AGMD device using tap water. The system also includes a water tank (33 L capacity) for tap water storage. The coolant flow-rate and temperature in the AGMD system can be adjusted to 200 L/h and 10 ± 2^{o}C.

This MD system incorporates a 'solid steel casing', including one cooling serpentine and one cooling surface on each side. In between both cooling surfaces is placed a plastic cassette, which is covered by the membrane in both sides [30]. The total available membrane surface of every cassette is 0.1955 m^2. Figs. 3 b) and 3 c) illustrate the 'solid steel casing' and a membrane cassette used in the lab-scale AGMD unit. Each of the air gaps (4 mm wide) creates a gap between the membrane and the cooled condensation surfaces. The purpose of the stagnant air gap is to act as a thermal insulation layer [32].



Figs. 3. a) Lab-scale AGMD system; b) solid steel casing; and c) membrane cassette to be placed in the solid steel casing.

Polyvinylidene fluoride (PVDF) membranes supplied by Hangzhou Anow Microfiltration Co., Ltd. (China) were used for these desalination experiments. Table 3 shows the main features of these membranes.

Table 3
AGMD Membranes characteristics

Membrane reference	Material	Pore size	Thickness	Bubble point test
JMV045	PVDF	0.45 µm	0.09-0.11 mm	≥0.06 MPa (Alcohol)

Note: Bubble point test has often been used to estimate the integrity of membrane filters [33]. This test has to be performed under gas pressure and the filter has to be initially wetted with an appropriate fluid [34]. This test determines the minimum pressure at which a continuous stream of bubbles was initially seen downstream of the wetted filter [33].

The operation of the lab-scale AGMD unit is illustrated in Fig. 4. 25 L of RO concentrate was added to the feed water tank (Batch 1). During the process, the feed water (RO concentrate) enters in the lower inlet of the cassette and leaves via the upper outlet. This allows direct contact between the feed solution and the membrane surface. In batch mode operation, the feed water is returned to the tank and re-circulated again through the cassette. This allows the progressive concentration of the solution in the feed water tank. Concurrently, there is a decrease in the water level in the feed water tank because of permeate production and water losses by evaporation. Once the feasible concentration factor (*CF*) is achieved, the feed water tank is cleaned and refilled with fresh RO concentrate (Batch 2). A previous study reported that a semibatch membrane distillation process has a lower thermal energy consumption than a steady process (one pass through system). In addition, a lesser amount of feed water was required to generate the same amount of permeate [28]. As shown in Fig. 4, the lab-scale AGMD unit allowed the measurement of temperature. The permeate flux was recorded by means of an electronic balance (model Ohaus Pioneer^{TM} PA4102C) and a stopwatch. Feed water and coolant flow-rate were determined using a 1 L glass cylinder and a stopwatch while all conductivity determinations were undertaken in the laboratory.

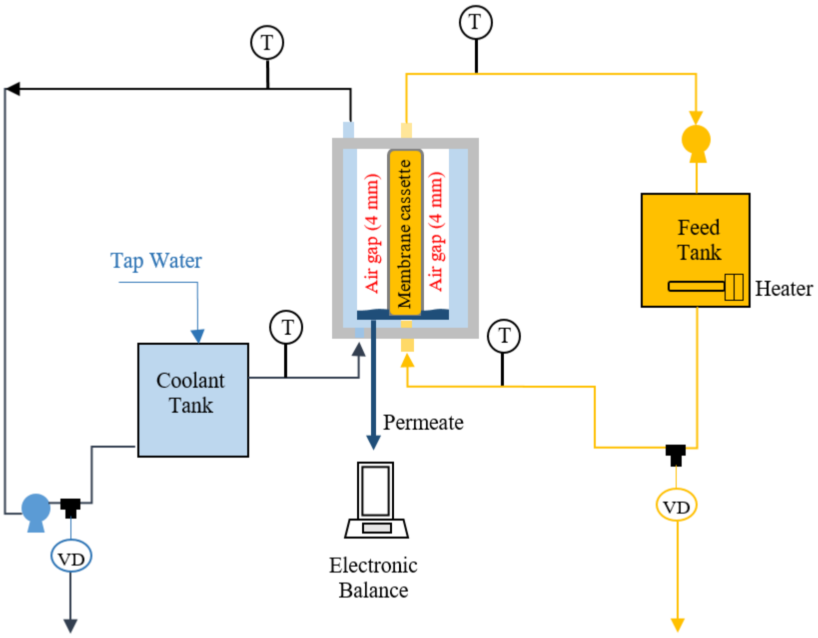


Fig. 4. Experimental set up of the batch AGMD unit. T = thermocouples type Y.

3.3 Analytical methods

Analytical methods and laboratory equipment utilized in this research were described in our previous publications [4, 35]. All pH and conductivity analyses were undertaken using a multi-parameter meter model Eutech PC2700. SEM-EDX analyses of MD membranes (new and scaled) and precipitates were carried out using a scanning electron microscope (JEOL model SEM-JCM6000). This technique allows the analysis of the morphology structure and composition of the surface of the membrane [9, 18]. The presence/absence of membrane scaling on the membrane surface can be confirmed by SEM images of the membrane surfaces [8]. Finally, FTIR spectra of MD membranes and precipitates were carried out using a FTIR spectrophotometer (Shimadzu model IRAffinity-1S). To perform all spectra, 45 scans were taken for both the background and the samples. In addition, FTIR spectra resolution was adjusted at 4 cm^{-1}.

3.4 Experimental protocols

3.4.1 'High-pH pretreatment' studies

All precipitation tests were conducted in the water laboratory available at the University of Southern Queensland, in a controlled environment (23±0.5°C). A jar-test flocculator (model VELP SCIENTIFICA JLT series), containing six 1-litre PVDF beakers was used for the demineralization of RO concentrate using lime and soda ash. Required $Ca(OH)_2$ (2.2 g/L) and Na_2CO_3 (0.44 g/L) doses were calculated according to standard methodology [36]. Previous research that we performed with RO concentrate of similar characteristics had proved that this option was more favourable than the NaOH softening treatment. The latter option resulted in an increase in conductivity and total alkalinity of the softened RO concentrate, and also led to a negative impact on the Langelier Saturation Index (*LSI*) and the Stiff & Davis Stability Index (*S&DSI*) [4]. Jar testing was comprised of the following steps shown in Table 4.

Table 4
Jar test protocol followed to study the efficiency of 'High-pH pretreatment' of RO concentrate

Step	Treatment	Duration time (minutes)	Mixing speed (rpm)
1	Addition of lime - rapid mixing	2	150
2	Slow mixing	30	50
3	Addition of soda ash - rapid mixing	2	150
4	Slow mixing	30	50
5	Settling	60	--
6	Collection of supernatant samples for experiments within the AGMD lab-scale unit	--	--

All jar test trials were conducted several times in order to gather enough volume of softened RO concentrate for the MD experiments. The removal of scale-forming constituents such as magnesium, SiO_2, calcium, strontium and barium was measured, and ROSA software used for saturation indexes (*SI)* calculation. Table 5 shows the composition of the softened RO concentrate following pH readjustment to 8.1 by HCl/NaOH addition.

Table 5
Characteristics of the softened RO concentrate. (Lime & soda ash softening treatment + pH readjustment to 8.1).

Parameter	RO concentrate characteristics
pH (Units)	8.1
Conductivity (mS/cm)	15.3
Turbidity (NTU)	1.5
TDS (mg/L)	9325
Alkalinity (mg/L $CaCO_3$)	37
Potassium (mg/L)	15
Sodium (mg/L)	3549
Magnesium (mg/L)	12
Calcium (mg/L)	20
Strontium (mg/L)	0.7
Barium (mg/L)	0.11
Chloride (mg/L)	5106
Fluoride (mg/L)	0.6
Sulphate (mg/L)	574
Silica (mg/L SiO_2)	4.5

3.4.2 Batch AGMD studies for RO concentrate minimization and scale control

Two different samples were desalinated in the lab-scale AGMD unit: (a) Treatment 1: RO concentrate (pH 8.1 and 'SpectaGuard SC' AS added); and (b) Treatment 2: RO concentrate treated by the lime and soda ash softening process (the pH level of softened concentrate was readjusted to 8.1 and 'SpectraGuard SC' AS added). For comparison purposes, both samples were desalinated at the same pH level. 'SpectraGuard SC' is a phosphate free AS that can control the precipitation of $CaCO_3$, $CaSO_4$, $BaSO_4$, CaF_2 and silica to a certain extent [37]. In all experiments 3 mg/L of AS were added to the feed water. As justified in Section 4.1, feed water temperature was adjusted to 50^oC in the first case (Treatment 1) and 56^oC in the second case (Treatment 2). Feed water flow-rate was set within the range 30-40 L/h in all experiments. Coolant temperature and flow-rate were adjusted to 10^oC and 200 L/h respectively. For every test, 25 L of sample were added to the feed water tank (Batch 1) and the solutions were progressively concentrated. MD experiments were interrupted when the AGMD unit achieved a *CF* of about 3.0-3.2. Further RO concentrate minimization was not possible due to the technical limitations imposed by the heating element and the submergible pump located in the feed water tank. At this point the feed water tank was cleaned and refilled with 25 L of fresh RO concentrate and the process re-started again (Batch 2). On completion of the experiments, precipitated solids collected from the feed water tank, and heating element and produced layer of scale generated on the membranes surface were analysed by FTIR and SEM-EDX technology. Produced AGMD permeate and the super-concentrated solution were also analysed and a mass balance performed.

Before commencing these experiments, the integrity of all tested PVDF membranes and cassettes was verified for two hours treating tap water (feed solution) in the lab-scale AGMD unit. To this purpose, permeate flux was recorded every fifteen minutes under the standard operation conditions previously mentioned.

4. Results and discussion

4.1 Selection of the intermediate 'High-pH pretreatment' for scale control

Calculation of *SI* levels at 25ºC showed that the RO concentrate (Table 2) was initially saturated with respect to (a) $CaCO_3$ with *LSI* and *S&DSI* levels of 1.8 and 1.3 respectively; and (b) $BaSO_4$ with a *SI* level of 4.66. Calculation of silica, CaF_2 and $CaSO_4$ *SI* levels reached values of 0.79, 0.30, and 0.04 respectively. On the other hand, the softened RO concentrate (Table 5) was only saturated with respect to $BaSO_4$ with a *SI* level of 3. As a consequence of the chemical demineralization treatment and the pH adjustment to 8.1, the *LSI* and the *S&DSI* resulted in negative values. In addition, silica and CaF_2 *SI* levels decreased from 0.79 and 0.30 to 0.03 and 0.01 respectively.

Extra volumetric reduction of the RO concentrate could be attained by AGMD technology. Figs. 5 and 6 show the evolution of the *S&DSI* and silica *SI* levels as the RO concentrate (black markers) and the softened RO concentrate (red coloured markers) are further minimized. Both $CaCO_3$ and silica solubilities depend on solution temperature, though $CaCO_3$ exhibits an inverse solubility to temperature ratio. This means that the heating element in an AGMD system could be more prone to $CaCO_3$ scaling due to the higher temperatures achieved [7]. According to the bibliography, $CaCO_3$ scales could also be prevented by decreasing the pH level of the solution [15]. However, considering the feed water quality as shown in Table 2 at its natural pH level of 8.1 and commercial AS capabilities, both $CaCO_3$ and/or silica may pose a scaling risk, limiting freshwater recoveries during the AGMD concentration experiment (Treatment 1).

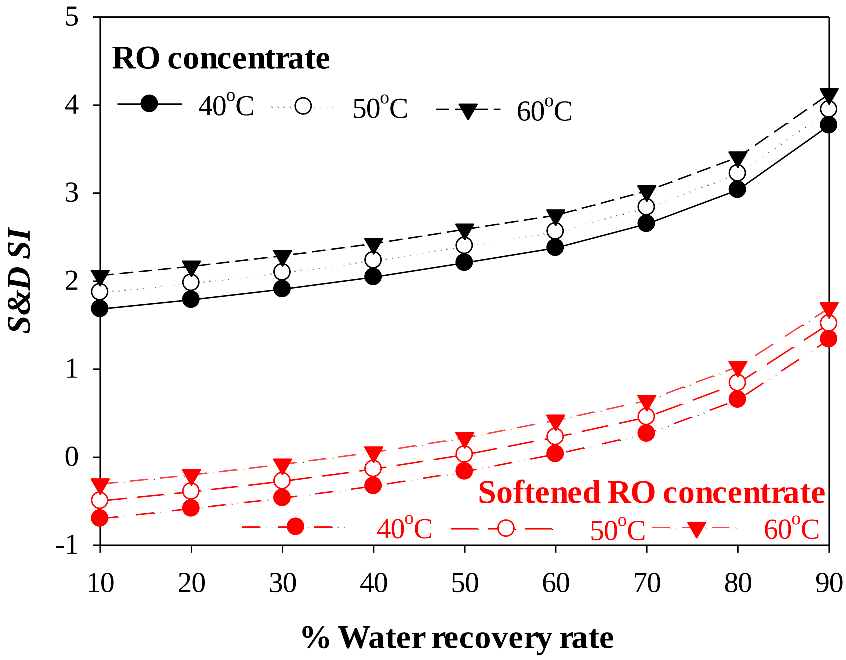


Fig. 5. RO concentrate minimization (black markers) and softened RO concentrate minimization (red coloured markers). *S&DSI* calculation at different temperatures.

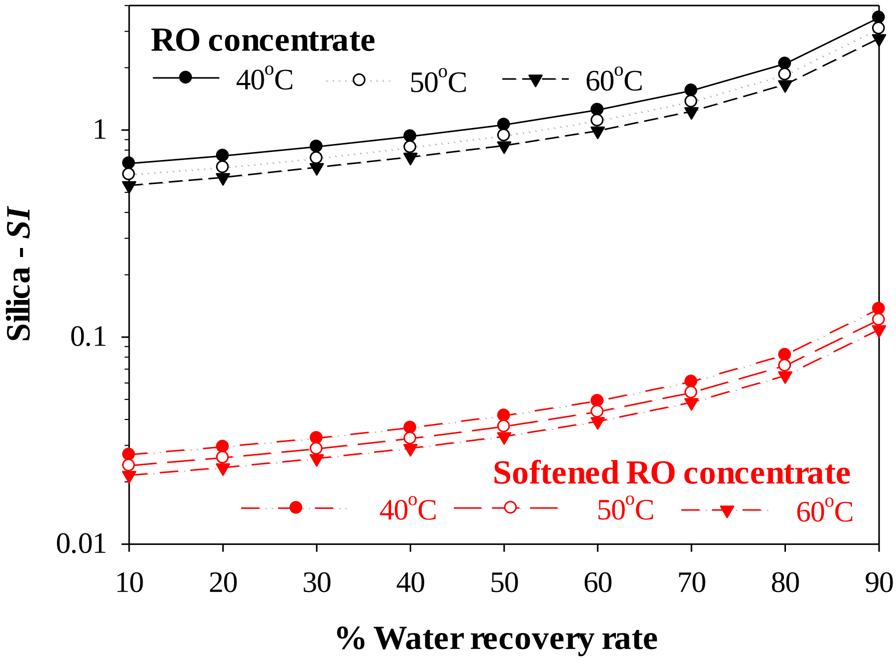


Fig. 6. RO concentrate minimization (black markers) and softened RO concentrate minimization (red coloured markers). Silica *SI* calculation at different temperatures.

Fig. 7 shows CaF_2 and $BaSO_4$ *SI* levels calculated at different temperatures as the RO concentrate (black markers) and the softened RO concentrate (red coloured markers) are further minimized. Although $BaSO_4$ exhibits a negative correlation of solubility with temperature [18], ROSA software provided similar CaF_2 and $BaSO_4$ *SI* levels regardless of the change in the solution temperature (40 to 60°C). Nevertheless, it was noted that following a 'High-pH pretreatment' of the RO concentrate, the risk of barite and/or fluorite precipitation was reduced as a consequence of the lowered *SI* levels achieved. Having said this, the risk of CaF_2, and $BaSO_4$ scaling during the RO concentrate minimization experiments could be controlled to a certain extent by using commercial scale inhibitors [15] such as VITEC 4000 [38].

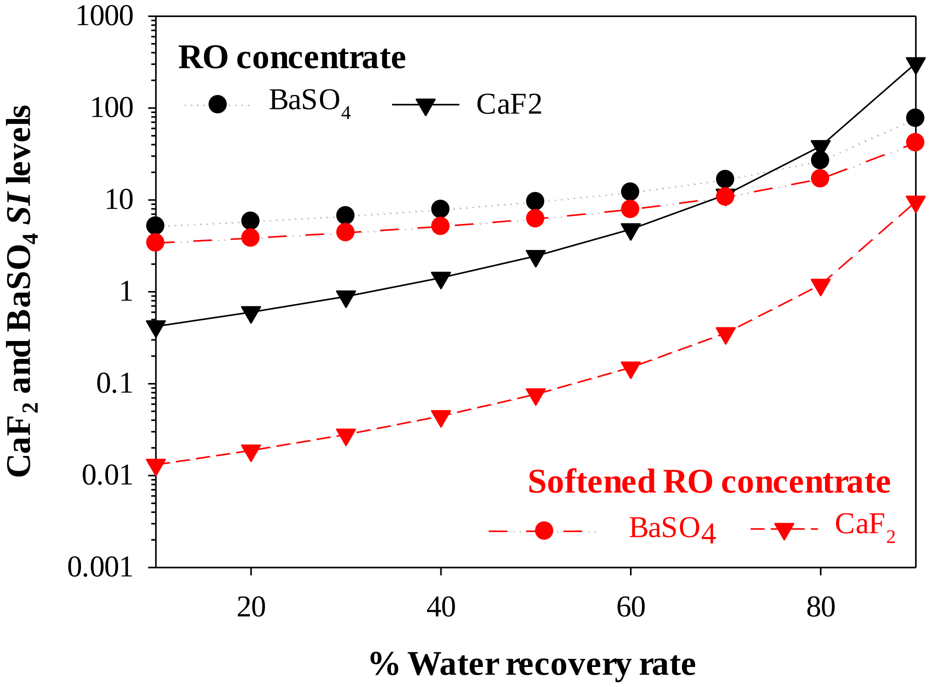


Fig. 7. RO concentrate minimization (black markers) and softened RO concentrate minimization (red coloured markers). CaF_2 and $BaSO_4$ *SI* calculation in the range of temperatures between 40 and 60°C.

Balancing (a) the fact that the permeate flux in an AGMD unit is favoured for higher feed water temperature [29]; (b) the propensity for both silica and $CaCO_3$ to scale as shown in Figs. 5 and 6; and (c) the technical limitations imposed by the lab-scale MD system, a feed water temperature of 50°C was selected to perform the RO concentrate minimization experiments following AS addition (Treatment 1). For Treatment 2 ('High-pH pretreatment' followed by pH normalisation to 8.1 and AS addition to the RO concentrate), a higher feed water temperature of 56°C was selected, considering the much lower scaling potential of the softened RO concentrate. Higher temperatures were discarded, considering that the feed water pump can only be operated to a maximum of 60°C. In addition, taking into account the possible utilization of clean sources of energy such as solar thermal energy in a real system located in a remote area [28] and the high groundwater volumes involved in inland desalination, higher temperatures might be seen as excessive.

Overall, to cope with the limitations imposed by AS utilization, an intermediate 'High-pH pretreatment' (followed by pH adjustment to 8.1 and AS addition) altered the physicochemical properties of the RO concentrate resulting in reduced scaling propensity in the AGMD system. Correspondingly, the MD system could be operated at higher feed water temperatures, considering the much lower scaling potential of the softened RO concentrate.

4.2 Comparison of Treatment 1 (pH 8.1 and AS addition to the RO concentrate); and Treatment 2 ('High-pH pretreatment' of the RO concentrate followed by pH adjustment to 8.1 and AS addition)

4.2.1 Salt precipitation in the AGMD unit: feed water tank, feed water pump and heating element

Significant salt precipitation and deposition was observed on the heating element, feed water flow-meter, and the walls and bottom of the feed water tank following Treatment 1 (Batch 1 and 2). This phenomenon, initially observed once the *CF* increased above 1.33 (equivalent to 25% fresh water recovery rate), was attributed to the higher *S&DSI* and *LSI* levels achieved. It seemed that in that scenario the AS capabilities for $CaCO_3$ scale control were overcome (*LSI* >2.5). In addition, the feed water pump was damaged, and was twice replaced by a new one. Therefore, the operation of the AGMD system for RO concentrate minimization solely by preliminary AS addition was demonstrated not to be sustainable under these operating conditions. In contrast, no mineral salt scales were visually observed on the heating element or the walls and bottom of the feed water tank following Treatment 2 to the RO concentrate. Thus, the operation of the batch AGMD system for the minimization of softened RO concentrate could be guaranteed at least to a *CF* of 3.2 under these operating conditions. Figs. 8a and 8b show images of the feed water tank and the heating element at the end of the AGMD concentration experiments following both strategies.

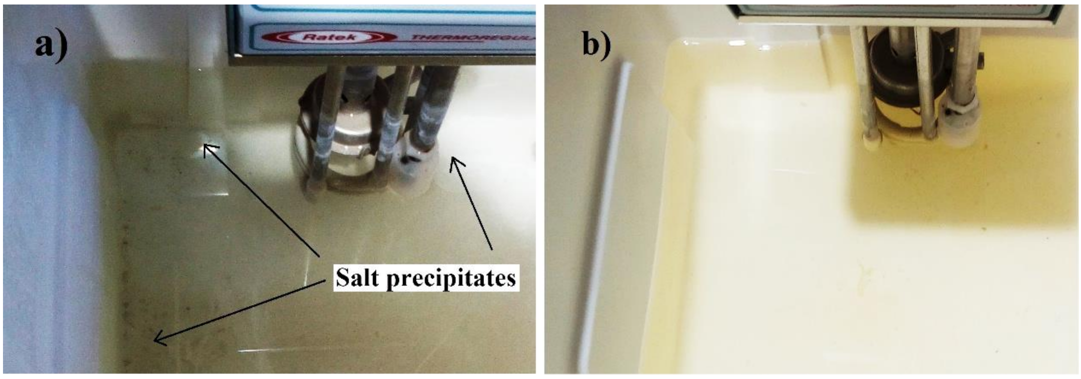


Fig. 8. Photos of the walls/bottom of the feed water tank, and surface of the heating element at the end of the AGMD concentration experiments. a) Treatment 1; and b) Treatment 2.

SEM images and EDX spectra of precipitated solids collected in the feed water tank and on the surface of the heating element following Treatment 1 to the RO concentrate were presented in Figs. 9a and 9b. In both cases, EDX analyses in selected points of both samples resulted in amorphous and heterogeneous precipitates containing calcium, magnesium and silicon.

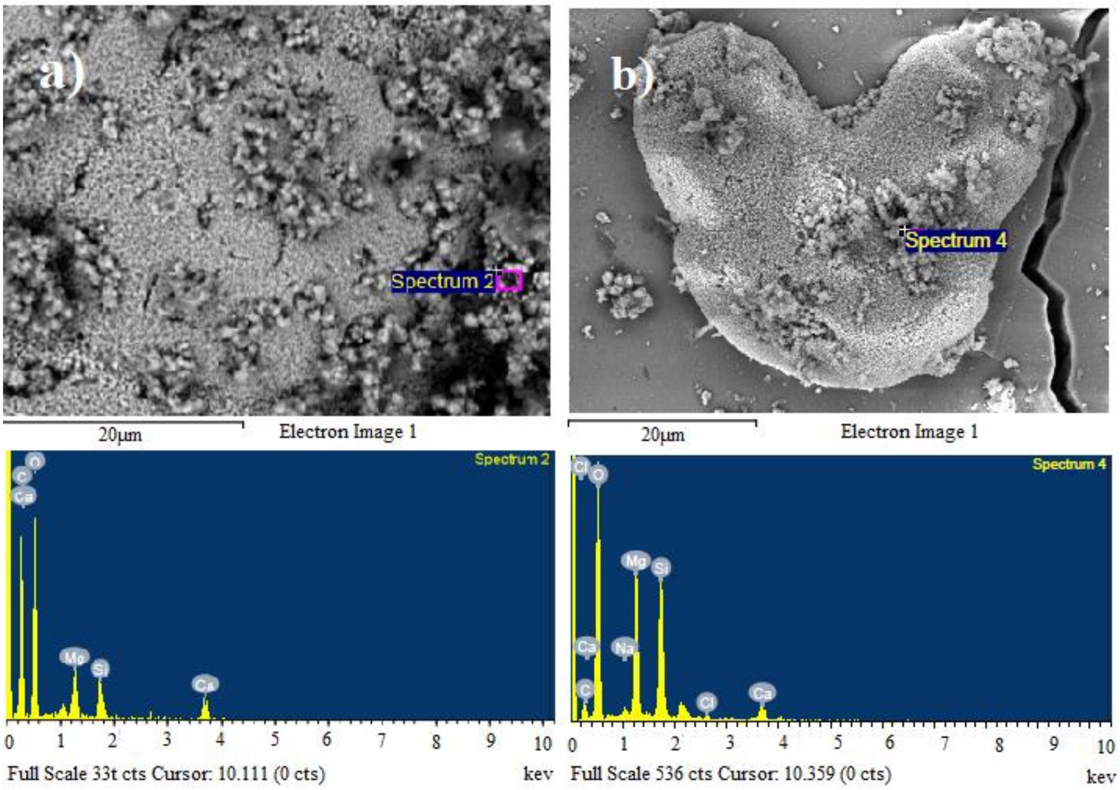


Fig. 9. SEM images and EDX analysis of the a) precipitated solids collected in the bottom of the feed water tank; and b) precipitated solids collected on the surface of the heating element during Treatment 1.

FTIR spectra of a sample of precipitated solids collected in the bottom of the feed water tank following Treatment 1 was provided in Fig. 10a. Silicate ion bands were identified in group frequencies ranging from 1,000 to 900 cm^{-1}, while carbonate ion bands were identified in group frequencies ranging from 1,490 to 1,410 cm^{-1} [39]. This could ratify the possible precipitation of calcium carbonate and silicates in the AGMD system following Treatment 1 to the RO concentrate. A slight increase in the pH level was recorded in the course of the volumetric concentration experiments (Batch 1 and 2) from the initial value of 8.1 to a final value of about 9.0. According to the bibliography, as the pH increases above neutral values, silicic acid dissociates into silicate anions. Thus, insoluble silicate could have been formed in the presence of metals like calcium or magnesium [40]. On the other hand, FTIR analysis of the solids precipitated on the surface of the heating element (Fig. 10.b) matched with a 75 % similarity to $CaCO_3$. This could be explained by the higher temperature achieved in this component, which enhanced $CaCO_3$ precipitation due to its inverse solubility to temperature ratio.

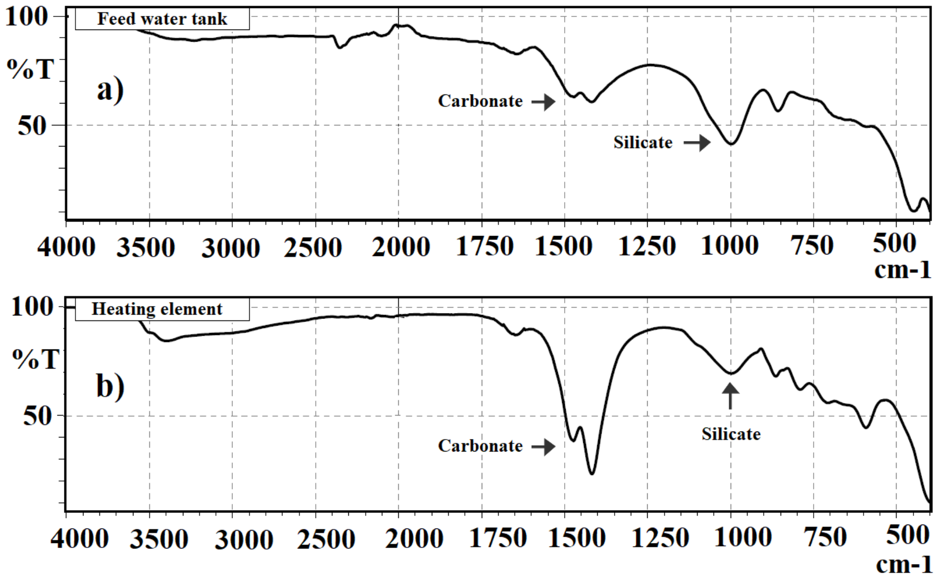


Fig. 10 FTIR (transmission) spectra of: (a) precipitated solids collected in the bottom of the feed water tank; and (b) precipitated solids collected on the surface of the heating element. Treatment 1.

4.2.2. *Salt precipitation on the AGMD membrane*

Figs. 11a and 11b show SEM images and EDX spectra of the PVDF (new) membrane, and the same membrane at the end of the AGMD concentration experiment following Treatment 1 to the RO concentrate. Carbon and fluoride peaks were clearly identified in the new membrane. However, as shown in Fig. 11b, mineral salt scales containing ions such as calcium, magnesium and silicon were detected on the surface of the wasted membrane.

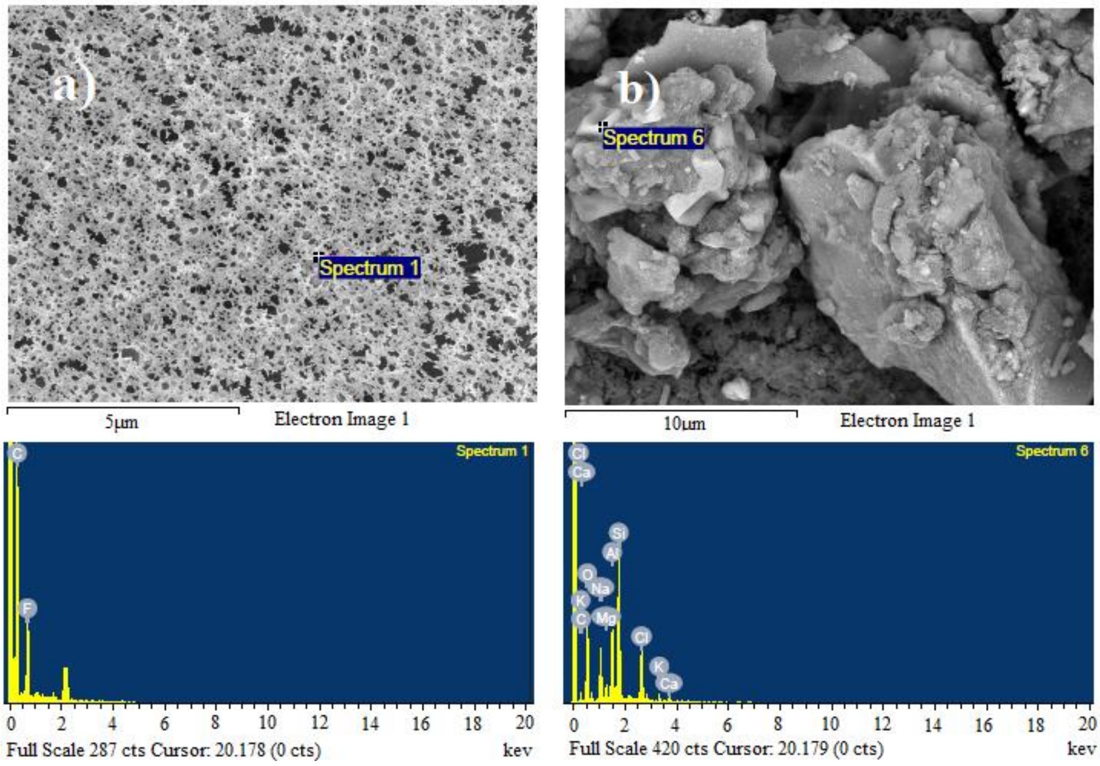


Fig. 11. SEM images and EDX analysis of the a) PVDF new membrane; and b) PVDF wasted membrane at the end of the AGMD experiment. Treatment 1.

Fig. 12 compares SEM images of the PVDF membranes at the end of the AGMD concentration experiments following both strategies. As demonstrated in Figs. 12c and 12d, the integration of a ‘High-pH pretreatment’ strategy followed by pH normalization and AS addition minimized the formation of mineral salt scales on the AGMD membrane. The FTIR spectra of the PVDF wasted membrane after completion of this second round of experiments (Treatment 2) was shown in Fig. 13b. The FTIR spectra did not show indications of membrane scaling and was analogous to the FTIR spectra of the PVDF new membrane (Fig. 13a).

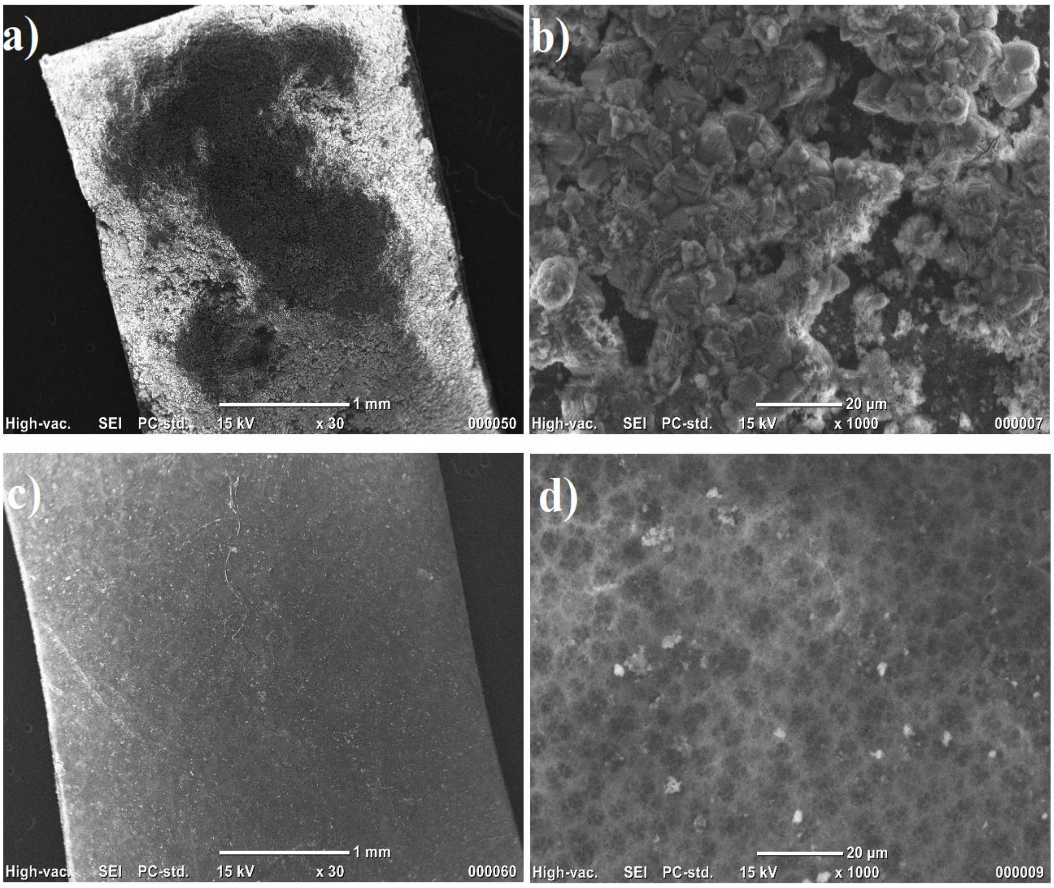


Fig. 12. SEM images of the PVDF membrane at the end of the AGMD experiments: a) and b) Treatment 1; c) and d) Treatment 2.

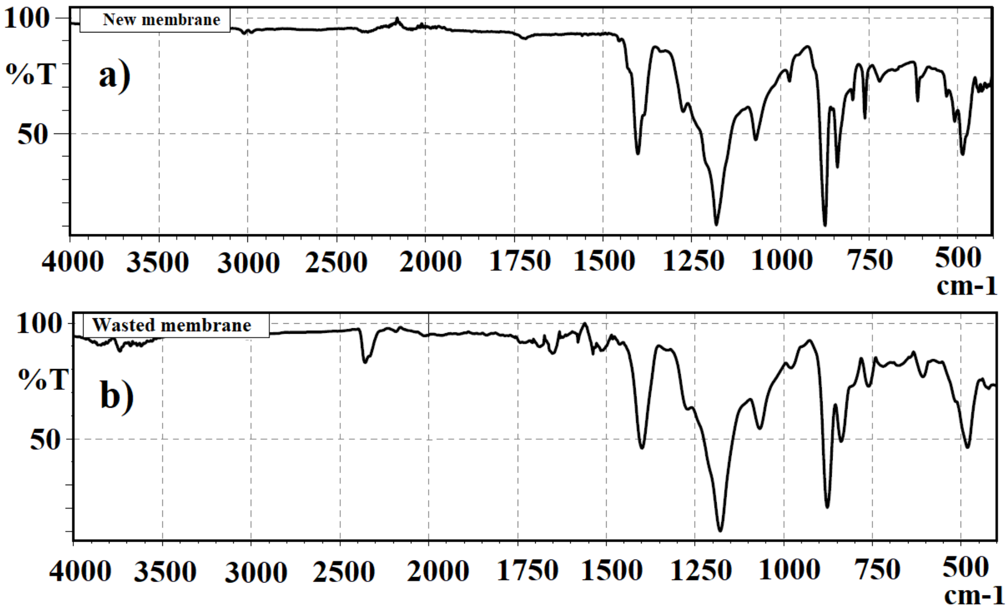


Fig. 13. FTIR (transmission) spectra of: a) PVDF new membrane; and b) PVDF wasted membrane at the end of the AGMD experiment during Treatment 2.

4.2.3 Influence of Treatment 1 and 2 on permeate flux and permeate water quality.

Fig. 14a illustrates the evolution of permeate flux in the AGMD system following Treatment 1 of the RO concentrate. A linear equation was selected to approximate permeate flux, resulting in a standard error of 0.1 kg/m^2.h. Permeate flux recorded a maximum value of 1.06 kg/m^2.h and a minimum value of 0.53 kg/m^2.h. In addition, the permeate flux was about 18 % lower at the beginning of Batch 2 than at the beginning of Batch 1. Overall, a slight decline in permeate flux was observed throughout the volumetric concentration experiment. Possible reasons for the continuous decline in permeate flux might have been: (a) the progressive increase in feed water salinity; (b) a decrease in feed water flow-rate; and (c) membrane scaling phenomenon. Firstly, the increase in feed water salinity resulted in a decrease in water activity and a lower transmembrane partial vapour pressure, which is the driving force in MD technology [13]. Secondly, the operation of the feed water submersible pump was affected as the water level in the feed water tank decreased. Cavitation and a small reduction in feed water flow-rate were observed. This circumstance could have led to a slight decrease in permeate flux due to the increased temperature and concentration polarization phenomena [12]. Finally, membrane scaling decreased the active surface for water vapour transport through the AGMD membrane. In addition, the deposited layer on the membrane surface would have created extra thermal resistance and increased mass transfer resistance through the membrane [9]. However, the permeate flux did not decrease sharply to zero or almost zero once the feed water concentration reached the saturation point. This phenomenon related to membrane scaling was previously reported in different studies [8, 9, 17, 23], most of them performed with DCMD configuration at much higher permeate fluxes. In the present study, the higher available membrane surface and the lower permeate flux avoided the drastic reduction in permeate flux.

Fig. 14b illustrates the evolution of permeate flux in the lab-scale AGMD unit following Treatment 2 of the RO concentrate. Permeate flux was also approximated by a linear equation, resulting in a standard error of 0.09 kg/m^2.h. On this occasion, permeate flux recorded a maximum value of 1.38 kg/m^2.h and a minimum value of 0.72 kg/m^2.h. Furthermore, there was no significant difference between permeate flux at the beginning of Batch 1 and 2. Firstly, it is important to highlight that the operation of the lab-scale AGMD unit at a higher temperature (56^{o}C) resulted in a 37% increase in permeate flux during the first hour of the experiment. Secondly, a slight flux decline was also observed in the AGMD system during Batch 1 and 2. In a similar way to Treatment 1, the slight decline was attributed to: (a) the increase in feed water salinity which led to a reduction in water activity and a lower transmembrane partial vapour pressure; and (b) a decrease in feed water flow-rate as a consequence of the technical limitations imposed by the feed water pump. However, the formation of scales on the AGMD membrane was controlled following Treatment 2 of the RO concentrate.

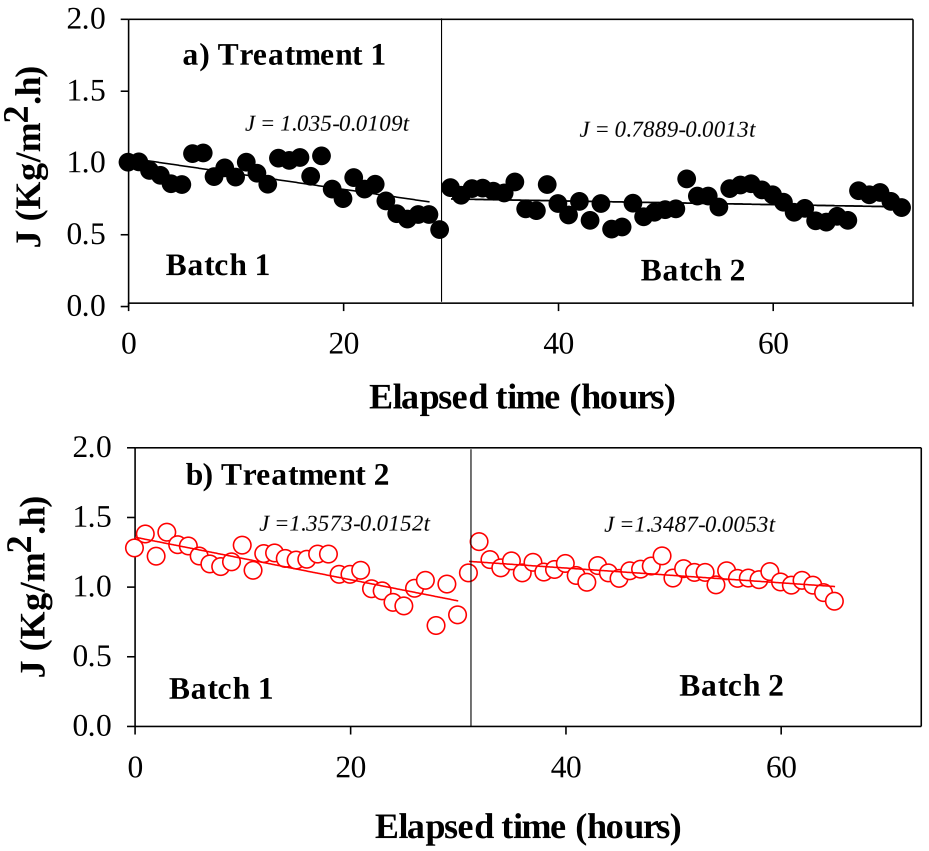


Fig.14 Evolution of the AGMD permeate flux (*J*) during the RO concentrate desalination experiment: a) Treatment 1; and b) Treatment 2.

As shown in Fig. 15a, a deterioration in permeate conductivity was recorded in the course of the AGMD concentration experiment following Treatment 1 of the RO concentrate. This deterioration in product water quality was attributed to membrane pore wetting due to membrane scaling [8, 9]. During this experiment, a maximum permeate conductivity level of 530 µS/cm was measured. On the other hand, permeate conductivity following Treatment 2 of the RO concentrate was plotted in Fig. 15b. Since pore wetting was prevented as a consequence of the softening treatment, permeate conductivity remained almost steady during the experiment. Only, a slight increase in permeate conductivity was observed during Batch 1 and 2 that was attributed to the higher feed water salinity recorded. A maximum permeate conductivity level of 303 µS/cm was recorded following Treatment 2 of the RO concentrate.

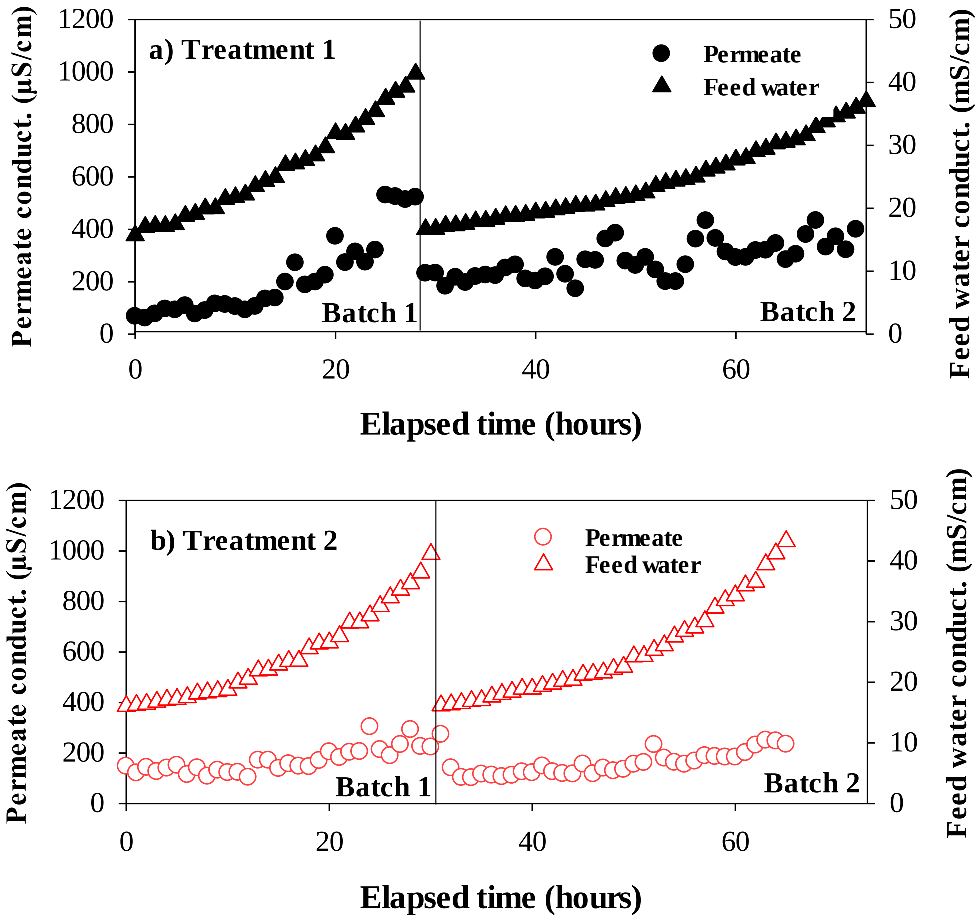


Fig. 15 Variation of AGMD feed water and permeate conductivity during the RO concentrate desalination experiments: a) Treatment 1; and b) Treatment 2.

Overall, it was demonstrated that 'High-pH pretreatment' (followed by pH adjustment to 8.1 and AS addition) enabled us to operate the lab-scale AGMD unit at a higher temperature (56°C), and thus permeate flux also increased. In addition, permeate conductivity remained almost steady during the volumetric concentration experiment.

4.2.4 Discussion of characteristics of the AGMD concentrated waste and produced permeate.

Table 6 illustrates the main characteristics of the AGMD concentrated waste and produced permeate following Treatments 1 and 2 of the RO concentrate. Firstly, a significant decrease in calcium, magnesium, silica, barium, strontium and fluoride concentration was measured in the AGMD concentrated waste, with respect to the predicted result following Treatment 1 of the RO concentrate. This phenomenon was attributed to salt precipitation in the AGMD system. Such a reduction could be related to calcium carbonate and silicate precipitation during the volumetric minimization process. Conversely, barium and strontium concentration decline might have occurred via co-precipitation with $CaCO_3$ [41], while fluoride reduction might be related to adsorption onto magnesium precipitates [4]. Secondly, the concentration of calcium, magnesium, silica, barium, strontium and fluoride in the AGMD concentrated waste clearly increased with respect to the initial concentration of the softened concentrate shown in Table 5. Thus, it was demonstrated that Treatment 2 was more effective than Treatment 1 in preventing mineral salt precipitation in the lab-scale AGMD system under these experimental conditions.

Table 6
General characteristics of the AGMD concentrated waste and permeate following: Treatment 1; and b) Treatment 2. All samples were collected after Batch 1.

	Treatment 1		Treatment 2	
Parameter	Concentrated waste characteristics	Permeate characteristics	Concentrated waste characteristics	Permeate characteristics
pH (Units)	9.0	7.3	8.7	6.6
Conductivity (µS/cm)	41400	210	40200	181
Turbidity (NTU)	10.7	0.1	7.7	0.1
TDS (mg/L)	29141	115	26731	82.5
Alkalinity (mg/L $CaCO_3$)	2400	< 40	220	< 20
Potassium (mg/L)	42	<1	54	<1
Sodium (mg/L)	10445	36	10990	36
Magnesium (mg/L)	861	4	40	< 1
Calcium (mg/L)	14	0.8	65	0.6
Strontium (mg/L)	1.6	<0.5	2.8	<0.5
Barium (mg/L)	<0.2	<0.2	<0.2	<0.2
Chloride (mg/L)	14061	53	13705	47
Fluoride (mg/L)	2.05	<0.02	2.15	<0.02
Sulphate (mg/L)	1721	6.8	1637	5.3
Silica (mg/L SiO_2)	82.5	1.1	28	< 1

Table 7 presents a mass balance of different ions in the AGMD system following Treatment 1 of the RO concentrate, assuming the initial concentration of the scale-forming ions in the RO concentrate is 100%. The percentage (%) of these ions presumably precipitated in the AGMD unit is presented in the last column of Table 7. In contrast, Treatment 2 successfully removed the scale-forming precursors and so the deposit into the system was greatly reduced.

Table 7
Mass balance of different ions in the AGMD system following Treatment 1.

Parameter	Concentrated waste (%)	Permeate (%)	% of ion precipitated in the Unit (%)
Calcium (mg/L)	2.91	0.11	96.97
Magnesium (mg/L)	82.87	0.26	16.87
Strontium (mg/L)	9.86	2.09	88.05
Fluoride (mg/L)	50.51	0.33	49.15
Silica (mg/L SiO_2)	22.09	0.20	77.70

We could conclude that the desalination of the RO concentrate in the batch AGMD unit solely by AS addition was not sustainable considering the membrane scaling phenomenon and the significant mineral salt precipitation observed in the feed water tank, feed water pump and heating element. The consequences of this process could also be critical for the AGMD membrane if higher feed water volumes of RO concentrate were desalinated.

5. Conclusions

An intermediate ‘High-pH pretreatment’ between RO and batch AGMD desalination was assessed for the first time for high salinity RO concentrate minimization. Lime and soda ash were added to soften the RO concentrate. The process attained considerable reduction of scale-forming constituents including silica, calcium, magnesium, strontium, barium and fluoride. The ‘High-pH pre-treatment’ (followed by pH re-adjustment and AS addition) altered the physicochemical properties of the existing RO concentrate, resulting in reduced scaling propensity. As a result, the batch AGMD system was operated at a higher feed water temperature, initially allowing a 37% increase in permeate flux. This was with respect to the traditional strategy comprising solely AS utilization, which was not successful in preventing the formation of mineral scale. At the end of the experiment the volume of

RO concentrate with an initial TDS level of 10.8 g/L was minimized by a *CF* of 3.2 (equivalent to 69 % freshwater recovery without considering the water loses by evaporation). A slight decrease in permeate flux recorded during the experiment was attributed to the increase in feed water salinity, and a decrease in feed water flow-rate as a consequence of the technical limitations imposed by the feed water pump placed in the lab-scale AGMD unit. This intermediate demineralization treatment greatly reduced the formation of mineral scales in crucial components of the unit such as the AGMD membrane, feed water tank, feed water pump and heating element. Eventually, SEM-EDX and FTIR analyses also confirmed the suitability of 'High-pH pretreatment' for scale control in the AGMD membrane.

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5.3 Concluding remarks

An intermediate ‘High-pH pretreatment’ between RO and batch AGMD was tested, for the first time, for scale control and high salinity RO concentrate minimization. The results confirm that RO concentrate treated with lime and soda ash, results in significant removal of scale-forming precursors including silica, calcium, magnesium, strontium, barium and fluoride. The ‘High-pH pre-treatment’ (followed by pH re-adjustment and AS addition) prevented the formation of mineral scales in the lab-scale AGMD system. It also allowed the operation of the batch AGMD system at a higher feed water temperature, facilitating an increase in permeate flux. These results contrast with the traditional strategy comprising solely of AS utilization, which was not successful in preventing the formation of mineral scales.

The results from SEM-EDX and FTIR determinations also confirm the suitability of ‘High-pH pretreatment’ for scale control in the AGMD membrane. These findings show that ‘High-pH pretreatment’ could have a positive impact on the longevity of the MD membranes. Eventually, this should lead to an optimization of the Opex costs. A study on a pilot plant scale would be required to assess whether an intermediate ‘High-pH pretreatment’ between RO and batch AGMD would be cost-effective.

CHAPTER 6

'High-pH softening pretreatment' for boron removal in inland desalination systems

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PAPER IV

Rioyo, J., Aravinthan, V., Bundschuh, J., & Lynch, M. 2018. 'High-pH softening pretreatment' for boron removal in inland desalination systems. Separation and Purification Technology, 205, 308-316. (Published).

6.1 Introduction

This paper investigates, for the first time, the feasibility of a 'High-pH pretreatment' for boron removal from magnesium-dominated groundwater samples obtained from an existing desalination facility. Different alkaline reagents are trialled with brackish groundwater initially containing 5 mg/L of boron.

The optimization of the process is researched with the addition of $MgCl_2 \cdot 6H_2O$ before the softening process. In addition, a secondary polishing treatment by means of adsorption with MgO is investigated. This 'High-pH pretreatment' could facilitate compliance with strict boron standards in inland facilities using RO or ED technology.

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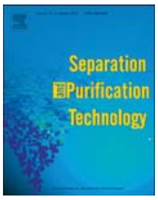

‘High-pH softening pretreatment’ for boron removal in inland desalination systems

Javier Rioyo[a,*], Vasantha Aravinthan[a], Jochen Bundschuh[a], Mark Lynch[b]

[a] University of Southern Queensland, School of Civil Engineering and Surveying, Faculty of Health, Engineering and Sciences, West St, Toowoomba, Queensland 4350, Australia
[b] University of Southern Queensland, School of Agricultural, Computational and Environmental Sciences, Faculty of Health, Engineering and Sciences, West St, Toowoomba, Queensland 4350, Australia

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ABSTRACT

Boron removal from water remains a challenge. In fact, it is largely unclear whether softening pretreatments enhance boron removal in groundwater desalination systems. We therefore investigated the feasibility of a high-pH softening pretreatment for boron removal from magnesium dominated groundwater samples obtained from an existing desalination facility. Different alkaline reagents were trialled with brackish groundwater initially containing 5 mg/L of boron. The results indicated that the lime and soda ash softening treatment was a better option than the caustic soda alternative, achieving 33% boron removal by sorption of hydroxyborate ions onto precipitated magnesium silicates. The process could be further optimized by the addition of $MgCl_2{\cdot}6H_2O$ before the softening process. In addition, a secondary polishing treatment by means of adsorption with MgO was investigated. A total of 9% extra boron removal was achieved in both cases. This ‘high-pH softening pretreatment’ could enhance compliance with strict boron standards in inland facilities using reverse osmosis or electrodialysis technology.

1. Introduction

Boron can produce harmful effects on human health depending on both the frequency and extent of the exposure [1]. Since the influence of boron on human health is not completely understood, most of the existing guidelines are still provisional. Therefore, it is anticipated that future standards in drinking water will become even more stringent over the next few years [2] which will necessitate the development of improved removal technologies. According to the World Health Organization (WHO), the concentration of boron in drinking water should not exceed 2.4 mg/L [3]. The European Union (EU) Drinking Water Directive was revised in 1998 including a new standard for boron concentration in drinking water of < 1 mg/L [4,5]. Stricter guidelines have been adopted in countries, such as Israel and Saudi Arabia, where the permitted boron concentration in drinking water was limited to 0.3 mg/L [6] and 0.5 mg/L [7] respectively.

Boron can be present in water due to either natural or anthropogenic sources [8,9]. While the average boron concentration in seawater is approximately 4.6–4.7 mg/L [7,10], its concentration in groundwater has been reported to vary from 0.3 to 100 mg/L [3,11,12]. Generally boron levels in groundwater are very low (< 0.1 mg/L) [13], though there are some exceptions reported in the bibliography. In a study carried out in South Texas (USA), boron concentrations ranging from 5 to 16.2 mg/L were measured in 18 out of 112 water wells [14]. In Kizildere and Balçova (Turkey), boron levels of 24.8 and 9.4 mg/L respectively were detected in natural groundwater [8]. In Italy, Cyprus and Greece, boron levels up to 8 mg/L were measured in regional groundwater [10]. In geothermal water, due to the underground contact between rocks and hot fluids, boron concentration can also be quite high [15].

Different industrial processes use boric acid or boron salts [10] and thus water contamination is possible [12,16]. Currently more than 50% of the production of boron compounds is used in the glass industry, although it can also be found in other manufacturing processes, such as electronics, ceramics, semiconductors and cleaning products [3,12]. Previous research involving the Minerata boron plant in Argentina reported boron values in groundwater of 6.2 mg/L inside the contamination area [13,17]. In domestic wastewaters boron levels up to 2 mg/L can also be found [10].

Boron is an important micronutrient for plant growth. Very low concentrations are required in irrigation water for healthy plant growth. However, boron becomes toxic if its concentration in irrigation

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[*] Corresponding author.
E-mail address: Javier.RioyoRumayor@usq.edu.au (J. Rioyo).

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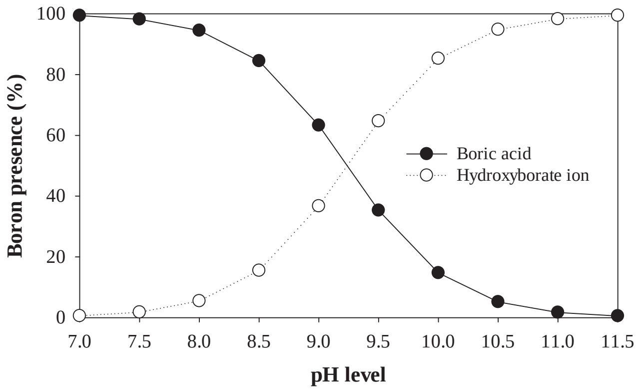

Fig. 1. Distribution of boric acid and hydroxyborate ion vs. pH.

water is higher than required [10]. Citrus trees in particular are very sensitive, showing leaf damage at boron levels of more than 0.3 mg/L [15].

Boric acid has an acid-dissociation constant of 5.8×10^{-10} at 20 °C. In water, boric acid forms the hydroxyborate ion by the addition of OH^- [18]. Boric acid behaves as a weak Lewis acid according to the following equation [7]:

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \quad (1)$$

For concentrations below 250 mg/L, boron will only be present in water as boric acid or hydroxyborate ion, while polyborate anions are formed at higher concentrations [18]. At low pH, it exists in the aqueous environment as un-dissociated boric acid [15] with a trigonal planar structure [19]. By contrast, anionic hydroxyborate ion becomes the predominant species at high pH levels [15,20], adopting a tetrahedral structure [19]. As shown in Fig. 1, both species can co-exist as an equilibrium mixture at pH levels ranging from 7.0 to 11.5.

Some authors have studied different state of the art technologies for boron removal from different kinds of waters [4,7,9,11,12,15,21]. Different technologies, such as coagulation and electrocoagulation, adsorption, solvent extraction or membrane processes, including reverse osmosis (RO) or electrodialysis (ED) have been investigated, although the use of boron-selective ion-exchange resins seems to provide the most effective treatment [15]. Boron removal from water is very difficult [7]. In seawater desalination systems, boron concentration can be reduced by combining multi-pass RO with pH adjustment. The first RO pass is operated at a lower pH for salt removal while the second RO pass is operated at higher pH for effective boron removal [22]. Alternatively, RO technology can be combined with ion exchange technology [23,24]. The latter solution can reduce overall capital and operating costs in seawater desalination systems [24].

In brackish water (BW) desalination systems a second pass at higher pH is not considered a feasible solution due to (a) the required higher water recoveries for minimizing the RO concentrates for eventual disposal; (b) the lower boron rejection of brackish RO membranes; and (c) the presence of scaling ions in the permeate [22]. In addition to this, it is not economically viable for groundwater containing high boron concentrations [6]. Cengeloglu et al. [8] tested BW30 membranes (The Dow chemical company, USA) in a RO pilot plant for boron removal from synthetic waters with boron initial concentrations ranging from 5 to 40 mg/L. Results showed that boron removal does not depend on its initial concentration in feed water. A 73% boron removal was achieved at pH 5.5 and 2 MPa. Experiments also showed that boron rejection was enhanced for increasing operating pressures and for pH levels above 9 [8]. Oner et al. [25] also tested BW30 membranes for boron and silica removal from geothermal water at its natural pH level (8.6). Boron and silicon initial concentrations were respectively 10.25–11 and 56–65 mg/L. Average boron and silica rejections achieved during the RO treatment were respectively about 65.6 and 99% at 1.5 MPa. An increase in the operating pressure up to 3 MPa raised boron removal up to 78.5% [25]. Finally, Teychene et al. [26] studied arsenic (III) and boron removal from synthetic brackish water containing 2.6 mg/L of boron by using BW30 membranes among others. Around 72% boron removal was achieved at pH 7.6 and 2.4 MPa (operating pressure). In this case, boron rejection was also enhanced for increasing transmembrane pressure and feed water pH values [26]. However, in real water desalination systems using brackish water membranes the boron rejection can be limited to 15–20% [22]. Consequently, RO technology using BW membranes alone is not sufficient to fulfil current or future boron removal guidelines in some countries. In that case, further boron removal from RO permeate could be achieved by implementing ion-exchange technology. Alternatively, the process could be optimized in certain plants by the implementation of additional RO stages using seawater membranes capable of achieving ‘high boron rejection’ followed by additional boron removal by selective ion exchange membranes where required [6]. Overall, seawater RO membranes can provide the highest boron removal followed by BW membranes at standard operating conditions (low pH). In that scenario, boron rejection by nanofiltration (NF) membranes is negligible [2].

Conversely to the previously mentioned technologies, a softening treatment for boron removal has only been reported in a few studies, and for different kinds of waters, such as seawater, brackish water and groundwater [4,20,27–29]. The efficacy of this treatment in magnesium dominated groundwater is the least explored. In that regard, the effectiveness of softening treatments for boron removal in groundwater, and in particular when magnesium concentration is higher than calcium concentration, is yet to be explored thoroughly. Overall, the mechanism of boron removal may be related to magnesium precipitation during the softening treatment. At high pH levels, hydroxyborate ion could be removed by sorption onto precipitated magnesium compounds [27]. The common presence of dissolved magnesium in brackish groundwater could facilitate the boron removal process. A recent study involving the treatment of seawater achieved 61% boron removal by precipitation softening at a pH of 11.0 [28].

In addition, boron removal by adsorption of hydroxyborate ions onto magnesium oxide may also be a suitable method [19,20]. However, the process is influenced by reagent quality, contact time, temperature, and pH level [19]. Rodarte and Smith reported that the addition of magnesium chloride (before softening treatment) for boron removal required two-thirds the dose and one-sixth the cost than MgO utilization. The former study was performed with flow back and produced water (oil and gas industry in the USA) containing 60 mg/L of boron [20]. Eventually, one of the main disadvantages of MgO addition is that it cannot be regenerated using acids [7,19]. In addition, this process requires large amounts of reagent per gram of boron removed [7,20,30].

The aim of this study was to investigate the implementation of a high-pH softening pre-treatment in existing or future inland desalination plants treating magnesium dominated waters with relatively high boron concentrations (5 mg/L), to meet stringent boron-specific standards (< 1 mg/L). The mass ratio Ca/Mg in the brackish well water was 3/4. The main objectives of this study were (a) to investigate the removal of boron from groundwater by a softening treatment; (b) to optimize the boron removal process during the softening step by the addition of magnesium chloride; (c) to examine a final polishing step for boron removal from softened water by adsorption of hydroxyborate ions onto magnesium oxide; and (d) to assess the combined effect of these chemical treatments with other membrane processes such as ED using a non-selective membrane.

If successful, this chemical pre-treatment could be retrofitted into existing or future inland desalination plants dealing with relatively high boron concentrations (~5 mg/L) to ensure compliance with strict standards, such as indicated by the EU Drinking Water Directive. Eventually, if extra boron reduction is required by more advanced technologies, such as ‘seawater RO membranes’ or ion exchange

Table 1
Characteristics of brackish groundwater.

Parameter	Well water quality
pH (Units)	7.4
Conductivity (mS/cm)	3.4
Turbidity (NTU)	< 1
TDS (mg/L)	1780
Alkalinity (mg/L $CaCO_3$)	360
Sodium (mg/L)	496
Potassium (mg/L)	4.3
Calcium (mg/L)	61
Magnesium (mg/L)	82
Strontium (mg/L)	2.1
Barium (mg/L)	< 0.2
Sulphate (mg/L)	154
Chloride (mg/L)	834
Fluoride (mg/L)	0.5
Silica (mg/L SiO_2)	34.5

technology, this softening pre-treatment could minimize the requirements of such downstream processes.

2. Material and methods

2.1. Brackish groundwater characteristics

This research was performed with well water collected at a desalination plant located in the Darling Downs region of Queensland (QLD), Australia. Table 1 shows the main characteristics of tested groundwater.

2.2. Softening studies

Softening tests were undertaken in the University of Southern Queensland chemical laboratory at a controlled room temperature (22 °C). A jar-test unit (VELP A – model JLT6), containing six 1-L plastic beakers, was used in all softening trials. Boron was initially spiked to the brackish groundwater in order to increase its concentration up to 5 mg/L, measured as dissolved boron. Powder boric acid supplied by MERCK was used as a source of boron. Such a concentration was used to avoid the formation of poly-borates in the groundwater samples. The initial boron concentration of 5 mg/L was selected in order to investigate a likely case-scenario of groundwater with high natural boron concentration in drinking water. For example, Italy and Cyprus may find it difficult and expensive to comply with the EU Drinking Water Directive (< 1 mg/L) [5]. In such countries boron levels up to 8 mg/L can be found in regional groundwater [10].

The boron spiked groundwater was softened with different amounts of NaOH (1N) to provide six different pH values: 10.0, 10.2, 10.5, 10.8, 11.1 and 11.4. Silica and boron removal were then investigated in triplicate. A second round of experiments was also undertaken, applying both the lime and the lime-soda ash softening treatments to the brackish groundwater. Required lime and soda ash doses were calculated following standard methodology [31]. All chemicals were added during the first two minutes of the initial rapid-flash mixing at 150 rpm, then slow mixing was carried out for 30 min at 50 rpm. Following that, softened waters were allowed to settle in the jars for 60 min. Finally, supernatant samples were collected for chemical analysis. In addition, samples of precipitated flocs were collected by vacuum filtration and dried at 50° C for analysis by (a) Fourier transform infrared spectroscopy (FTIR); (b) X-ray diffraction (XRD); and (c) scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX).

2.3. Preliminary $MgCl_2 \cdot 6H_2O$ addition to enhance boron removal during softening pretreatment

The optimization of boron removal during a 'high-pH softening pretreatment' was also investigated. In order to increase the dissolved magnesium concentration in groundwater, a soluble magnesium salt was added before commencing the softening experiments. This strategy was only applied to the groundwater softened by the lime and soda ash softening treatment. Initial jar test experiments, shown in Section 3.1.1, had demonstrated that this alternative could be more efficient than the caustic soda softening treatment. To this end, 100 and 200 mg/L of $MgCl_2 \cdot 6H_2O$ were initially spiked to the groundwater jars to improve both silica and boron removal during the softening process. All jar tests were repeated in triplicate following the same methodology described in Section 2.2.

2.4. Polishing treatment for boron removal by means of adsorption with MgO

Previous studies have demonstrated that boron removal by adsorption of hydroxyborate ions onto magnesium oxide is possible [19,20]. To quantitatively corroborate this approach, groundwater pretreated by the lime and soda ash softening process was put in contact with EMAG45 supplied by Swancorp. EMAG45 is a salt rich in MgO (80% by weight). This chemical is currently used on an industrial scale for different applications, such as animal feed production, as a fertilizer, or in sewage treatment [32]. Considering that this adsorption treatment achieves optimum boron removal at high pH level [19,20], a preliminary pH adjustment of softened groundwater (pH 11.2) following the high-pH softening pre-treatment was not required.

Three different Mg/B molar ratios were tested for these experiments: 25, 75 and 125. For every test, 100 mL of softened groundwater was mixed with EMAG45 for 30 min using a magnetic stirrer. During the adsorption experiments, the mixing speed was adjusted to the minimum required to keep the EMAG45 in suspension. Following a 30 min sedimentation time, the solution was filtered. All these adsorption tests were conducted in triplicate at room temperature.

2.5. ED experiments for boron removal

Research on both boron and silica removal by ED technology was conducted using a bench ED pump unit, model PCCell B-ED 2–3. This apparatus incorporates a Manson switching modem power supply unit, model 1–30 VDC 20A/ HCS-3402. Fig. 2 illustrates the ED pilot plant. This laboratory-scale pilot plant uses a non-selective membrane

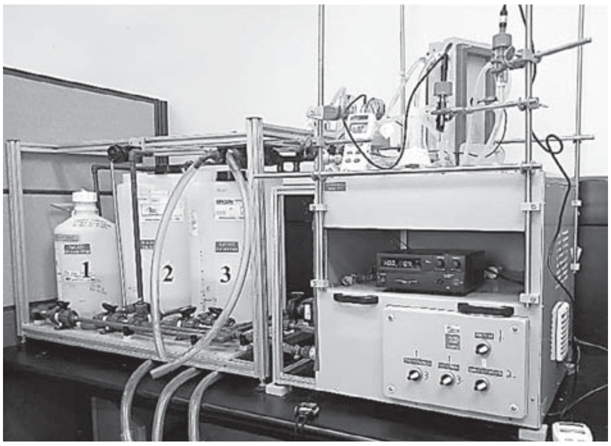

Fig. 2. Bench ED pump unit. Water containers 1, 2 and 3 correspond respectively with: (a) the electrode rinse; (b) the diluate; and (c) the concentrate streams.

Table 2
Two Chamber ED cell characteristics [33]

Parameter	Characteristics
Membrane size	262 × 125 mm
Active membrane area	207 cm^2 per membrane
Processing length	220 mm
Cell thickness	0.5 mm
Anode material	Pt/Ir- coated titanium
Cathode material	V4A Steel
Electrode housing material	Polypropylene

(Reference: Laboratory Scale Electrodialysis Cell PCCell 200). The two chamber ED cell includes 10 cell pairs with standard anion and cation exchange membranes [33]. Table 2 shows the characteristics of the ED membrane. During the electrochemical separation process, the ions are transferred through the ion exchange membranes with a direct current voltage [34].

The ED unit was operated in batch mode at room temperature. To perform the experiments, the diluate container was filled with two different samples: (a) 5 L of groundwater softened by the lime and soda ash softening treatment (the pH level of softened groundwater was initially reduced to 7.8); and (b) 5 L of groundwater softened by the lime and soda ash softening treatment (the pH level of softened groundwater was reduced to 10.0). In this study, pH levels above 10 were prevented in order to avoid damaging the ED unit.

The electrolyte rinse solution assisted in the demineralization process. It consisted of a solution of 14.2 g sodium sulphate/L [35]. The concentrate tank consisted of a leftover solution from a previous experiment with a conductivity that ranged between 32 and 33 mS/cm. The flow-rates for the diluate and concentrated streams were approximately 40–50 L/h in all experiments. Conversely, the flow-rate for the electrolyte rinse circuit was 130 L/h. The voltage in the system was set to 10 V and the current (Amperes) was recorded after 0, 10, 20, 30, 45, 60 and 120 min together with the pH level and conductivity in the diluate stream. The pH level and conductivity were recorded using a portable pH electrode and a portable conductivity meter, model Sper-Scientific in both cases. Diluate samples were also collected at these intervals for boron and silica analysis. In all experiments the electric current decreased.

2.6. Analytical methods and chemical reagents

'Reagent-grade' chemicals were supplied by Chem-Supply, HACH, Australian Chemical Reagents and Sigma Aldrich. The azomethine-H method was applied for all boron determinations using a HACH DR spectrophotometer according to Method 10274 [36]. Reactive silica was analysed according to the HACH silicomolybdate Method 8185 [37]. The pH and conductivity were determined using a pH electrode and conductivity meter, model Eutech PC 2700. A Lovibond turbicheck-meter was used for the analysis of turbidity. Total alkalinity determinations were performed by titration with H_2SO_4 [38]. This method was validated and the sulphuric acid standardized by using an alkalinity standard (1000 mg/L as $CaCO_3$) supplied by Sigma Aldrich. Total dissolved solids analysis was carried out in accordance with the Standard Methods: 2540 C 'Total Dissolved Solids Dried at 180 °C' [39].

Cation analyses in water samples were undertaken using a Shimadzu atomic absorption spectrophotometer, model AA-7000. Fluoride was measured using a HACH test, according to the USEPA SPADNS method [40]. Other anions such as chloride and sulphate were determined by ion chromatography. A Dionex ICS-2000 apparatus was used to perform these analyses according to Thermo Scientific application note n-154 [41].

A scanning electron microscope, model SEM-JCM6000, was used to undertake SEM-EDX observations in precipitated solids. A Philips X'Pert apparatus with radiation $CuK_\alpha = 1.542$ A, operating at 40 kV and 20 mA in the 10–80° 2-theta scanning range was used to perform powder XRD determinations of precipitated solids. The X'Pert HighScore Plus software was used for pattern identification using the powder diffraction files (PDF) from the International Centre for Diffraction Data (ICDD) as references. A Shimadzu RF-6000 spectrophotometer was used to undertake FTIR analysis of solid samples as KBr discs. This apparatus incorporates the LabSolutions IR software for surface functional groups analysis. All solid samples were prepared mixing 200 mg of KBr and 2 mg of sample.

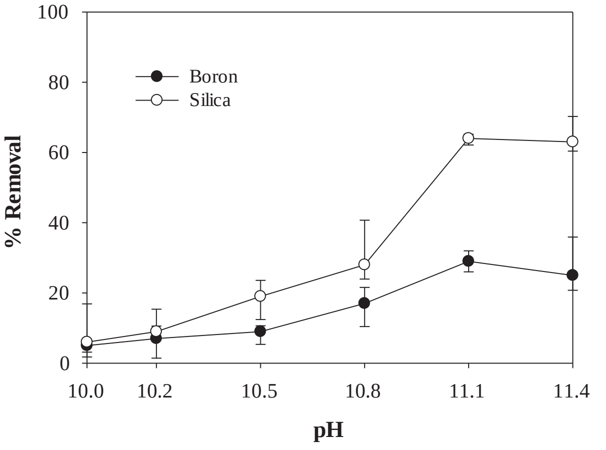

Fig. 3. Boron and silica removal (%) vs the pH level. NaOH softening pretreatment at different pH levels. (Boron and silica initial concentrations were 5 and 34.5 mg/L, respectively).

3. Results and discussion

3.1. 'High-pH softening pretreatment' for simultaneous removal of boron and silica

3.1.1. Softening alternatives

Fig. 3 shows the experimental results of the caustic soda softening pretreatment, in which the percentage removal of boron and SiO_2 is plotted against the groundwater pH level. The highest boron removal, ranging from 26 to 32%, was achieved at pH 11.1. SiO_2 removal also reached a maximum at pH 11.1, oscillating between 62 and 65%. In any case, both trends plotted in Fig. 3 appeared to follow a similar tendency as the groundwater pH level was increased.

Fig. 4 compares the concurrent removal of boron, SiO_2, calcium and magnesium, following a softening pretreatment with (a) caustic soda at pH

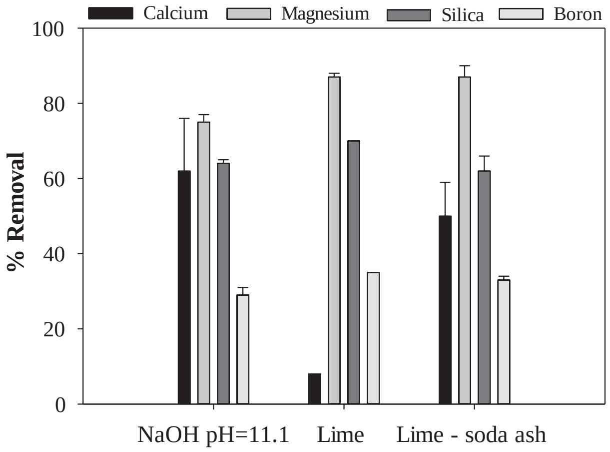

Fig. 4. Calcium, magnesium, silica and boron removal (%) by three different softening pre-treatments: (a) NaOH softening (pH 11.1); (b) lime softening (pH 11.2); and (c) lime and soda ash softening (pH 11.2). (Boron and silica initial concentrations were 5 and 34.5 mg/L, respectively).

Table 3
Boron removal from water by different softening treatments.

Study	Water tested	Softening treatment	Boron initial concentration (mg/L)	% Boron removal	Reference
This study	Brackish groundwater	Lime and soda ash at pH 11.2	5	33	–
Nevgen at al.	Brackish water	Lime softening	1.7	12	[29]
Kitano et al.	Seawater	Batch test of calcite precipitation	—	Insignificant	[4]
Ayoub et al.	Seawater	Softening at pH 11	5.1	61	[28]
Parks et al.	Ames Iowa water treatment plant	Lime softening at pH 10.8	0.130	56	[27]
Waggot.	Wastewater	Lime softening	1.6	0–16%	[29]
Unknown	Wastewater	Mg^{+2} addition required	1.2	50	[4]

Table 4
pk_{sp} values of possible compounds formed and calculated molar solubility's.

Name	Formula	pK_{sp} [43]	Molar solubility (mmol/L)
Brucite	$Mg(OH)_2$	11.6	0.0856
Antigorite	$Mg_3Si_2O_5(OH)_4$	34.5	0.0191
Forsterite	Mg_2SiO_4	26.9	6.8×10^{-7}
Enstatite	$MgSiO_3$	16.6	5×10^{-6}
–	CaH_2SiO_4	8.16	0.083

Note: The molar solubilites presented in Table 4 have been calculated from pK_{sp} values.

11.1; (b) lime (pH 11.2); and (c) lime and soda ash (pH 11.2). The required lime dose, 0.6 g/L as $Ca(OH)_2$, was added during the first two minutes of the initial flash mixing in order to remove carbonate hardness. Na_2CO_3 addition (0.14 g/L) together with $Ca(OH)_2$ was also needed during the lime and soda ash softening treatment for removal of non-carbonate hardness. Average boron removal during both the lime and the lime and soda ash softening treatments were 35% and 33% respectively, which are higher than those achieved during the NaOH softening of around 29%. In addition, silica removal accounted for an average of 70, 62 and 64% in the three scenarios previously mentioned. The highest calcium removal, accounting for an average 62%, was achieved in the groundwater samples softened only with caustic soda at pH 11.1. On the other hand, soda ash addition during the lime and soda ash softening facilitated a 42% increase in calcium removal with respect to the groundwater sample softened only with $Ca(OH)_2$. Finally, magnesium removal (%) in groundwater samples softened with (a) caustic soda at pH 11.1; (b) lime; and (c) lime and soda ash were respectively 75% in the first case and 87% in the second and third softening treatments.

Based on the experimental results, the caustic soda softening pretreatment showed some drawbacks with respect to the lime and soda ash softening pretreatment. Firstly, total alkalinity (measured as mg/L $CaCO_3$) accounted for 700 and 150 mg/L respectively, in the samples softened with (a) caustic soda at pH 11.1; and (b) lime and soda ash at pH 11.2. The higher alkalinity in samples softened with NaOH led to an increase in the Langelier saturation index (*LSI*). Secondly, conductivity also increased from 3.4 up to 4.1 mS/cm in samples softened with NaOH at pH 11.1. This higher salinity also increased energy requirements and operating costs during the desalination treatment. Finally, pH adjustment using hydrochloric acid or sulphuric acid, together with antiscalant addition, were required before desalinating softened groundwater by RO. Taking into account the higher alkalinity of the samples softened with NaOH, the cost for final pH adjustment also increased.

Table 3 shows a comparison of the results obtained in this study and by other researchers using conventional softening treatments for boron removal from different kinds of water.

There are inconsistencies about the efficacy of softening treatments for boron removal [4,29] perhaps due to the different raw water characteristics of brackish, sea and wastewater matrices. It has been hypothesised that boron removal is closely related to magnesium precipitation during a softening treatment [27,28]. A previous study treating synthetic water has also demonstrated that regardless of the calcium concentration, no silica or boron reduction was observed when magnesium was absent in the raw water [27]. The higher magnesium concentration present in seawater could have facilitated the relatively higher boron removal shown in Table 3. That circumstance would also be applicable to the present study since it was performed with a magnesium dominated groundwater.

3.1.2. Silica and boron removal mechanisms

Silica is believed to be removed from water during a 'high-pH softening treatment' by two different mechanisms: (a) by co-precipitation as calcium and magnesium silicate; and (b) by adsorption/enmeshment in precipitated magnesium hydroxide and/or calcium carbonate [42–44]. As shown in Table 4, precipitation of antigorite, forsterite or enstatite is more thermodynamically feasible than $Mg(OH)_2$ precipitation or calcium silicate precipitation when both calcium and magnesium ions are present in solution [43]. According to Parks and Edwards, silica can be precipitated as an amorphous magnesium silicate during a softening treatment when the molar ratio Si/Mg is higher than 1/6 [27,44,45]. In that case, boron would be partially removed from water by sorption of hydroxyborate ions onto freshly precipitated magnesium silicate [27]. Silica removal by adsorption on $Mg(OH)_2$ requires a higher magnesium concentration. In this regard, Chen et al. reported a molar ratio Si/Mg of 1/22 for adsorption of silica on $Mg(OH)_2$ [44,45]. Considering groundwater quality (shown in Table 1), enough dissolved magnesium was available to precipitate most of the silica as amorphous magnesium silicate, and thus to partially remove boron by sorption of hydroxyborate ions onto this precipitated magnesium silicate. The initial mass ratio Si/Mg in the groundwater was 1/5, corresponding to a molar ratio of 1/6.

Fig. 5 shows SEM images of precipitated flocs obtained following

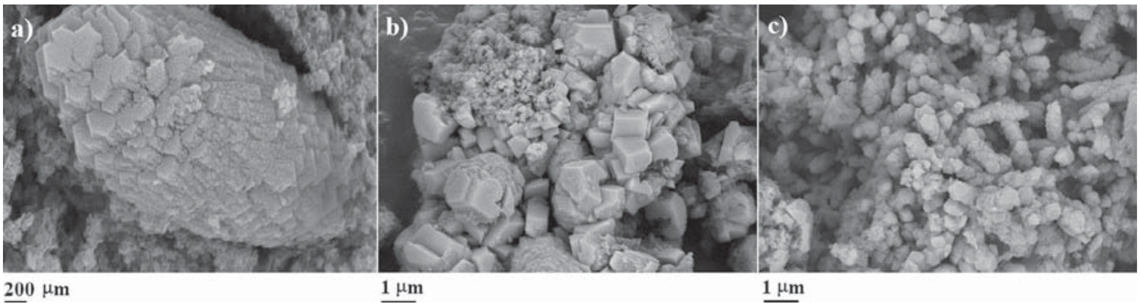

Fig. 5. SEM images of formed solids. Softening was performed with (a) NaOH at pH 11.1; (b) lime at pH 11.2; and (c) lime and soda ash at pH 11.2.

Table 5
Composition of formed solids (EDX analysis) during groundwater softening.

Softening pretreatment	Mg (% Atomic)	Si	Ca	Si/Mg
NaOH pH 11.1	12.6	2.16	4.36	1/6
Lime softening	7.21	1.38	11.21	1/6
Lime-soda ash softening	5.70	0.96	12.87	1/6

groundwater softening with (a) NaOH at pH 11.1; (b) lime; and (c) lime and soda ash. EDX analysis of precipitated solids was provided in Table 5. As indicated in Table 5, a similar Si/Mg atomic ratio of around 1/6 was observed in the three different softening scenarios. This means that precipitation as magnesium silicate appeared to be the main mechanism for silica removal. Therefore, boron removal from groundwater may have occurred by sorption of hydroxyborate ions onto formed amorphous silicate. The latter might involve either a co-precipitation mechanism and/or an adsorption process in which hydroxyborate ion adsorbs onto magnesium silicates as they are precipitating. It is important to mention that EDX technology can only identify elements with atomic numbers above 6, therefore boron cannot be identified by this technology [27].

XRD analyses of formed solids during groundwater softening with (a) lime; and (b) lime and soda ash were also undertaken. Calcite (PDF 00-005-0586) was identified in the two mentioned softening scenarios. This technique provides information about the crystalline material structure of solid samples [46]. Consequently, the crystalline phases as seen in Fig. 5(b) and (c) could correspond with calcite. Fig. 6 shows the FTIR spectra of a sample of precipitated solids obtained during the lime and soda ash softening treatment. Carbonate ion bands were also detected in the group frequencies ranging between 1490 and 1410 and 880–860 cm^{-1} [47]. This issue could ratify the presence of calcite in precipitated flocs. According to the bibliography, the band between 1100 and 900 cm^{-1} could be attributed to silicate ion [47]. This observation might also confirm the mechanism for silica removal by precipitation as magnesium silicate. Finally, the wide band around 3400 cm^{-1} could be attributed to O-H stretching vibration [47].

In summary, we can conclude that: (a) silica reduction, apparently through magnesium silicate polymerization; and (b) boron reduction by sorption of hydroxyborate ions onto formed magnesium silicate, were enhanced by the high-pH of the softening treatment and the initial Si/Mg molar ratio (1/6) in the groundwater. The former confirmed the importance of water chemistry in both silica and boron removal. In addition, based on the results of the experiments, the lime and soda ash softening treatment appeared to be a more efficient treatment than the caustic soda ash softening process.

3.1.3. *Optimization of the boron removal process during 'High-pH softening pretreatment' by initial $MgCl_2·6H_2O$ addition*

The initial addition of magnesium chloride can be a feasible strategy for boron removal from groundwater. However, the high chemical consumption and limited efficacy in the presence of SiO_2 are the main handicaps of this alternative [20]. This hypothesis was tested regardless of the initial Si/Mg molar ratio in the groundwater. In order to check this, the groundwater was spiked with 100 and 200 mg/L of $MgCl_2·6H_2O$ to increase the dissolved magnesium concentration from 82 mg/L to 94 and 106 mg/L, respectively. The higher magnesium concentration also increased the required doses of $Ca(OH)_2$ and Na_2CO_3 used during the lime and soda ash softening process.

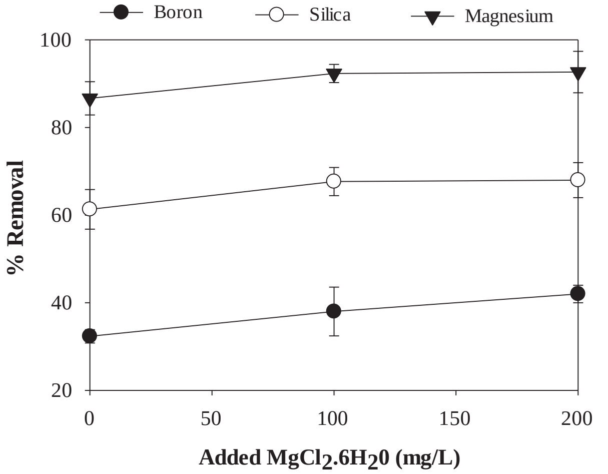

Fig. 7. Added $MgCl_2·6H_2O$ vs. (a) boron; (b) silica; and, (c) magnesium removal (%) during the lime and soda ash softening treatment (pH 11.2). (Boron and silica initial concentrations were 5 and 34.5 mg/L, respectively).

Boron, silica and magnesium removal (%) during the lime and soda ash softening treatment were plotted in Fig. 7. Both boron and silica removal improved slightly due to the higher achieved magnesium removal during the softening treatment following the addition of $MgCl_2·6H_2O$. When 200 mg/L of $MgCl_2·6H_2O$ was spiked to the groundwater, boron and silica removal respectively increased by an average of 9 and 6% in comparison to the softened sample with no added $MgCl_2·6H_2O$. Conductivity in softened groundwater also increased from 3.4 mS/cm to 3.6 mS/cm in that scenario.

A Si/Mg molar ratio of 1/8 was recorded in the EDX analysis of formed solids during softening and after the initial addition of 200 mg/L of $MgCl_2·6H_2O$. Such a ratio suggested that silica could have been removed by precipitation as silicate and/or adsorption on formed magnesium hydroxide during the softening treatment. According to the bibliography, a molar ratio Si/Mg of 1/22 is required for pure adsorption of silica on precipitated magnesium hydroxide [44,45], therefore, boron may have been removed by sorption of hydroxyborate ions onto these formed magnesium solids. This could be described either as a co-precipitation mechanism and/or adsorption process where hydroxyborate ion adsorbs to formed solids as they are precipitating.

Fig. 8(a) shows SEM images of formed solids during the softening treatment after the addition of 200 mg/L of $MgCl_2·6H_2O$, while Fig. 8(b) and (c) display images of elemental distribution (Mg and Si) in the same sample. The elemental distributions of Mg and Si provided by the X-ray mapping confirmed the concurrent removal of Mg and Si during the

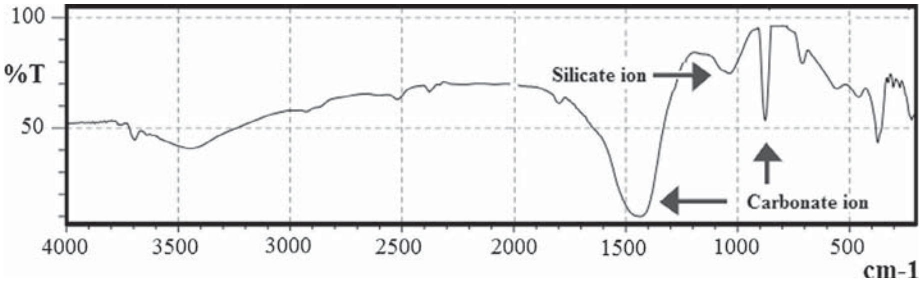

Fig. 6. FTIR spectra of formed solids obtained after treating the groundwater with lime and soda ash.

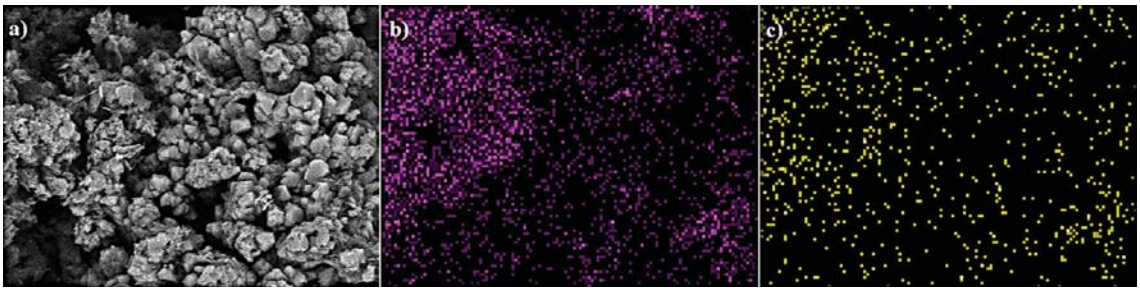

Fig. 8. (a) SEM image of precipitated solids and related; (b) Mg X-ray map; and (c) Si X-ray map following groundwater softening with lime and soda ash and an initial addition of 200 mg/L of $MgCl_2·6H_2O$.

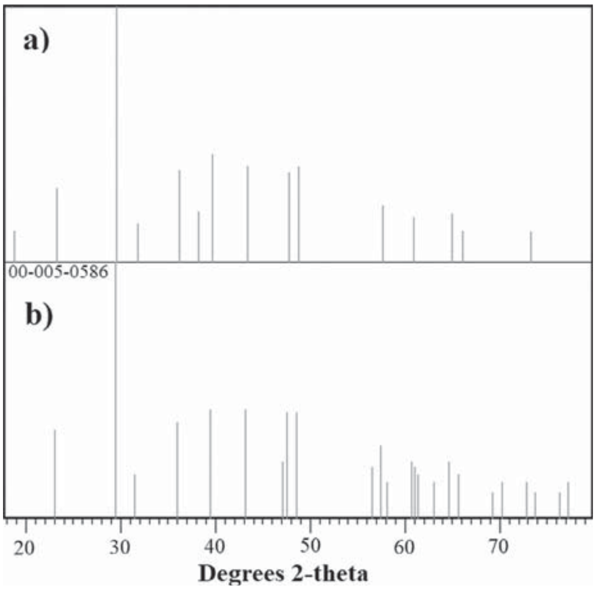

Fig. 9. (a) XRD diffractogram of precipitated flocs obtained after softening the groundwater with lime and soda ash and an initial addition of 200 mg/L of $MgCl_2·6H_2O$; and (b) XRD pattern of calcite (PDF 00-005-0586).

softening treatment. Carbonate ion bands, due to the presence of calcium carbonate, were also observed in the FTIR spectra of this sample. As shown in Fig. 9, the XRD diffractogram also showed 47% similarity with the XRD pattern of calcite (PDF 00-005-0586). In addition, the FTIR spectra also showed a band between 1100 and 900 cm^{-1} that could be attributed to the presence of silicate ion in precipitated solids [47].

Overall, we can conclude that the addition of $MgCl_2·6H_2O$ marginally improved silica and boron removal during the lime and soda ash softening. However, this alternative increased reagent costs and sludge production during the lime and soda ash softening treatment.

3.2. Polishing treatment for boron removal by means of adsorption with MgO

A two-step process was tested to enhance boron removal. In that regard, the groundwater was initially softened with lime and soda ash, and then softened groundwater was mixed with EMAG 45. EMAG45 has an approximate 80% content in MgO [32]. For this study, EMAG 45 doses were calculated according to the following Mg/B molar ratios: 25, 75 and 125. Fig. 10 shows silica and boron removal (%) combining the lime and soda ash softening treatment followed by polishing treatment by means of adsorption with EMAG45. By applying this secondary treatment, an extra 9% boron removal and a 15% silica removal were achieved when softened groundwater was mixed with EMAG45 in a molar Mg/B ratio of 125.

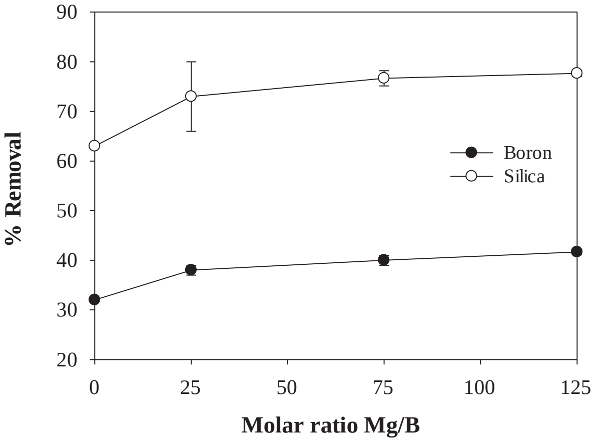

Fig. 10. Added EMAG 45 to the softened groundwater (pH 11.2) vs. boron and silica removal from groundwater. (Boron and silica initial concentrations were 5 and 34.5 mg/L, respectively). Note: The molar ratio Mg/B = 0 shown in Fig. 10 corresponds with the lime and soda ash softening treatment (first step) without secondary treatment by EMAG 45 addition. In that case and based on groundwater quality provided in Table 1, the initial molar ratio Mg/B was 7.3.

Previous research performed by de la Fuente García-Soto and Muñoz Camacho has demonstrated that boron can be removed by adsorption of hydroxyborate ion onto added magnesium oxide at pH levels ranging between 9.5 and 10.5. At this pH and low boron concentration, $B(OH)_4^-$ is the predominant ion. The same study also showed that high boron removal could also be achieved at pH levels of approximately 11.0 [19]. Therefore, considering the initial pH level of the softened groundwater (pH 11.2), no pH adjustment was carried out in this study before the secondary adsorption step.

Boron removal using MgO is insignificant for pH levels below 8, since $B(OH)_3$, is the predominant species, presents a low electrical activity [19]. However, the electrostatic adsorption reaches a maximum when the pH is raised. This occurs at pH levels of around 10 when negatively charged $B(OH)_4^-$ ion concentration rises [20]. For pH levels above 10, the concentration of $(OH)^-$ ions are increased relative to the concentration of $B(OH)_4^-$ ions. There may be competition between these anions for adsorption sites in such a scenario, and thus boron removal may decrease [19].

The efficacy of the adsorption process also depends on the quality of the added reagent and the contact time. According to de la Fuente García-Soto and Muñoz Camacho, Mg/B molar ratios above 20 were shown to be effective for boron removal from synthetic waters containing 50 mg/L and 500 mg/L of boron. In that study, the higher boron removal was observed in the high concentration sample (500 mg/L). In addition, stirring and repose times of 2 and 48 h were adopted respectively [19]. However, taking into account the huge volumes of groundwater often treated in inland desalination systems, stirring and sedimentation times in this research were limited to only 30 min in order to provide a technically feasible solution. Finally, the lower boron concentration in softened groundwater (< 5 mg/L) also decreased the efficiency of the adsorption process.

Overall, similar boron removal was achieved by applying this adsorption strategy and by the addition of soluble magnesium salts before the softening treatment (Section 3.1.3).

3.3. Combined effect of 'high-pH softening treatment' and ED for boron removal

This set of experiments was conducted with the groundwater softened with lime and soda ash. Before commencing the ED experiments, the pH of two softened groundwater samples was reduced from the initial level of 11.2 to 10.0 and 7.8, respectively. Both ED tests were performed in batch mode operation. Fig. 11 represents the removal of boron in the ED system. Conversely, the diluate tank did not incorporate a system to control the pH level, therefore a fluctuation of the pH level was observed during the experiments and plotted in Fig. 12.

The efficacy of ED technology for boron removal depends on different factors like initial boron concentration, solution pH, presence of other ionic species and tested membrane [48]. As shown in Fig. 11, a sharp drop in boron initial concentration was observed in both experiments during the first minutes of the treatment, due to the higher pH levels recorded in the diluate stream. As a consequence of the higher initial pH levels, the concentration of $B(OH)_4^-$ ions was higher and the transport of boron through the anion exchange membranes was favoured [48,49]. After 30 min, the pH level dropped below 8.5 and consequently boron removal slowed down in both cases. The reason for this lies in the fact that under neutral or acidic conditions boron is present mainly as un-dissociate boric acid, and thus it is not properly removed by ED [50].

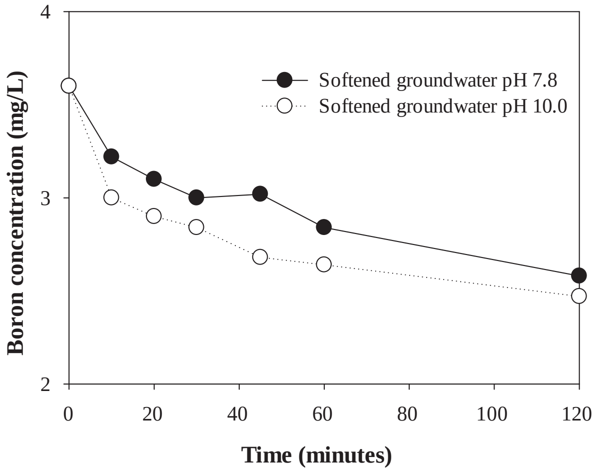

Fig. 11. Boron remaining concentration in the diluate stream vs. detention time in the ED unit.

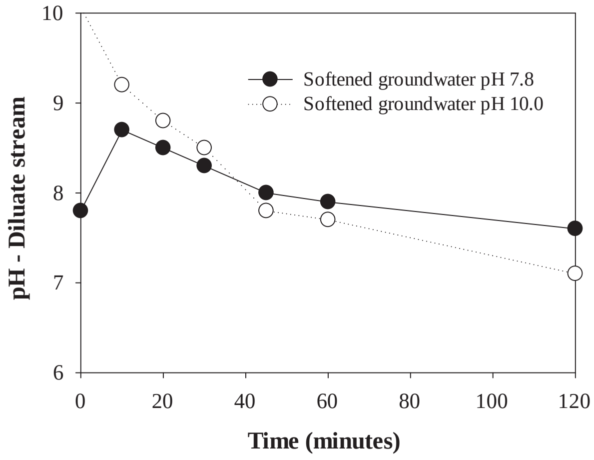

Fig. 12. The pH level evolution in the diluate stream vs. detention time in the ED unit.

The fluctuation of the pH level in the diluate stream could be explained by the migration of ions through the ED membrane. Eventually, total boron removal, achieved at the end of the experiments, were respectively 49 and 51% for the softened samples at initial pH levels of 7.8 and 10.0. Therefore, the efficacy of ED treatment in these experimental conditions was limited considering that around 30% of boron removal had been achieved during the softening treatment. On the other hand, diluate water conductivity and chloride concentration dropped below 300 μS/cm and 100 mg/L, respectively in both experiments. In addition, no silica reduction was observed at the end of the experiments. Since silica is a neutrally charged species, it cannot be removed by ED technology [51].

Kabay et al. [48] studied the effect of feed characteristics and interfering ions in boron removal by ED using batch mode operation. This study was also performed with a stack of 10 pair of cation exchange and anion exchange membranes. The highest boron transport through the anion exchange membranes was achieved at pH around 10.5. Boron removal was not feasible at pH 8.5. It was also demonstrated that boron removal by ED technology was favoured for higher initial boron concentrations. In addition, the presence of chloride in the feed water decreased boron removal and operation time became longer. Eventually, 40% boron removal was achieved when treating a synthetic solution containing a boron initial concentration of 25 mg/L at pH 10.5 [48].

Some investigators have stated that conventional ED can only remove about 42–75% of boron from water [52,53]. Therefore, a lime and soda ash softening pretreatment could facilitate compliance with strict boron standards in existing ED desalination systems.

4. Conclusions

A 'high-pH softening pre-treatment' was trialled for the first time for boron removal from samples collected in an inland desalination system. Brackish magnesium dominated groundwater spiked with 5 mg/L of boron was softened with different alkaline reagents in order to remove boron and other scale forming precursors including SiO_2. Since SEM-EDX and FTIR determinations of formed solids showed that precipitation as silicates appeared to be the main mechanism for SiO_2 removal, boron may have been removed during the softening process by sorption of hydroxyborate ions to formed magnesium silicates. The latter might involve either a co-precipitation mechanism and/or an adsorption process in which hydroxyborate ion adsorbs onto magnesium silicates as they are precipitating. Based on the experimental results, the lime soda and ash softening treatment was proved to be more suitable than the caustic soda treatment, achieving average boron and silica removal of 33 and 62%, respectively. On this subject, the caustic soda softening treatment increased groundwater conductivity and alkalinity. Conversely, an additional 9% boron removal was feasible by (a) magnesium chloride addition before the softening treatment; or (b) a final polishing step based on adsorption of hydroxyborate ions onto magnesium oxide.

Finally, the application of the lime and soda ash softening pretreatment to groundwater samples in combination with latter pH adjustment to 10.0 and ED technology achieved a total boron removal of 51%. Since the diluate tank in the ED system did not incorporate a system to control the pH level, the boron removal in the ED system was limited to around 21%. Based on previous research further boron removal could have been possible if the pH in the diluate stream would have been kept around 10.5 during the desalination step. From this research, we can also conclude that even if additional boron removal is required in existing inland desalination plants by more advanced technologies like 'seawater RO membranes' or ion exchange technology, this 'high-pH softening pre-treatment' could reduce the requisites of such downstream complex processes.

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Additional note regarding a minor error in the published paper.

A minor error was recently discovered in the published paper. The FTIR spectrophotomer used for these experiments was a Shimadzu model <u>IRAffinity-1S</u>.

6.3 Concluding remarks

This paper investigated the performance of 'High-pH pretreatment' for boron removal from groundwater samples collected in an inland desalination facility. Magnesium-dominated groundwater, initially spiked with 5 mg/L of boron, was softened with different alkaline reagents to remove boron and other scale-forming precursors including SiO_2. The outcomes of this research suggest that the lime and soda ash softening treatment is more suitable than the caustic soda treatment; achieving average boron and silica removal of 33 and 62 %, respectively. SEM-EDX and FTIR determinations of precipitated solids showed that precipitation as silicates appeared to be the main mechanism for SiO_2 removal. At the same time, boron may have been removed during the softening process by sorption of hydroxyborate ions to formed magnesium silicates.

The results also show that an additional 9% boron removal was possible by magnesium chloride addition before the softening treatment, or by a final polishing step based on adsorption of hydroxyborate ions onto magnesium oxide.

From this research, we can conclude that 'High-pH pretreatment' of groundwater can facilitate compliance with strict boron standards in inland facilities using RO or ED technology.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the contribution of this thesis and discusses the important recommendations for future work.

7.1 Conclusions

The efficacy of 'High-pH pretreatment' in existing or future inland desalination facilities for scale control, RO concentrate minimization, specific pollutants removal (such as boron) and by-products recovery, was investigated in-depth in this study. Groundwater and RO concentrate collected in a municipal desalination facility run by the Western Downs Regional Council (Australia) was used to carry out this research. In contrast to previous studies, the groundwater and RO concentrate used for these experiments had a magnesium concentration higher than the calcium concentration. No studies have been conducted to discover the effect of magnesium-dominated water in scale control, RO concentrate minimization, specific pollutants removal (such as boron) and by-products recovery following a 'High-pH pretreatment' strategy. The study was conducted in four phases:

- Phase 1: The differences between inland and seawater desalination were highlighted and the existing strategies for RO concentrate minimization towards ZLD in inland desalination were critically reviewed. This phase also compared two different scale control technologies: acid/AS addition, and 'High-pH pretreatment'
- Phase 2: 'High-pH pretreatment' of RO concentrate followed by secondary RO was tested to increase overall water *Rw* in an existing inland desalination system. It was hypothesized that *Rw* could be enhanced in facilities treating magnesium-dominated waters since magnesium-bearing minerals that precipitate at high pH could concurrently remove other scale forming precursors including silica through precipitation and adsorption/enmeshment. In addition, $CaCO_3$ and CaO recovery from

precipitated sludge could be possible through CO_2 gas injection to selectively dissolve magnesium

- Phase 3: Two different scale control strategies: 'High-pH pretreatment', and AS addition were evaluated for RO concentrate minimization in a lab-scale AGMD system. The inorganic precipitation mechanism in MD systems may be different from those of pressure driven membrane technologies, such as RO, due to variation in operating conditions such as temperature
- Phase 4: 'High-pH pretreatment' was evaluated, at a laboratory scale, for boron removal from magnesium-dominated groundwater samples. Before commencing the experiments, the brackish groundwater was spiked with 5 mg/L of boron. To date, it is largely unclear whether a softening pretreatment at High-pH can facilitate boron removal from groundwater.

The first phase of this study showed that water *Rw* in inland desalination is limited by AS efficacy, and large volumes of RO concentrate are frequently disposed of into evaporation ponds. Overall, no matter which concentration technology is selected for RO concentrate minimization, it must address the scaling potential problem. The integration of a 'High-pH pretreatment' between consecutive RO stages or between RO and another advanced concentration system could overcome AS limitations and increase water *Rw,* while simultaneously enhancing salt recovery options.

Therefore, in the second phase of the study, magnesium-dominated RO concentrate was treated with different alkaline reagents, such as NaOH, $Ca(OH)_2$, and Na_2CO_3. As a consequence, the concentration of scale-forming precursors including magnesium, calcium, strontium, barium, and SiO_2 was reduced by precipitation and adsorption/enmeshment. SEM-EDX and FTIR determinations performed on the generated solids showed that precipitation as silicates appeared as the main mechanism for SiO_2 removal. Overall, the lime and soda ash softening treatment showed more advantages than the caustic soda treatment for the High-pH precipitation treatment. NaOH addition increased RO concentrate alkalinity and conductivity with a consequent negative impact on the LSI/S&DSI, achievable water *Rw* and energy requirements during the RO desalination process. Software simulations performed with ROSA 9, demonstrated that following RO concentrate treatment with lime and soda ash, pH readjustment and AS addition, overall water *Rw* could be further increased from 80% to 97% using secondary RO. Eventually, $CaCO_3$ recovery from the precipitated sludge during the lime and soda ash treatment was shown to be possible through CO_2 injection to selectively dissolve magnesium. Recovered $CaCO_3$ could be used in agriculture as a pH stabilizer for soil or re-calcined as quicklime at 900°C. Overall, the second phase of the study positively answers the first two research questions regarding the efficacy of 'High-pH pretreatment' of RO concentrate followed by secondary RO to increase overall water *Rw* in an existing inland desalination system and regarding the capacity to facilitate recovery of by-products.

The scaling risk must also be reduced when applying other advanced desalination technologies like MD. The third phase of this study investigated an intermediate 'High-pH pretreatment' between RO and batch AGMD desalination for high salinity RO concentrate minimization. RO concentrate was treated with lime and soda ash, resulting in significant removal of scale-forming precursors. The 'High-pH pre-treatment' (followed by pH readjustment and AS addition) permitted the operation of the batch AGMD system at a higher feed water temperature, initially allowing a 37% increase in permeate flux. This was compared to the traditional strategy of AS utilization only, which was not successful in preventing the formation of mineral scales. Consequently, the volume of RO concentrate with an initial TDS level of 10.8 g/L was minimized by a *CF* of 3.2. A slight decline in permeate flux recorded during the experiment was attributed to the increase in feed water salinity and a decrease in feed water flow-rate as a consequence of the technical limitations imposed by the feed water pump placed in the lab-scale AGMD unit. This intermediate chemical treatment greatly reduced the formation of mineral scales in different components of the system such as the AGMD membrane, feed water tank, feed water pump and heating element. SEM-EDX and FTIR analyses also confirmed the suitability of 'High-pH pretreatment' for scale control in the AGMD membrane. Therefore, the third research question has been answered confirming that 'High-pH pretreatment' can be combined with AGMD for RO concentrate minimization in an inland desalination system.

The final phase of this study investigated the efficacy of 'High-pH pre-treatment' for boron removal from groundwater samples. Boron can be present in groundwater from natural or anthropogenic sources. In this study, brackish groundwater spiked with 5 mg/L of boron was softened with different alkaline reagents to remove boron and other scale forming precursors including SiO_2. Based on the experimental results, the lime and soda ash softening appeared as the best option achieving average boron and silica removal of 33 and 62%, respectively. SEM-EDX and FTIR analyses of formed solids showed that precipitation as silicates appeared as the main mechanism for SiO_2 removal. Consequently, boron might have been removed during the softening process by sorption of hydroxyborate ions to formed magnesium silicates. This might involve a co-precipitation mechanism and/or an adsorption process in which hydroxyborate ion adsorbs onto magnesium silicates as they are precipitating. An additional 9% boron removal was made feasible by: a) magnesium chloride addition before the softening treatment; or b) a final polishing step based on adsorption of hydroxyborate ions onto magnesium oxide. These results have answered the last research question of the project regarding the effectiveness of 'High-pH pretreatment' in removing boron from magnesium-dominated groundwater. Finally, the combination of the lime and soda ash softening pretreatment of groundwater samples followed by pH adjustment to 10.0 and ED technology achieved a total boron removal of 51%. Since the diluate tank in the ED system did not incorporate a system to control the pH level, the boron removal in the ED system was limited to around 21%. Based on previous research, further boron removal could have been possible if the pH in the diluate stream had been kept at around 10.5 during the (batch mode) desalination step.

7.2 Recommendations for further study

The results obtained in this study with magnesium-dominated groundwater and RO concentrate showed that the integration of a 'High-pH pretreatment' in existing or future inland desalination systems for scale control, RO concentrate minimization, pollutants removal (such as boron) and by-products recovery could be considered to be promising alternative. However, while working on the project, several aspects were identified for further exploration. The following aspects are worthy of further investigation in future work:

1. The second phase of this study reported the recovery of calcium carbonate from pretreatment sludge through CO_2 injection to selectively dissolve magnesium. Carbonated sludge, mainly $CaCO_3$, was collected by filtration and a magnesium bicarbonate solution was collected from the filtrate. The study of possible

applications for this magnesium bicarbonate solution could be worthwhile. It could be tested as a coagulant in industrial water treatment

2. The scaling risk also has to be reduced when applying other advanced desalination technologies like Forward Osmosis (FO) or Mechanical Vapour Recompression (MVR) evaporators. In this regard, the third phase of this study investigated an intermediate ‘High-pH pretreatment’ between RO and batch AGMD desalination for high salinity RO concentrate minimization. Therefore, it is recommended to further extend this phase of study, evaluating the combination of ‘High-pH pretreatment’ with thermal desalination systems such as MVR evaporators and crystallizers for RO concentrate minimization and by-products recovery
3. The total cost of desalination depends on factors such as: a) energy requirements, b) feed water salinity and water quality, c) economies of scale, d) operating and maintenance costs, and e) environmental regulations. A study on a pilot plant scale would be required to assess whether ‘High-pH pretreatment’ of the RO concentrate would be cost-effective for this desalination project. The increase in capital, energy, operator/maintenance and chemical costs should be compensated by a reduction in the cost of RO concentrate management and disposal. Moreover, the influence of ‘High-pH pretreatment’ on (secondary RO) membrane productivity, membrane replacement and membrane cleaning frequency is also an important factor that has to be carefully evaluated.
4. Most inland desalination systems have low treatment capacity and are often located in isolated places. To cut energy costs, it could be effective to use solar energy to provide power to inland desalination plants, thus avoiding any greenhouse gas emissions. Therefore, testing the integration of the ‘High-pH pretreatment’ at pilot plant scale while taking advantage of solar energy to reduce the environmental impact of the desalination process, could be worthwhile
5. Episodes of groundwater contamination have been widely reported in the literature. To date, the possible advantages of a ‘High-pH pretreatment’ during the desalination of sewage contaminated groundwater are largely unclear. Therefore, it could be useful to investigate the integration of a ‘High-pH pretreatment’ (followed by pH readjustment and AS addition) in inland

facilities dealing with sewage contaminated groundwater. The process could provide microbial disinfection of groundwater and nutrients removal. The efficacy of this chemical approach in terms of biofouling prevention could be evaluated in a pilot plant using RO technology.