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Strategies for the Management and Treatment of Coal Seam Gas Associated Water

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Coal seam gas (CSG) is a growing industry in Queensland and represents a potential major employer and deliverer of financial prosperity for years to come. CSG is a natural gas composed primarily of methane and is found trapped underground in coal beds. During the gas extraction process, significant volumes of associated water are also produced. This associated water could be a valuable resource, however, the associated water comprises of various salt constituents that make it problematic for beneficial use. Consequently, there is a need to implement various water treatment strategies to purify the associated water to comply with Queensland's strict guidelines and to mitigate environmental risks. The resultant brine is also of importance as ultimately it also has to be dealt with in an economical manner. In some ways it can be considered that the CSG industry does not face a water problem, as this has inherent value to society, but rather has a "salt issue" to solve. This study analyzed the options involved in both the water treatment and salt recovery processes. A brief overview of the constituents present in Queensland CS water was made to illustrate the challenges involved and a range of treatment technologies discussed. Water treatment technologies examined included clarification (ballasted flocculation, dissolved air flotation, electrocoagulation), membrane filtration (ultrafiltration), ion exchange softening and desalination (ion exchange, reverse osmosis desalination and capacitance deionization). In terms of brine management we highlighted reinjection, brine concentration ponds, membrane techniques (membrane distillation, forward osmosis), thermal methods, electrodialysis, electrodialysis reversal, bipolar membrane electrodialysis, wind assisted intensive evaporation, membrane crystallization, eutectic freeze crystallization and vapor compression. As an entirety this investigation is designed to be an important tool in developing CS water treatment management strategies for effective management in Queensland and worldwide.

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Highlights

- Detailed overview of the challenges in treating CSG associated water
- Examination of associated water pre-treatment options
- Evaluation of desalination opportunities and issues
- Critical analysis of brine management strategies

Key Words
Coal seam gas; coal bed methane; produced water; pre-treatment; desalination; brine management

1. Introduction

1.1 Coal Seam Gas - Overall Process

The development of unconventional gas resources such as shale gas and coal seam gas has boomed over the past few years [1]. Coal seam gas (CSG) also known as coal bed methane (CBM) is comprised of natural gas that is extracted from low to high rank coal beds [2, 3]. The coal seam depth typically ranges from 300 to 1000 m underground and the CSG is typically comprised mainly of methane [2]. The gas is adsorbed and withheld in the pore structure of the coal by potentiometric pressure [4]. In order to extract the gas the coal seam requires depressurization which is achieved by extracting the water within the coal seam [5] [Figure 1]. On some occasions it may also be necessary to apply hydraulic fracturing for CSG operations to facilitate the flow of gas from the coal beds [6]. Hydraulic fracturing involves injection of a mixture of water, additives and proppant sand under sufficiently high pressure to crack the coal bed and create flow paths for the gas and water to rise to the surface [7, 8].

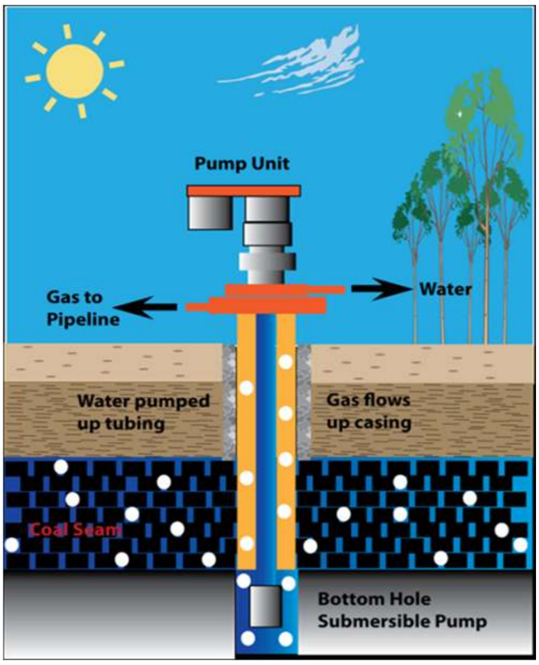


Figure 1: Illustration of the Coal Seam Gas (CSG) Extraction Process

1.2 Coal Seam Gas in Australia

Australia has vast deposits of CSG with approximately 200 peta-joules (PJ) produced for the domestic market per year and in addition to this there has been a 10 % increase in CSG production for the export market [3]. Continued growth is expected until 2030 in order to cope with increasing global demand for CSG [3]. The extraction of CSG has developed in a number of countries including China, Australia, USA, Canada and India [2]. The USA is the world's largest CSG producer followed by Australia [3]. Australia is estimated to possess 4 trillion m^3 of CSG resources with a current yearly production of 6.2 billion m^3 [3]. Recently Australia has been utilizing CSG at an increasing rate, however there are concerns for potential environmental issues [5]. The Eastern states of Australia have the largest reserves of coal seam gas, with Queensland clearly leading industry development [7].

1.3 Coal Seam Gas in Queensland

Queensland's CSG industry represents great economic potential to Australia [9] with presently four major companies involved; Santos GLNG; Queensland Gas Corporation (QGC); Arrow Energy and Australia Pacific LNG (APLNG). The Surat and Bowen Basins in Queensland together comprise 90 to 97 % of CSG production for the nation [3, 10]. In 2007, the Queensland government implemented a "smart energy policy" that required a minimum gas-fired generation contribution of 15 % of the Queensland power supply by 2010 which in turn accelerated the exploration by CSG operators [11] and increased power generation using CSG to 35 % of the total operating capacity [10]. The Surat Basin located in Queensland has been estimated to hold over 64 % of Australia's coal seam gas reserves [11]. The bulk of the CSG produced in Queensland is destined for export in the form of Liquefied Natural Gas (LNG) with extensive LNG facilities located at Curtis Island [10].

2.0 Coal Seam Gas Produced Water and Constituents

2.1 Water Production

Coal seam gas extraction is accompanied by the production of significant volumes of water as a by-product [3]. The water produced usually cannot be immediately used or disposed, and thus must undergo further treatment due to its high salinity [4, 12]. It is estimated that over the next 25 years, up to 7,500 giga-litres (GL) of water will be produced from the Australian CSG industry [13]. In Queensland alone, approximately 12.5 GL of CS water was produced in 2007 [4]. For a single coal seam, water production decreases with time and gas production increases with time. Therefore the quantity of water produced at the start of the lifetime of a well will be less than the water produced at the end of its lifetime. Water production can continue for as long as 15 years depending on geographic location [3].

2.2 Overall Water Quality

To understand how to effectively manage and treat CSG produced water it is critical to understand what components are in the water and how to adhere to the rules and regulations. CSG produced water management is an environmental challenge due to the inherent salt content [4]. Commonly CS water has a total dissolved solids (TDS) concentration in the brackish range of 200-10,000 mg/L and characterized by alkaline pH values up to *ca*. 9 [5, 14, 15]. CS water salinity is variable and is dependent upon geological factors and conditions [9]. Therefore, to propose a "universal strategy" to treat CS water is impractical due to the variation in water qualities. Coal seam gas associated water has the potential to cause surface water, underground and ecosystem damage [3]. The water that is produced from the coal seam requires treatment and can be an important and costly aspect of the CSG industry [7]. CSG produced water needs to be treated with effective technologies to allow for beneficial reuse and for this reason CS water is commonly desalinated [4]. The constituents present in Queensland's CSG produced water which may make it unfit for immediate beneficial uses are discussed below.

2.2.1 Total Suspended Solids

Total suspended solids (TSS) is a water parameter which has been studied for many years [16]. Elevated TSS in water causes turbidity and if irrigated on crops can inhibit plant growth as a reduction in photosynthesis can occur [17]. TSS must also be removed prior to any water demineralization process in order to prevent clogging and fouling of membranes [18]. Dahm *et al*. [19] analyzed a series of coal seam water samples from various Basins in the USA and determined that TSS values were up to 580 mg/L. Notably, the actual TSS value measured ranged from below detection limits to several hundreds of ppm, thus no general statement regarding trends in TSS content could be made.

2.2.2 Total Dissolved Solids

Total dissolved solids (TDS) is the total amount of salts or mobile charged ions dissolved in the water [20]. TDS is a water parameter that is commonly measured by specific electrical conductivity [21], and the term salinity is often associated with TDS [22]. Commonly CS water as outlined above has a TDS concentration in the brackish range of 200-10,000 mg/L [5, 15], albeit samples from wells in the USA have been characterized with TDS levels of up to 39,260 mg/L [19]. TDS majorly includes species such as sodium, potassium, magnesium, calcium, strontium, barium, iron, aluminium, bicarbonate, chloride and sulphates [3, 15, 23, 24]. Trace elements can also be present such as dissolved metals, metalloids and boron [25, 26]. Saline water can cause physiological effects in humans and livestock through consumption [27]. Also, elevated TDS concentrations in irrigation waters may cause adverse effects on plants and crops by inducing saline soils [27].

2.2.3 Sodium Adsorption Ratio (SAR)

Soil sodicity indicates the accumulation of sodium in the soil structures and can cause problematic issues for soils and detrimental impacts upon plants and crops [22]. Sodium is the most common cation found in coal seam water and the elevated salinity and SAR value can cause an increase in the exchangeable sodium percentage (ESP) of the soil [28, 29]. The Sodium Adsorption Ratio is calculated as shown in Equation 1, where all concentrations are expressed in terms of meq/L [30].

Equation 1:

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{1}{2}[Ca^{2+} + Mg^{2+}]}}$$

Sodium chloride is the most dominant salt in soils and the buildup of this salt induces soil sodicity [28]. Salt affected soils can therefore be classified as sodic soils and can be evaluated by pH, SAR and the electric conductivity (EC) [31]. Elevated concentrations of salt in soils may result in decreased osmotic potential which induces decreased water uptake by plants, ion competition, issues with microbial activity and turnover of soil organic matter [31]. Soils that produce an ECe (saturated extract) > 4 dSm^{-1} and SAR > 13 are regarded as saline-sodic [32]. A high SAR value causes structural degradation to soil structures for irrigation purposes and should be managed accordingly [33]. SAR values reported for CS water by King *et al*. [34] ranged from 5 to 70 whereas Vance *et al*. [30] found that coal seam water in the Powder River Basin region ranged from 17 to 57. In contrast, the CS water from the Surat Basin in Queensland has been analyzed as having a SAR value of 107-116 [14]. Dahm *et al*. [19] examined a range of coal seam water sources from the Rocky Mountain region of the USA and confirmed that SAR values were highly dependent upon location and could exhibit large variations from 0.2 to 452.8.

2.2.4 Total Hardness

The water hardness in an important parameter that needs to be addressed in the water treatment industry [35]. Water hardness originates from cations in the water such as magnesium, calcium, bivalent and trivalent cations [35]. The water hardness initiates scaling in industrial equipment such as pipes, boilers and heat exchangers [36], and total hardness (mg/L) is effectively the sum of calcium and magnesium hardness in the water [5]. $CaCO_3$ causes scale precipitation on reverse osmosis membranes hence the use of anti-scalant chemicals is often required to minimize scale deposition [37], or water softening using ion exchange [38, 39]. Millar *et al*. [40] published an analysis of coal seam water from the Surat Basin, which indicated that the levels of calcium and magnesium ions in solution were actually relatively low (2.93 mg/L calcium and 0.83 mg/L magnesium ions). Alternatively, Rice [41] found that concentrations of calcium and magnesium ions in CS water from the Ferron field in USA were typically much higher than those reported from Queensland, with values up to 480 mg/L calcium and 290 mg/L magnesium, with average values in the range 20 to 100 mg/L. Dahm *et al*. [19] a large range of values for calcium ions for example in coal seam water, with the most extreme concentration being 5530 mg/L for a sample from the San Juan Basin. Chinese samples of CS water studied by Yang *et al*. [24] from the Liulin coalfield were in contrast relatively soft as hardness values were typically below 201 mg/L $CaCO_3$.

2.2.5 Fluoride

Fluoride ions are commonly found in soil, vegetation and water [42]. Fluoride in drinking water has been recognized as a problem to human health around the world and is classified as a contaminant by the World Health Organization [43]. The World Health Organization guideline for fluoride in drinking water is <1.5 mg/L [43]. When ruminants ingest fluoride it is either excreted or transported to calcium deposits such as bones and teeth [44].

Fluorosis is a chronic disease that occurs through elevated and persistent amounts of fluoride intake by animals such as cattle [45], causing acute intoxication and chronic intoxication [44]. Acute intoxication occurs from the gastro-intestinal tract, symptoms include vomiting, diarrhea, thirst, excess salivation, painful spasms and weakened pulse [44]. Chronic intoxication through long exposure times can lead to mottling/staining of teeth, loss of appetite, lameness and cachexia [45]. Symptoms depend on exposure times, dosages and livestock [45]. In plants, fluoride can cause varying effects depending on the concentration in the cell sap [42]. The excess fluorine can be absorbed by the plant causing physiological, biochemical, structural damage and even cell death [42]. Fluoride is commonly found in groundwaters and thus the presence of this species in CS water is not unexpected. For example, Millar *et al.* [40] recorded 5.69 mg/L fluoride ions in a CS water sample from the Surat Basin. On the other hand, Nghiem *et al.* [14] indicated that fluoride levels in a Surat Basin CS water were less than 1 mg/L, which illustrates the variability of CS water composition not only from Basin to Basin but also from different sites within the same Basin. Dahm *et al.* [19] discovered an even wider range of fluoride concentrations in USA CS water samples, ranging from 0.4 to 20 mg/L, depending upon the gas field investigated.

2.2.6 Boron

Boron in small quantities is a necessary nutritional requirement for crop species, as it produces the rhamnogalacturonan II complex that is needed by plant cells for growth [46]. However, there is a fine line between toxicity and deficiency of boron in plants [47]. If boron is in excess then plants will develop effects that are detrimental for crop productivity and growth [47]. Other elements have negative and positive charges which limits the permeability through the cell membrane and controls the influx into the cells of the plant [46], while boron has no charge, and therefore the degree of control of influx to the plant cells is absent [46]. The toxicity for boron develops from its interaction with hydroxyl groups (cis-formation) in metabolites such as ribose, which has the net result of interference with translation and transcription of the plant species [46]. The effect of boron varies amongst species of plants with some being more sensitive than others [47]. Irrigation water is a primary source of excess boron in soils and must be managed effectively to govern crop productivity [48]. Boron toxicity in plants may not occur immediately but through time and accumulation [47]. . Boron toxicity affects the morphological and physiological aspects of the plant [47], with a typical visible toxicity being leaf burn (chlorotic and necrotic patches) [48]. Other affects include decreased shoot and root growth, reduction of photosynthesis, elevated membrane permeability, minimized root cell division, oxidative damage and changed antioxidant enzymes [47]. Consequently, boron needs to be managed to reduce its detrimental impact on crop and plant species. Boron has been noted to be present in CS water samples by several research teams. For example, less than 1 mg/L boron was reported to be present in a sample of CS water from the Surat Basin [40]. Nghiem *et al*. [14] did not present any data for boron content in Australian CS water but did mention that concentrations of cs. 0.2 mg/L were found in Powder River Basin CS water from the USA. Boron levels of up to 4.7 mg/L were analyzed by Dahm *et al*. [19] for the Raton Basin.

2.2.7 Silica

Silica is present in various forms such as particulate matter, colloidal silica or reactive silica (dissolved silica). Dissolved and particulate silica species are commonly found in CS water [40, 49]. Surat Basin CS water was shown to contain 10.57 mg/L dissolved silica [40] whereas Powder River Basin CS water was quoted to be slightly higher with 12 mg/L silica [14]. The Greater Green River, Powder River and Raton Basins were all reported to produce CS water with silica in the range 4.11 to 12.79 mg/L, with higher concentrations of silica found in the San Juan Basin [19].

2.2.8 Organic Carbon

Organic carbon is generally characterized in terms of total organic carbon (TOC) and dissolved organic carbon (DOC) in water and wastewater samples. Since coal seam water has been in contact with coal for long periods, the possibility of contamination by organic species cannot be ignored. Orem *et al*. [50] examined produced water from the Powder River Basin and found several organic species such as polycyclic aromatic hydrocarbons (PAHs), phenols, and aromatic amines among others. Recently, Orem *et al*. [51] analyzed the total organic carbon (TOC) content for a wide variety of coal seam gas operations in the USA and found 0.25 to 21 mg/L with mean values mainly in the range 1.5 to 4.5 mg/L. This latter data was in accord with the comparable results from Dahm *et al*. [19] wherein the dissolved organic carbon (DOC) values ranged from 0.3 to 11.41 mg/L and total organic carbon (TOC) from 0.25 to 13 mg/L.

2.3 Alkalinity and pH

Solution pH has a strong influence on the solubility and toxicity of various constituents in the aquatic environment [52]. High alkalinity is usually associated with CS waters with a pH ranging from 7.5 to 9.5 [40, 41], albeit there are reports of some CS water types in the USA characterized by slightly acidic pH values [19]. Dahm *et al*. [19] recorded total alkalinity values from 51 to 11,400 mg/L $CaCO_3$ in the San Juan Basin. The alkalinity and pH of the CS water also need to be within the regulatory guideline limits. Total alkalinity is usually expressed by the amount of hydroxide, bicarbonate and carbonate and is typically represented in terms of mg $CaCO_3$/L [53]. For the Surat Basin CS water, the alkalinity present was predominantly bicarbonate [40] due to the pH value of 9.03.

2.4 Impact upon Aquifers

There exists public anxiety that CSG mining may impact the levels of bore water and potentially promote inter-aquifer exchange as coal seam gas wells can penetrate overlying aquifers [54]. As stated by Vink [55] a critical concern in Queensland has been the potential threat to the Great Artesian Basin (GAB) aquifers which supply water to some of Australia's premium agricultural land. The Queensland government has set up the Office of Groundwater Assessment (OGIA) to monitor and control the situation [56]. According to their recent report relating to the Surat Basin, of the estimated 21,000 water bores only 528 bores are predicted to experience a decline in water level of more than the trigger threshold of 5 m for consolidated aquifers and 2 m for unconsolidated aquifers, as a result of CS water extraction [57]. Herckenrath *et al*. [58] recently provided an improved modelling tool which allows simulation of the impact of coal seam gas extraction upon neighboring groundwater sources.

3. Queensland CSG Guidelines and Social Issues of CSG Operations

The Queensland Department of Heritage and Protection (DEHP) has published regulations in relation to the beneficial use of coal seam water [59]. The main objective of the state government is stated as *"to encourage the beneficial use of CS water in a way that protects* *the environment and maximises its productive use as a valuable resource".* Letts [54] has elegantly summed up the Queensland regulatory regime surrounding the CSG industry and outlined the preferred water management strategies as: (1) Reinjection of CS water or treated water into underground structures such as aquifers in a manner which does not harm the environment; (2) Reuse of CS water if possible without altering the composition; (3) Desalination or amendment of the CS water to make it suitable for reuse; (4) Provision of water of suitable quality to facilities such as water supply dams. Letts also highlighted the non-preferred options such as evaporation ponds and discharge to surface waterways [54]. Comino *et al*. [60] have also pointed out that while CSG exploration and extraction is regulated by the Petroleum and Gas (Production and Safety) Act 2004 (Qld), other aspects such as environmental impacts are regulated under the Environment Protection Act 1994 (Qld). If the CSG operation is located on cropping land then further legislation in the form of the Strategic Cropping Land Act 2011 (Qld) must be considered. Recently, the Queensland government has amended guidelines so that CS water with an electrical conductivity < 15,000 µS/cm and pH from 6 to 10.5 is no longer classified as a regulated waste [61]. A beneficial use approval (BUA) changes the waste material to a valuable commodity that can be used [59, 62].

Environmental and personal health concerns due to CSG activities, have naturally been of significant concern. Werner *et al*. [63] conducted an extensive survey of existing literature from around the globe in regards to unconventional natural gas development. The main conclusion from the latter work was that published studies rarely had been based on rigorous and methodical investigation of gas exploration activities. On the other hand, there also was insufficient evidence to dismiss the possibility that gas operations do cause health issues. The summary of possible hazards and means by which these could be transferred in Queensland by Navi *et al*. [64] similarly acknowledged the potential for environmental health impacts, but again indicated the need for more comprehensive studies. Everingham *et al*. [65] focused more on the social aspects of CSG development in Queensland. These authors found that various factors such as CSG company practices, management practices and community engagement were important in facilitating successful growth of both the CSG and agricultural industries.

Summarized below are the main beneficial uses used proposed for water use in the CSG industry.

3.1 Coal Washing & Dust Suppression

The reduction of dust from various sources is of practical importance [66]. For example, construction processes that are associated with CSG development and exploration can utilize dust suppression from CS water [67]. Notably, due to the possibility of detrimental impacts to the local ecology or soil degradation, usually it is required for CS water to be treated prior to dust suppression [67]. The BUA specifically says that the CS water must not damage any vegetation or produce visible signs of salt deposition [59]. The produced water from CSG operations can also be used for coal washing at mine sites as long as there is effective drainage to capture and manage the water [67]. CS water has similar characteristics to the water being used in mine sites and therefore provides minimized environmental risks [67].

3.2 Irrigation

Salinization and sodicity are the two major problems that can occur in irrigation [3]. As discussed earlier, high concentration of sodium in irrigation water can change soil characteristics by effecting properties such as soil permeability, soil infiltration and aggregate stability, ultimately impacting plant growth [3]. Vance *et al*. [30] studied the impact of CS produced water irrigation over several years upon soil properties. In each case the electrical conductivity and sodium adsorption ratio (SAR) values increased. Concomitantly, the soil infiltration rate was reduced as was the Darcy flux. Johnston *et al*. [68] further investigated the application of soil amendments along with the coal seam water and showed that addition of gypsum (calcium sulphate) could reduce soil sodicity. Santos GLNG has initiated a CSG irrigation project at Fairview and Springwater stations [69] which encompasses a drip irrigated 240 hectare plot growing mainly leucaena and Chinchilla white gums. Approximately 2 million trees will ultimately be planted and sufficient forage generated for 1,500 cattle. Greenhouse gas reductions can rise to as high as 40,000 tonnes per annum of stored carbon from the atmosphere each year from the aforementioned irrigation project. Vickas *et al*. [70] provided an excellent overview of the issues associated with assessment of the greenhouse gas emissions from the Australian CSG industry.

Notably, it was discovered that a coherent approach to greenhouse assessments was lacking across the CSG industry, with a need to adopt more in depth methods such as Strategic Environmental Assessment (SEA). Zheljazkov *et al*. [71] found that both spearmint and peppermint could be irrigated with water comprising of 50 % CS water without impact upon growth characteristics. One concern is that irrigation with coal seam water can potentially result in transfer of this liquid to groundwater aquifers [64].

3.3 Livestock Watering

Livestock can tolerate high levels of saline water when compared to humans, however young, old, lactating and pregnant livestock are less tolerant to water quality [67]. The beneficial use approval (BUA) applies to both intensive livestock farming operations such as feedlots which are prevalent in Queensland and normal stock grazing on pastoral land. The one caveat is that the CS water should not be directly released to other waterways [59]. As expressed by Navi *et al*. [64] there is also a chance that contaminants present on coal seam water can enter the food chain. Significantly, consideration must be given to the identity of the livestock which will use the water, and their tolerance to different water qualities. For instance, beef cattle have been shown to prefer well water with TDS values of less than 3000 mg/L [72].

3.4 Industrial and Manufacturing Use

The use of CS water in the industrial and manufacturing sector represents a potentially large opportunity. Closed cycle operations such as cooling water and slurry pumping are tolerant to high saline water and therefore suitable industries can incorporate CS water [67]. The only condition set by the BUA is that the CS water should have a pH in the range of 6 to 9 which is typical of the majority of CS water found in Queensland [59].

3.5 Aquaculture

CS water characteristics lend themselves to be suitable for aquaculture, however, the indirect contact with the human population is also something worthy of consideration [67]. The BUA outlines that if coal seam water is used for aquaculture it should not be released to either another waterway or disposed on land, hence it applies to lined ponds or tanks [59]. Furthermore, the range of fish species which can be grown in such medium is limited. Navi *et al*. [64] mentioned that both Barramundi and Mulloway have been demonstrated to grow in CS water, whereas in contrast another Australian native, the Murray Cod, could not.

3.6 Injection into Depleted Aquifers for Recharge Purposes

Santos GLNG operates a managed aquifer recharge project near Roma that involves reinjection of water into the Gubberamunda sandstone aquifer which has been depleted over many years by the Roma township. On average, the Roma citizens deplete the aquifer by 3.5 ML per day whereas the Santos project aims to re-inject 10 ML per day [69]. Myers [73] discussed the management of groundwater from CSG operations in the Powder River Basin in the USA. He noted that one means to minimize the impact of CSG mining upon local river flux was to reinject produced water into depleted coal seams.

3.7 Drinking Water

There exists potential for CS water to be used to supplement local urban water supplies. For example, in Queensland, Sun Water has worked with QGC on the Kenya to Chinchilla Weir pipeline project [74]. CS water which has been treated by the Kenya Water Treatment Plant using reverse osmosis as the central desalination technology, has been made available to not only the local agricultural sector but also the Western Downs Regional Council for further treatment to produce drinking water.

4. Pre-treatment of Coal Seam Water

The main reason why pre-treatment is a necessity for treatment of CS water is the need to protect the central desalination process, whether it is reverse osmosis or ion exchange. Both systems are susceptible to fouling and scaling which results in process inefficiency, increased operational costs and potential environmental damage. Two generic process options for coal seam water treatment are illustrated in Figure 2 and Figure 3. Whether reverse osmosis or ion exchange is used, the overall treatment strategy is similar. The obvious question is when to apply reverse osmosis and when to use ion exchange and in this regard the screening tool by Plumlee *et al*. [75] is useful. In the USA, ion exchange has been the dominant technology in the coal seam water treatment sector. According to Dennis [76], the Higgins Loop Continuous Ion Exchange (CIX) process has been used in over 15 sites in the Powder River Basin. The primary objective was the removal of sodium bicarbonate species from the CS water which was achieved by use of a strong acid cation (SAC) column. The strong acid cation resin exchanged the sodium ions in the associated water with protons which lowered the solution pH and ultimately promoted the decomposition of the bicarbonate species to produce carbon dioxide.

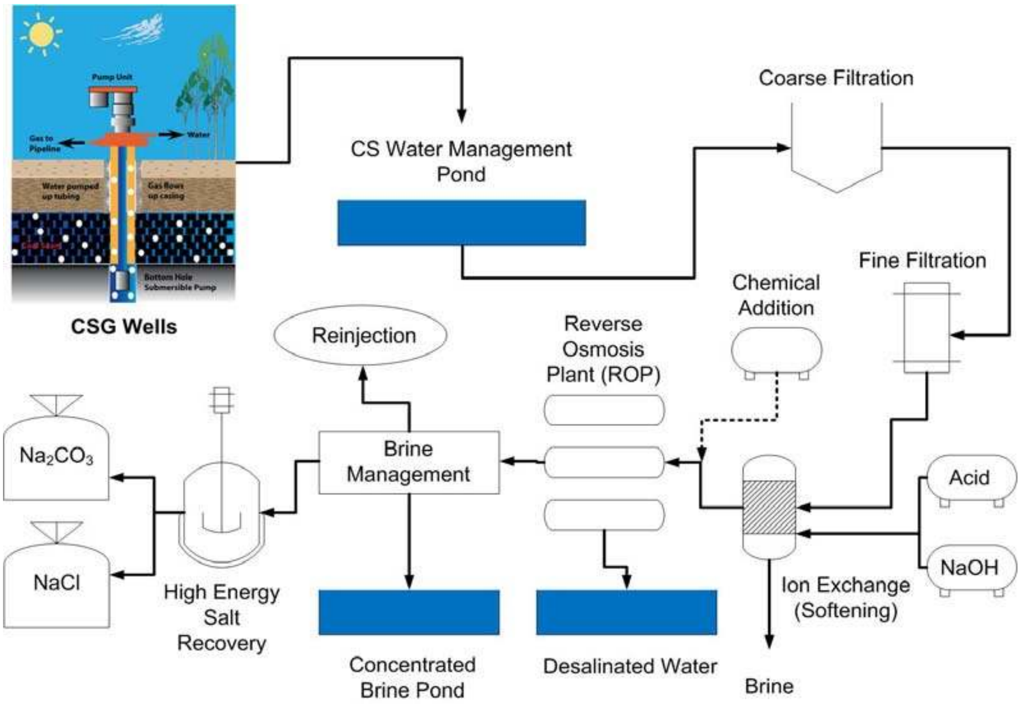


Figure 2: Process Flow for Coal Seam Water Treatment using Reverse Osmosis

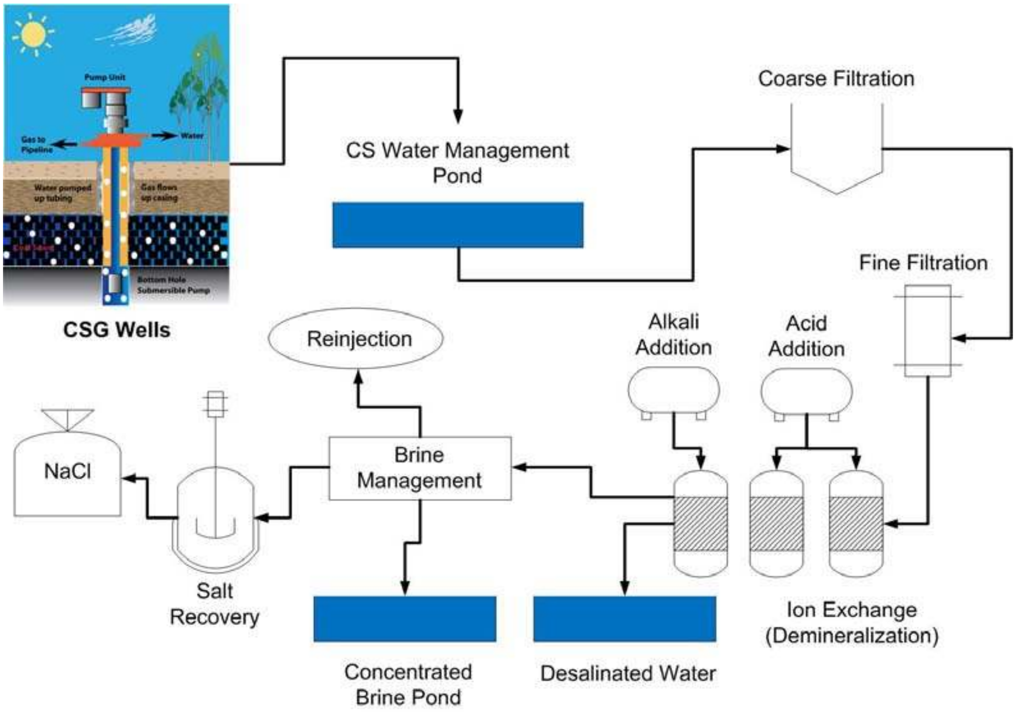


Figure 3: Process Flow for Coal Seam Water Treatment using Ion Exchange

However, in Queensland the coal seam water composition is quite different from the USA in that it consists mainly of sodium chloride with sodium bicarbonate usually present in lesser concentrations [3, 14, 40]. Thus, more complicated treatment strategies are required such as multiple ion exchange beds instead of a singular strong acid cation resin column. To date, reverse osmosis has been installed in several sites across Queensland as the central desalination step with ion exchange present if required for water softening and scale prevention [77]. Ion exchange is still under consideration for certain fields since as a general rule, ion exchange should be more cost effective for CS water compositions with lower total dissolved solids content. As the salinity of the water increases the operational benefits of ion exchange of low power consumption, minimal brine volume production and reduced capital expenditure tend to be neutralized by the cost of chemicals required for the regeneration stage.

A range of pre-treatment process options are discussed below and the application of each of these depends upon the composition of the CS water.

4.1 Clarification

The initial unit operation in a CS water pre-treatment train is typically some sort of coarse filtration stage which is designed to reduce suspended solids, remove algae and lower turbidity.

4.1.1 Microsand Ballasted Flocculation

In relation to CS water treatment, the Actiflo™ system marketed by Veolia has been implemented in Queensland. This technology is based upon a microsand ballasted flocculation clarification process [78]. Initially a coagulant such as alum or ferric chloride is injected in the coagulation tank followed by floc growth in the flocculation tank which is enhanced by addition of a microsand seed. The microsand has the added benefit of increasing the settling velocity of the particles thus allowing for more compact systems to be built. In the final stage is a counter current lamella system which accelerates the sludge settling. The resultant sludge is recycled to a hydrocyclone where the microsand is separated and returned to the Actiflo™ unit [Figure 4]. An example of an Actiflo™ pilot plant in operation has been given by Ko *et al*. [79] who evaluated the performance for drinking water treatment. In general, the Actiflo™ system worked according to vendor guidelines albeit a higher loading of microsand was required compared to full scale units (15 g/L relative to 3-5 g/L). Similarly, Imasuen *et al*. [80] evaluated the performance of Actiflo™ for high-rate clarification of a variety of wastewater streams. Using either ferric chloride or polyaluminium chloride (PAC) coagulants the unit consistently reduced turbidity, suspended solids and chemical oxygen demand (COD) to acceptable levels. Laboratory studies of Actiflo™ operation are relatively rare, albeit Desjardins *et al*. [81] have provided an interesting investigation which correlated modified jar tests at bench scale with full scale performance in several drinking water plants. The key criteria influencing the process were derived to be coagulant dosage, pH, microsand dosage and coagulant identity.

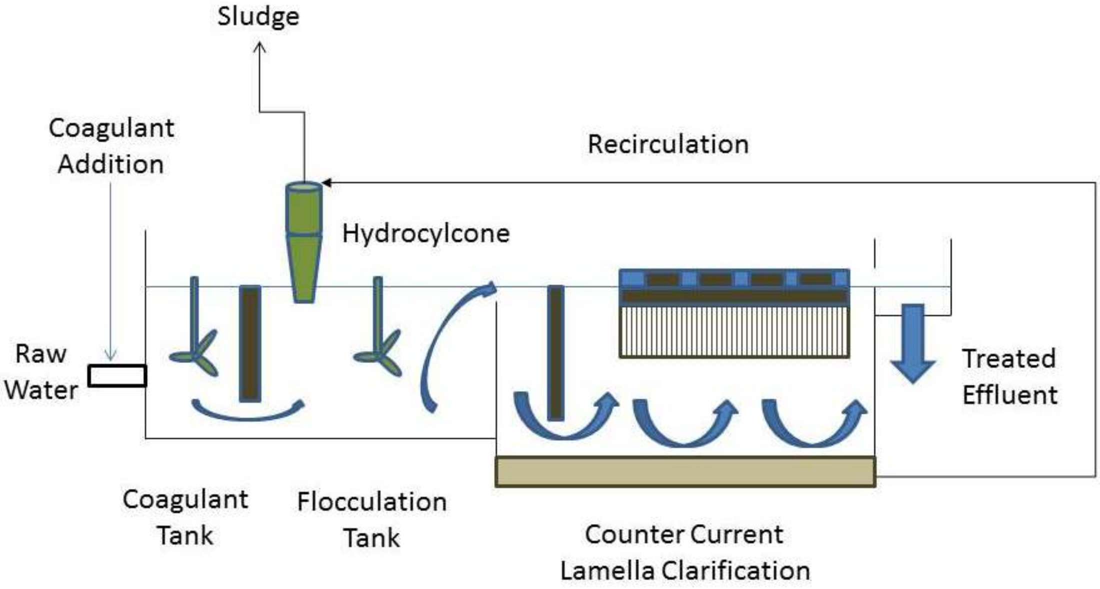


Figure 4: General Schematic of Actiflo™ High Rate Clarification Process

4.1.2 Dissolved Air Flotation

Dissolved air flotation (DAF) is a primary pre-treatment step for wastewater including drinking water and was used as early as the 1920's [82]. DAF removes constituents from water such as: impurities already present (TSS); coagulants/flocculants that were added prior; organic matter; turbidity; algae; Giardia and Cryptosporidium [82]. In a DAF tank there are two zones, the contact zone and the separation zone [82]. The contact zone permits collision between flocculating particles and produced air bubbles [82]. The separation zone is where the aggregates are separated from the water [83]. The flocculating particles and the air bubbles attach to each other and float to the top of the tank [53]. Gradually this float forms a sludge and is removed by an overhead skimmer [53]. Air bubbles (<100 µm) are produced by a saturator and are facilitated through the water in the contact zone [82]. The amount of air bubbles produced is correlated to the pressure set for the saturator and also the flow of the recycle stream [82].

Algae is a concern in the treatment of CS water as water management ponds are normally used to temporarily store water prior to demineralization, and these are subject to algal blooms. The presence of algae can produce small and colloidal particles that can cause significant fouling to membrane processes [84]. DAF can significantly reduce the turbidity, TSS and algae count in water prior to refined treatment methods hence reducing membrane fouling [85, 86].

The major advantage of DAF over sedimentation is claimed to be the time taken for the particles to flocculate [53]. DAF also offers a reduced footprint when compared to conventional sedimentation processes [53]. In the past decade there have been technological innovations and improvement to DAF processes [82]. High rate DAF processes exhibit major improvements wherein the hydraulic loading surface rate has increased and the flocculation times decreased to enhance efficiency and productivity [82].

4.1.3 Electrocoagulation

Electrocoagulation (EC) is a technology that was introduced in the early 19th century, which involves *in situ* generation of coagulants [87]. This approach can provide a more cost effective method when compared to conventional chemical coagulation methods [88]. Advantages of EC include, compact instrumentation, simplicity, automation and versatility [89]. EC induces coagulation through the use of electrochemical processes using sacrificial anodes such as aluminium or steel (iron) [87]. Essentially electrocoagulation is the total process of destabilizing species, contaminants, dissolved and suspended solids in the water by using metal ions (Fe or Al) and utilizing an electric current through the aqueous medium [90]. This current applied through the water, forces chemical reactions to occur forming stable compounds and elements [91]. These stable complexes and elements (hydrophobic) precipitate out of the water attaching to pollutants and can easily be filtered and removed through secondary separation techniques [91]. Species such as $Al_n(OH)_{3n}$ can agglomerate forming large surface areas that can aid in rapid adsorption of soluble compounds and efficiently capture colloidal particles [90]. The formation of H_2 gas provokes and aids flotation of the precipitates formed [35]. The entire EC process works by removing pollutants through the following processes: sorption; co-precipitation; precipitation; electrostatic attraction; coagulation and flotation [92].

Coal seam water appears to be highly amenable to treatment using electrocoagulation. For electrocoagulation to operate successfully the solution to be tested must have good conductivity. In many instances, researchers have added sodium chloride to test solutions whereas coal seam water already has sufficient salt content. In addition, the primary targets for removal from the CS water during the pre-treatment stage are alkaline earth ions (calcium, magnesium, strontium and barium), silica (both colloidal and reactive forms), algae, fluorine, boron and particulate matter. As can be seen from the studies cited below, most of these species have been shown to be amenable to removal using electrocoagulation.

Gao *et al*. [93] investigated the use of electrocoagulation to remove algae species from water and concluded that aluminium electrodes were considerably more efficient than steel (iron) electrodes. Algal removal was promoted by higher water temperature and enhanced current density. Zeboudji *et al*. [94] applied electrocoagulation to the treatment of a solution containing boric acid, and under optimum conditions boron was removed with an efficiency of 96 %. Xu *et al*. [95] confirmed the effectiveness of electrocoagulation for boron control in wastewater with 82 % removed in a single step and >99.9 % removed in a multi-stage process. Den and Huang [96] reported that silica nano-particles could be removed from a wastewater stream with efficiencies up to 95 % observed. In addition, sludge volumes were less, compared to chemical coagulation, and no pH adjustment was required. Den and Huang [97] also demonstrated the use of electrocoagulation as a pre-treatment stage for brackish water treated with a reverse osmosis unit. Application of EC was found to significantly stabilize performance of the system primarily due to prevention of silica scaling on the membrane surface.

Khatibikamal *et al*. [98] has shown that EC can be an effective process for the removal of fluoride in industrial wastewater. The optimal pH for fluoride removal was said to be 6 to 7 and the fluoride reduction was noted to be from 4 to 6 mg/L to less than 0.5 mg/L. Zhao *et al.* [99] further investigated the influence of common ions such as calcium and magnesium in solution upon the degree of fluoride removal using EC. Whereas calcium had little impact, magnesium was identified in significant concentration in the formed flocs and it was suggested that a layered double hydroxide (Mg-Al-F) may have been created.

Schulz *et al*. [100] studied the removal by EC of species responsible for scaling in process water including calcium, magnesium and silica. Another study conducted to analyze the removal of TSS and turbidity prior to reverse osmosis (RO) found 98 and 99% removal rates respectively [18]. EC can be used as a very effective pre-treatment for RO, reducing fouling and pressure changes in the membrane [18]. Recently our research group has applied electrocoagulation to the treatment of coal seam water sourced from the Surat Basin in Queensland [40, 101]. In general, electrocoagulation was demonstrated to be more effective than standard coagulation approaches at removing dissolved ions from the CS water. Aluminium electrodes were observed to reduce the concentrations of species such as alkaline earth ions and dissolved silica to a larger extent than mild steel electrodes. Depending upon the process conditions, removal rates for calcium, barium, magnesium and strontium ions from solution and dissolved silica could be >90 % [40]. In contrast to the aforementioned EC studies of boron and fluoride, the removal rates for these latter species from coal seam water was recorded to be relatively low. Factors such as elevated pH and the presence of competing ions in the CS water were cited as being responsible for the disparity in observations between simple solutions and actual coal seam water.

5. Membrane Technologies

Membrane technologies play a major role in the water treatment industry including processes such as, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [102]. Of the outlined membrane technologies, ultrafiltration has been the focus of use in the CSG industry for pre-treatment of water prior to the reverse osmosis stage.

5.1 Ultrafiltration

Ultrafiltration (UF) has been a widely used water treatment method in industry and has been utilized for the removal of particulate matter including viruses, colloids, bacteria, high molecular weight organic compounds and turbidity [53, 103]. Ultrafiltration operates with a pressure range of 0.1-5 bar excluding species with a size range of 0.002–0.1 µm [104]. The feed water is commonly fed in a cross-flow action to the UF membrane producing high superficial velocities [104]. The permeate is passed through and the concentrated solution is sent to a waste tank [20]. Essentially the larger particles are excluded by the UF membrane pore size [104]. UF membranes can be made from hydrophobic, intermediate and hydrophilic polymers [104]. Polymers such as cellulose acetate, polypropylene, polyethylene, polysulfone, polyethersulfone, polyvinylidene fluoride and polyacrylontrile are implemented depending on operating conditions [104]. The membranes used in UF normally have a width of (0.1- 1.0 µm) and are applied on a porous layer 50 – 250 µm in width [20]. There are three types of membranes modules used: tubular; capillary and spiral wound [20].

The application of feed water with UF produces permeates that are of high quality and physically disinfected [105]. However, fouling occurs on the membrane depending on the quality of the feed water [106]. Fouling can be mitigated through pre-treatment methods, periodic cleaning and operating parameters [107]. Periodic cleaning and membrane replacements inevitably increase operating expenditure and should be minimized [103]. Agricultural organic matter is known to be a primary source of membrane fouling along with other species such as silica [103]. Chemical coagulants consisting of Fe and Al salts ($Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ and $FeCl_3$) have been added to the feed water as a pre-treatment to UF [103]. Coagulation of this type is called “in-line” coagulation and is used to increase performance of the membrane and reduce membrane fouling [108]. Flux decline in UF is commonly associated with concentration polarization of solute at the surface of the membrane [109]. This simultaneously occurs with irreversible fouling and cake layer formation on the surface of the membrane [109]. Algae cells (commonly associated with bio-fouling) and extracellular organic matter (EOM) are constituents that can be removed by ultrafiltration however the algae cells and EOM deposited on the membrane have the ability to cause severe fouling of the UF membrane [110]. It should be noted that the effects of membrane properties such as, pore size and hydrophobicity have an effect on the degree of fouling caused by EOM [110]. Bio-fouling is also a problem in reverse osmosis membranes and consists of the buildup of micro-organisms and organic material at the surface of the membrane causing a biofilm that decreases RO performance [85]. Hence, in the water treatment industry the design of RO desalination plants incorporates a double barrier pre-treatment system of UF and MF [85].

6. Water Softening

6.1 Ion Exchange (IX) Softening

Ion exchange is widely used in the water treatment industry through the use of softening to eradicate scale forming components on membrane processes such as RO and UF [111]. The removal of scale forming compounds prior to reverse osmosis mitigates flux problems, increases recovery rates and ultimately decreases brine waste [112]. The major salts that produce scaling in membranes are: calcium carbonate ($CaCO_3$); magnesium carbonate ($MgCO_3$); magnesium hydroxide ($Mg(OH_2)$) and calcium sulphate ($CaSO_4$) [112]. The latter salts precipitate on RO/UF membranes, which inhibits the productivity of the membranes [113]. IX can be used as a pre-treatment method for RO to reduce the hardness properties of the water and to prevent scale forming [38, 112]. The specific objective of water softening is to reduce the levels of magnesium and calcium in the feed water [53]. Typical exchange processes for water hardness removal in IX with Na^+ resin [53] are shown below:

$$\mathrm{C}a^{2+} + 2\,\mathrm{N}a^{+}\mathrm{R} \leftrightarrow 2\,\mathrm{Na}^{+} + \mathrm{C}a^{2+}R_2$$
$$\mathrm{M}g^{2+} + 2\,\mathrm{N}a^{+}\mathrm{R} \leftrightarrow 2\,\mathrm{Na}^{+} + \mathrm{M}g^{2+}R_2$$

The sodium cations (Na^+) on the resin exchanges with Mg^{2+} and Ca^{2+} in solution, thereby reducing scale formation on the membrane and increasing recovery rates [112]. Cation exchange is an alternative to chemical softening and produces smaller volumes of sludge [114]. Apell and Boyer [114] found that RO feed water without pre-treatment gave water recoveries of >35%, however, with IX pre-treatment recovery rates improved to *ca*. 90%. Weak acid cation (WAC) resins are commonly used for softening of water prior to a reverse osmosis unit [115]. However, strong acid cation (SAC) [116] and chelating resins such as those with iminodiacetic acid functional groups [117] can also be employed. Ghergeles *et al*. [118] demonstrated that geothermal water which was brackish in character, similar to CS water, could be softened successfully using a strong acid cation resin.

6.2 Lime Softening

Lime softening is currently employed at the QGC 92 ML/day water treatment plant located at the Kenya operations site near Chinchilla [119]. Lime softening normally involves the application of lime-soda ash to reduce the hardness of the water [20], through the precipitation of magnesium and calcium [120]. Mohammadadesmaeili *et al*. [121] investigated the ability of various lime-soda softening methods with the aim of selectively recovering pure salts which had commercial value. Simple addition of lime-soda resulted in collection of calcium carbonate and magnesium hydroxide mixtures of minimal worth. Modification of the solution pH, however, was found to offer some advantages in terms of recovery of desirable products such as relatively high purity calcium sulphate which could be used for building products.

7. Chemical Addition

Dissolved organic compounds (DOC) and hardness cause fouling in membranes and are recommended to be removed prior to any demineralization process [114]. Thus, anti-scalants are often added to the water in the aim to prevent precipitation of salts [112]. Hater *et al*. [122] evaluated a wide range of potential anti-scalants and discovered that several demonstrated effectiveness in the pH range 7.6 to 9.0. Biofouling is a well-known and extensively studied phenomenon which occurs during reverse osmosis treatment of salt laden water [123, 124]. When biofouling is present, membrane flux and salt rejection effectiveness are normally diminished. Consequently, addition of chemicals such as chlorine and ozone have been used for disinfection purposes in order to minimize fouling potential [124]. Hijnen *et al*. [125] examined the efficacy of chemicals for membrane cleaning and concluded that a mixture of sodium hydroxide and sodium dodecyl sulphate was optimal among the chemical combinations studied.

8. Ion Exchange Desalination

8.1 Principles of Ion Exchange

Ion exchange is a well-established technology for water treatment, especially for applications such as demineralization of brackish water [115, 126]. Ion exchange (IX) comprises a reversible process that exchanges ions stoichiometrically between solution and active sites on, for example, a synthetic resin [20, 127, 128]. The end result comprises unwanted ions left on the resin bed and desirable ions passing through the column [53]. The water flows through the resin beads allowing ions in the water to exchange with ions attached to the resin.

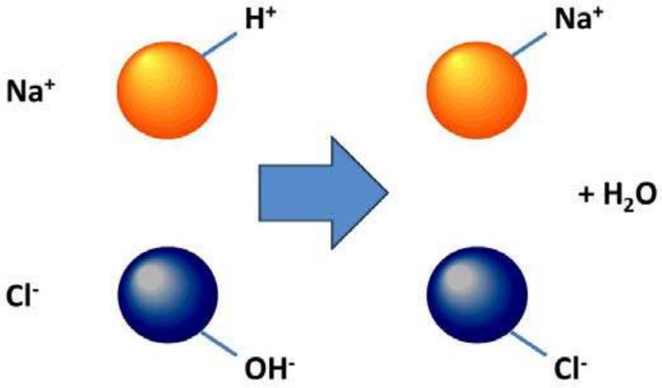


Figure 5: General representation of ion exchange desalination process

8.2 Functional Groups and Resins

Synthetic resins are the most popular material for commercial ion exchange processes due to their relatively low cost, ready availability, consistency and high level of technical support. The type of functional group attached to the resin determines its classification: strong acid cation (SAC); strong base anion (SBA); weak acid cation (WAC) and weak base anion (WBA). The functional groups present on a strong acid cation resin are normally sulphonic acid species ($SO_3^-H^+$) whereas on a weak acid cation resin carboxylic acid groups are typically present (CO_2H). As a general rule, the exchange capacity of strong acid cation resins (*ca*. 1.8 to 2 eq/L) is lower than weak acid cation resins (*ca*. 3.8 to 4.5 eq/L). However, strong acid cations have the advantage of operating at all pH ranges whereas for desalination processes weak acid cation resins perform best at alkaline solution pH values. Likewise, for weak base anion resins the functional group is typically a tertiary amine group with a capacity of approximately 1.3 eq/L. Strong base anion resins have quaternary amine functional groups and anion capacity of *ca*. 1.0 to 1.3 eq/L depending upon whether chloride or hydroxyl groups are present on the exchange sites.

Recent interest has extended to shallow shell technology (SST) resins supplied by Purolite [129]. The basis of the SST resins is that of a core-shell arrangement where the inner core of the resin has not been functionalized. One advantage of this latter resin architecture is that regeneration is potentially easier due to the shorter diffusion path lengths with the shallow shell concept and thus chemical consumption costs can be substantially reduced. Downey [129] also suggests that leakage rates (*i.e.* the concentration of ions in the treated effluent) from the resin bed are less compared with conventional resins, as well as reduced rinse volumes and increased running times. Of particular interest of the CSG industry is the claim that a shallow shell technology strong acid cation resin can be used as a water softening stage prior to reverse osmosis [130]. The key benefit is that the resin can be regenerated using RO reject brine instead of relatively expensive sodium hydroxide.

8.3 Ion Exchange (IX) Desalination

The most elementary process for almost complete desalination of coal seam water comprising mainly of sodium chloride and sodium bicarbonate, is the combination of a strong acid cation resin plus a weak base anion resin [Figure 6]. The strong acid cation resin would be expected to remove all major cations from solution and produce an effluent comprising of a mixture of strong and weak acids. As weak base anion resins operate optimally when the solution is acidic the removal of anions such as chloride, sulphate and phosphate is expected to occur [126]. One word of caution is that the passage of bicarbonate and carbonate ions through the acidic environment of the strong acid cation bed is expected to result in evolution of significant volumes of carbon dioxide. For safety reasons a degassing system is usually required between the two resin beds [115]. For CS water comprised mainly of sodium bicarbonate, use of only a strong acid cation resin was found to be satisfactory at removing not only cations such as sodium but also calcium while concomitantly destroying bicarbonate and carbonate species due to the low treated water pH produced [76]. Regeneration of the resin was achieved by use of hydrochloric or sulphuric acid solutions. Treated water quality was quoted to be pH between 7 and 7.5, less than 500 TDS and a sodium adsorption ratio less than 4.

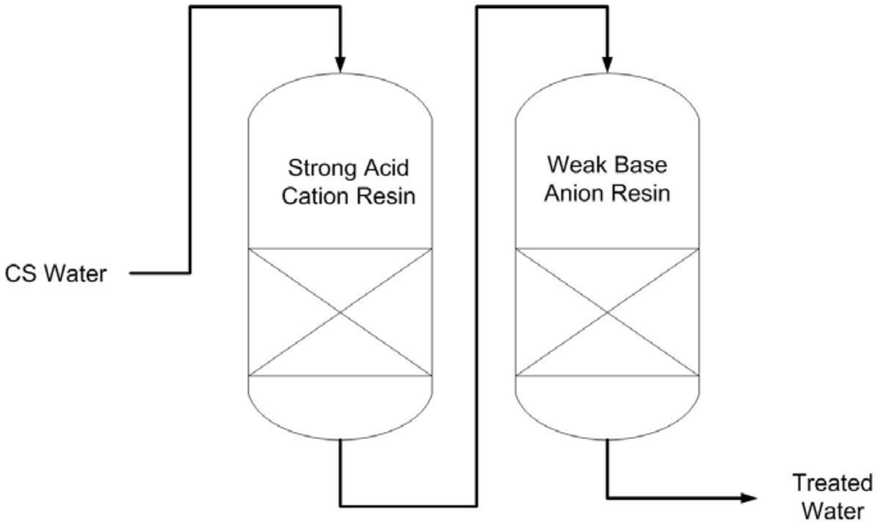


Figure 6: Strong Acid Cation and Weak Base Anion Resin configuration for Demineralization of Coal seam water

An alternate resin bed configuration is shown in Figure 7, wherein a weak acid cation resin bed is installed before the strong acid cation/weak base anion resin combination. The question arises as to the benefit of adding a weak acid cation resin to the treatment train as it inherently involves greater capital expenditure. It has known that weak acid cation resins do not demineralize solutions of sodium chloride due to competition from protons in solution. However, the alkaline sodium bicarbonate species which are a significant fraction of the salt content in Australian coal seam water are expected to interact with the weak acid cation resin surface [115].

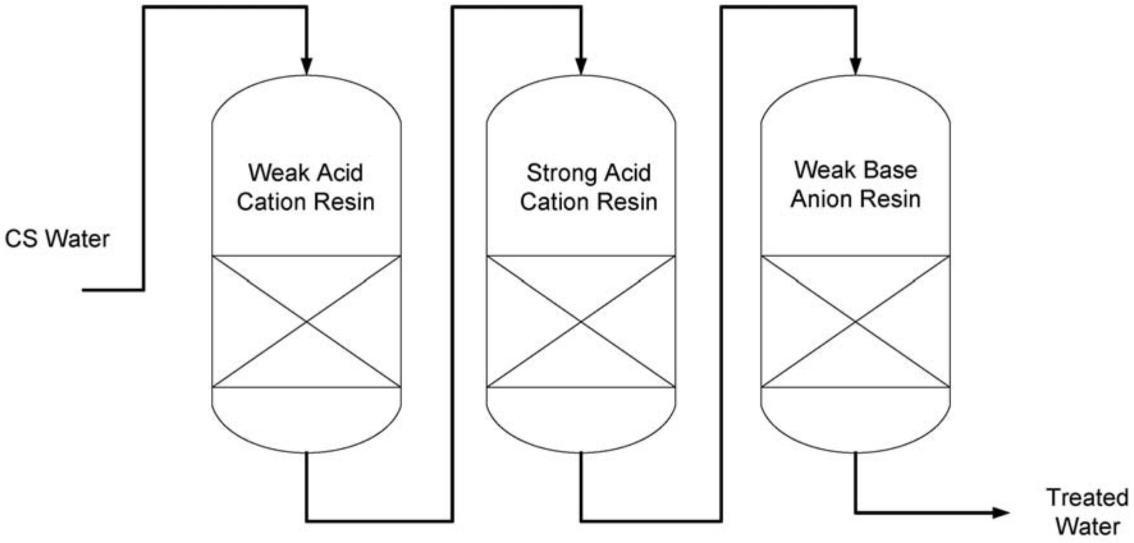


Figure 7: Weak Acid Cation, Strong Acid Cation and Weak Base Anion Resin configuration for Demineralization of Coal seam water

The process of IX can consist of two flow types: (1) In co-current flow the loading phase and the regeneration phase flow through the column in the same direction as each other [131]; (2) In counter-current flow the loading phase and the regeneration phase flow through the column in the opposite directions as each other [131].

8.4 Regeneration

Ion exchange resins have finite exchange capacity, hence once they are exhausted a specified regeneration solution is applied to regain full exchange capacity once again [53]. The amount of regenerate used and the resin replacement does depend on the concentration of undesirable ions in the feed water [132]. The regeneration of IX columns is a costly process and the source of the brine waste stream [132]. The exhausted resin is generally regenerated with acid or base [133]. The regeneration process encompasses the steps of backwashing to remove suspended solids and to repack the resin bed, regeneration of the exchange sites and finally rinsing [53]. Typically the rinse water is fed to the regenerant system to minimize water consumption in the process and to recover valuable regenerant chemicals.

Regeneration of the cation resin beds requires the use of either hydrochloric acid or sulphuric acid solutions. According to the resin manufacturer guidelines 5 wt% solutions are recommended. For the CSG industry, sulphuric acid is the most desirable chemical to handle as it is relatively cheap and more readily available in the remote areas where the gas fields are. However, use of concentrated sulphuric acid solutions to regenerate columns loaded with alkaline earth ions such as calcium can cause problems with precipitation of calcium sulphate.

Two possible regeneration strategies to explore are represented in Figure 8 and Figure 9. Figure 8 aims to minimize costs and reduce the scaling potential by regenerating the strong acid cation resin bed with sulphuric acid and the weak acid cation resin bed with hydrochloric acid. This latter strategy also has the benefit that in terms of brine management, two streams are produced which provides options for better handling and downstream application. One of which is relatively “clean” of alkaline earth species and the other “contaminated” with calcium, magnesium, barium and strontium. Alternatively, Figure 9 proposes the use of sulphuric acid in both resin beds with the more concentrated acid present in the strong acid resin bed and a significantly more dilute acid solution presented to the weak acid cation resin bed. Which is the optimum strategy needs to be decided by further research.

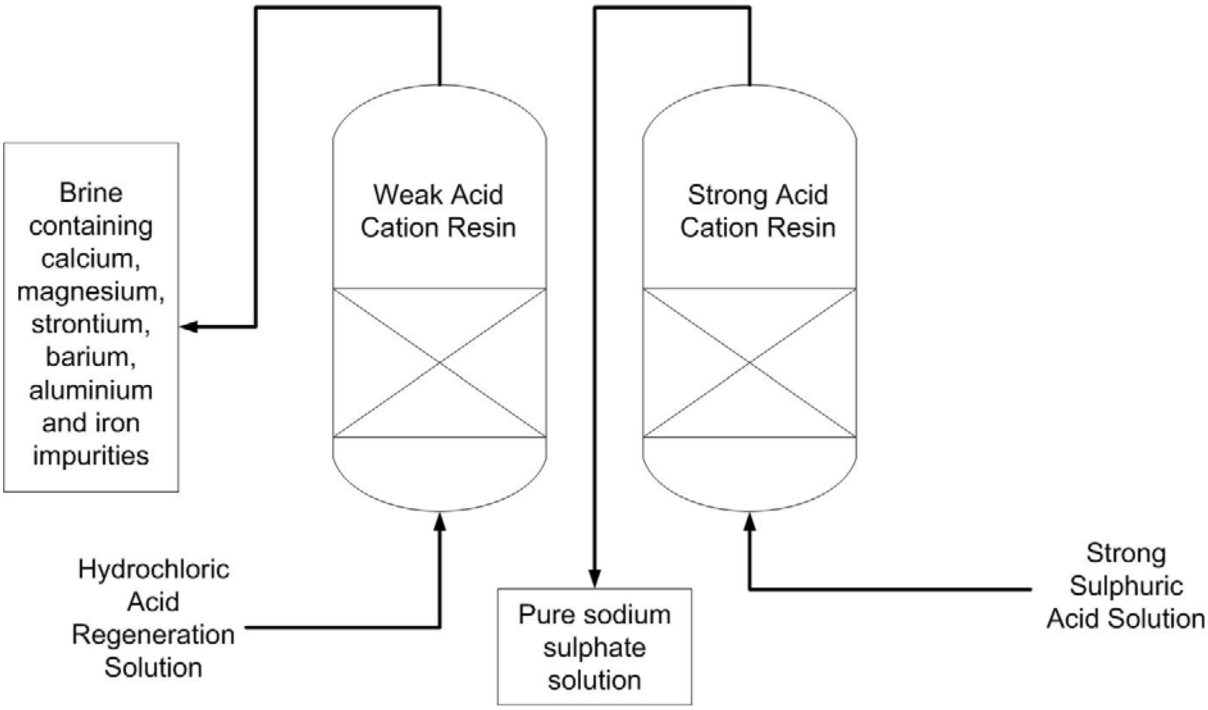


Figure 8: Regeneration Strategy for Production of "Clean" and "Contaminated" Brines

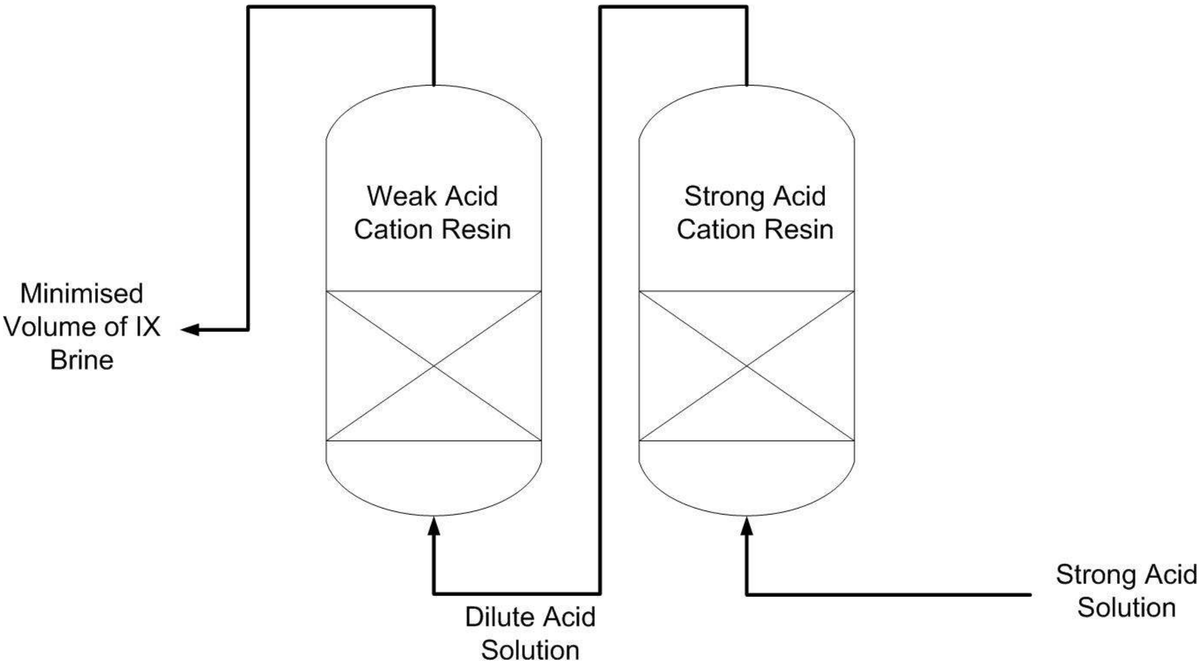


Figure 9: Regeneration Strategy for Minimizing Brine Volume

8.5 Fluoride removal

Fluoride removal using anion exchange resins appears problematic due to the order of selectivity of the ions: $Cl^- >> F^-$ [134] and the relative concentration of fluoride and chloride in CS water. Considering that chloride ions in CS water are typically present at concentrations of 500 to 2000 mg/L and fluoride ions are present mainly in the range 1 to 8 mg/L then there is minimal opportunity for fluoride ions to be retained. The option of adding an additional column to the treatment process is therefore a potential necessity if the fluoride ion concentration in the coal seam water is in danger of exceeding discharge limits. Commercially, the most commonly applied method for fluoride control in water involves the use of activated alumina [43, 135]. Alternatively, chelating type resins selective for fluoride uptake could also be implemented [134].

8.6 Boron Removal

Boron removal is problematic during reverse osmosis treatment due to the fact that it is uncharged and difficult for the membranes to reject [136]. Consequently, boron species are typically found in both permeate and brine streams. As the regulations for boron discharge to surface waters are strict (less than 0.5 mg/L) the presence of boron in permeate may prevent disposal [137]. To solve this issue, ion exchange technology has been developed and is potentially the most viable means for elimination of boron [138, 139]. Commercial resin vendors offer boron specific resins consisting of a macroporous polystyrene backbone functionalized with N-methyl glucamine [140]. These resins form a stable complex with boric acid and do not remove other ions such as sodium, potassium, chloride and sulphate due to its strong selectivity [140, 141].

8.7 Zeolites as Ion Exchange Materials

Ion exchange resins are not the only ion exchangers available [142]. Zeolites, whether natural or synthetic, are comprised of 3-dimensional alumino-silicate structures and can be used as absorbents, catalysts, ion exchangers and molecular sieves. Natural zeolites such as clinoptilolite are the most widely studied materials due to their abundance and relatively low cost [4]. Its cage like structure consists of AlO_4 and SiO_4 tetrahedra that contain exchangeable ions which are available for replacement by other ions in the water that are more attracted to the negative zeolite structure [4].

With regards to literature studies of coal seam water treatment using zeolites the Vance group has been the most active in this area. For example, Zhao *et al.* [143] investigated the performance of three calcium rich natural zeolites from the USA, and found the equilibrium loading capacity for the zeolites ranged from 9.6 to 12.3 g Na per kg zeolite. Column studies with synthetic coal seam water solutions suggested that the zeolites could reduce sodium concentrations to acceptable levels for reuse [143, 144]. Extension of column trials to actual coal seam water collected from ponds in the Powder River Basin confirmed the effectiveness of the natural zeolite materials [145]. Despite these positive outcomes, Huang and Natrajan [146] concluded from an economic perspective that natural zeolites could not compete with other options such as deep well injection or land amendment. In addition, natural zeolites exhibit several properties which make them less amenable to practical applications in the CSG industry compared with synthetic resins. First of all, natural zeolites are not homogeneous or indeed the same material when comparing different deposits worldwide. Hence, material consistency and repeatability is of concern. Second, natural zeolites exhibit lower cation exchange capacity compared to resins which means that larger columns would be required and increased storage capacity for materials on site. Third, the acidic nature of cation resins promotes the decomposition of bicarbonate species which reduces solution TDS and conductivity. In contrast, natural zeolites typically have a pH between 6 and 7 which is not normally sufficiently acidic to decompose bicarbonate species to produce carbon dioxide. The exchange kinetics for resins suggests only minutes to attain equilibrium conditions whereas with natural zeolites a day or more is required to saturate the zeolite surface sites due to diffusion limitations [143]. Consequently, during column operation full usage of the zeolite exchange sites is improbable. Recent work by Wang *et al*. [4] has addressed some of the above concerns by pre-treating natural zeolite to remove the calcium ions from the exchange sites. By this latter procedure the exchange capacity was found to exhibit a three-fold increase in cation exchange capacity. Further work is required to understand if this approach makes zeolites more attractive for implementation in the CSG industry.

9. Reverse Osmosis

Reverse Osmosis (RO) has expanded substantially in recent years as water shortages for drinking water are more widespread, and thus the need to recycle and reuse water has increased for an increasing population growth has accelerated [147]. This paper will only provide a basic overview of RO technology and focus more upon the issues which are relevant to the coal seam gas industry. The reader is referred to numerous excellent articles concerning reverse osmosis theory and operation for more in depth analysis [147-150]. The advantages of RO water treatment include small footprint, high recovery rates, wide range of contaminant exclusion, excellent water quality and modularity [138]. Some disadvantages of RO include high power cost, maintenance expense and the need for routine membrane replacement [138].

9.1 Principles of Reverse Osmosis

Reverse osmosis is a common tertiary water treatment method utilizing membrane technology [150]. Reverse osmosis (RO) technology is commonly used for sea water and brackish water desalination offering advantages such as high salt rejection efficiency and recovery rates [151]. Essentially reverse osmosis overcomes osmotic pressure to drive the water through a semi-permeable membrane where the contaminants are rejected [152]. The semi-permeable membrane separates the feed water into two streams: permeate (purified water) and brine (rejected salts and remaining compounds) [150]. The brine quality and composition is dependent upon the quality of the feed water and the various chemical pre-treatments implemented [150]. Reverse osmosis plant performance is typically characterized in terms of "% water recovery" which refers to the ratio of water fed to the process and water recovered in the permeate stream. As can be seen from Figure 10 as the degree of water recovery increases the concentration of the salts in the brine solution is concomitantly intensified.

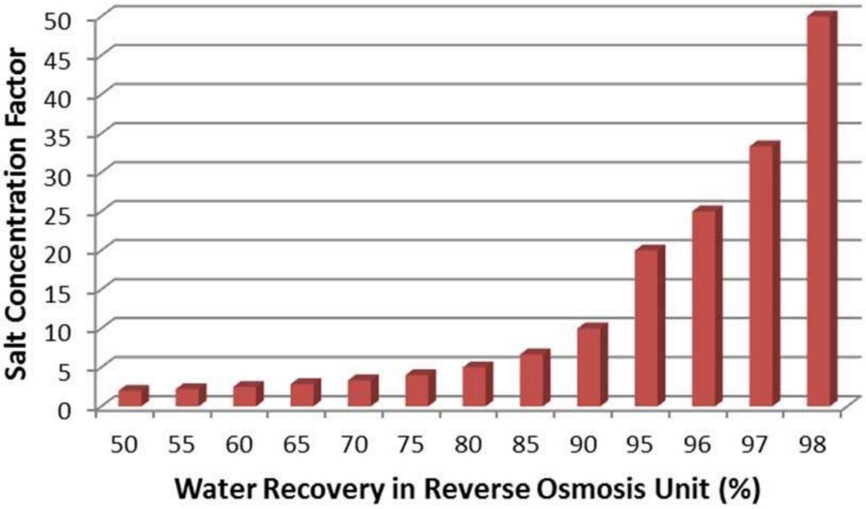


Figure 10: Relationship between Degree of Water Recovery during Reverse Osmosis Plant Operation and Concentration of the Brine Produced

The % water recovery in an RO unit depends upon many factors such as feed composition & temperature, pre-treatment technologies applied to protect the membranes, feed pressure, membrane type, RO plant configuration and limitations imposed by brine disposal options [149].

9.2 Membrane types and Configuration in RO Relevant to CS Water Treatment

There are two common types of membrane material used in RO operation: cellulose tri-acetate (CTA) – chlorine tolerant and TFC/TFM – non-chlorine tolerant. Cross flow filtration is the most common membrane configuration in RO operation [149]. Spiral wound membranes dominate the RO market due to the fact that they have a high surface area, are easy to replace and produced by many manufacturers in the water treatment industry [153]. Spiral wound membranes essentially consist of membrane sheets wrapped around a collecting permeate tube. The membrane sheet resembles an envelope and is glued at three edges with a cloth filling the permeate channel [154]. One side of the membrane envelope is fixed onto the perforated inner permeate tube [154]. A spacer is placed between the sheets to keep them from touching [155]. Spiral wound membranes are placed in series (typically 4-8 modules) forming an element that is enclosed in a pressure vessel [155]. The permeate and brine leave from the end of the pressure vessel with the precise ratio depending upon initial water composition and pressure employed [151]. The number of elements per pressure vessel and the arrangement of the RO system is dependent on the recovery rate required [156].

9.3 One and Two Stage Reverse Osmosis

Reverse osmosis normally is operated as a 1 [Figure 11] or 2-stage system [Figure 12].

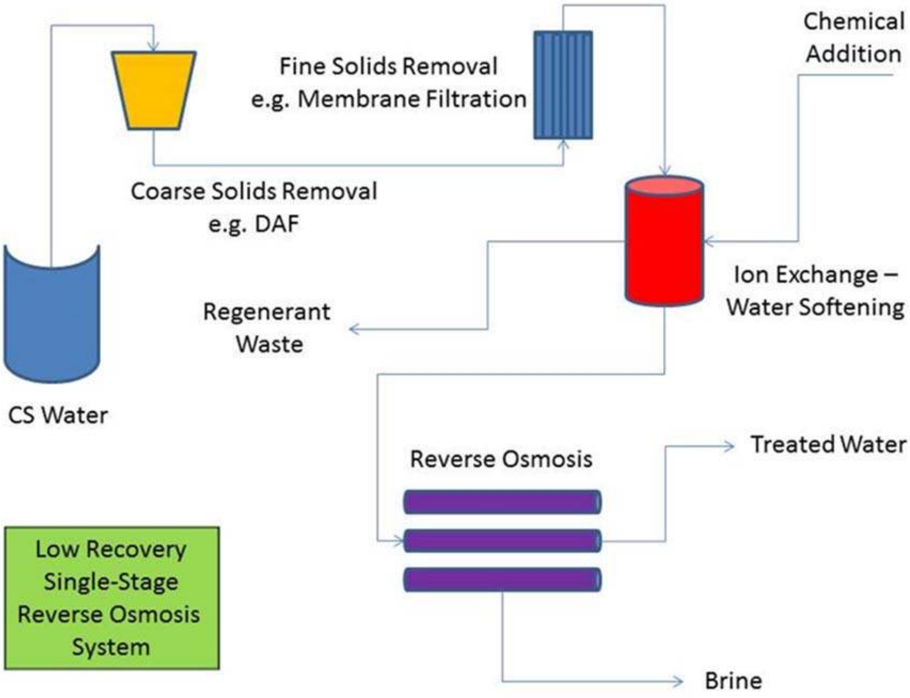


Figure 11: General Process for a Single-Stage RO Treatment Unit

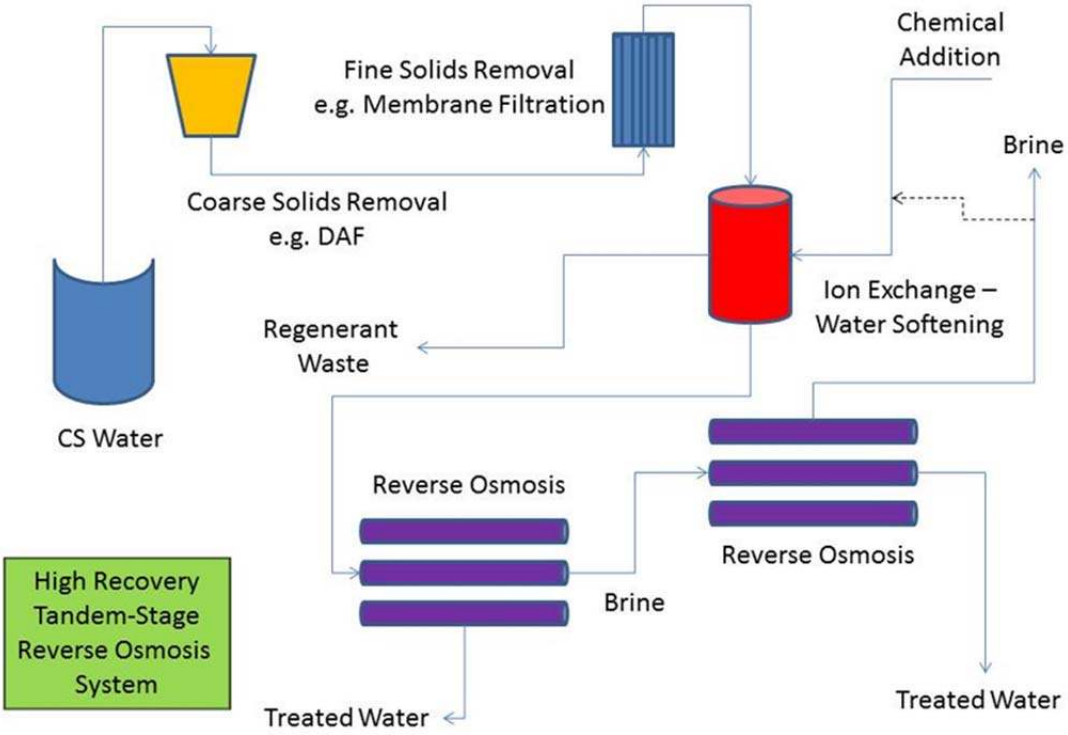


Figure 12: General Process for a Tandem-Stage RO Treatment Unit

For the treatment of brackish water such as coal seam water, the feed to the second stage is the brine reject from the first stage. This configuration is different from seawater RO (SWRO) units wherein the second stage feed is typically the permeate from the first stage [149].

9.4 High Recovery Reverse Osmosis (Zero Liquid Discharge)

Zero-liquid discharge (ZLD) is a new innovative approach that aims to provide the highest water recovery and the lowest disposable waste volume through multistage processes [150]. The aim to increase water recovery rates in RO plants is a substantial factor with regards to minimization of operational expenditure by decreasing brine production and hence disposal costs [113]. ZLD strategies include the use of processes such as crystallizers, brine concentrators, spray driers, thermal evaporators, electrodialysis (ED) and electrodialysis reversal (EDR) [149]. The downside to ZLD technology is the need for increased capital expenditure in addition to the central desalination unit [149].

9.5 Reverse Osmosis in the Coal Seam Gas Industry

Reverse osmosis has been implemented in both the USA [157] and Australia [77]. Welch describes the evolution of reverse osmosis plant design for the Powder River Basin in Wyoming [157]. The initial RO system design used acid injection to control scale formation whereas the second unit located at Mitchell Draw eliminated acid use by the application of a resin softener stage prior to the RO membranes. The higher solution pH in the second process design was stated to have the advantages of increasing the solubility of silica and dissolved organic components while facilitating boron rejection by driving equilibrium towards borate and not boric acid species. Silica in the feed, in particular, was highlighted as a cause of decreasing water conversion in the reverse osmosis plant with even the addition of anti-scalants said to be unable to control this detrimental effect when the silica levels were too high. Kimball [158] has described strategies for reverse osmosis plant operation at high recovery rates for coal seam bed methane water treatment from the Powder River Basin in the USA. The author highlighted the following challenges to achieving economically viable and stable reverse osmosis plant performance: (1) the need for improved filtration strategies to deal with coal fines and clay particulates in the produced water; (2) the requirement to control scaling due to barium sulphate and calcium carbonate;

(3) the detrimental impact of adding acid to bicarbonate laden produced water to inhibit calcium scaling and (4) the process limitations due to silica content in relation to precipitation and fouling of RO membranes.

Queensland Gas Corporation [159] has recently announced the operation of their major reverse osmosis treatment facility for the Kenya gas field west of Brisbane. The plant is designed to treat 92 ML per day of water and consists of ultrafiltration, ion exchange softening, reverse osmosis and brine concentration technologies. Santos GLNG are also operating reverse osmosis facilities for desalination of coal seam water at Pony Hills in Queensland [160]. The treated water is used as part of a large irrigation project with the aim of increasing crop yields [161]. Similarly, Arrow Energy have opened various reverse osmosis facilities including a small 2 ML/day at Moranbah which includes application of chemical dosing, ultrafiltration, reverse osmosis and activated carbon [162].

Le *et al*. [163] described the use of a mobile reverse osmosis treatment unit to treat various coal seam water storage dams in the Roma region of Queensland. The RO plant was designed to treat at least 1.5 ML of CS water per day with a minimum water recovery of 65 % at 8000 µS/cm. Pretreatment options included acidification, chloramination, microfiltration and anti-scalant doing. Notably, hydrochloric acid was chosen over the cheaper sulphuric acid for pH adjustment of the water, as it did not significantly increase the scaling potential of the system. In addition, chloramine was chosen as it was shown to be a more effective solution to the bio-fouling problem compared to non-oxidizing biocides.

Chalmers *et al*. [12] elegantly outlined the development of an integrated membrane treatment system for coal seam water produced at the Origin Energy Spring Gully site in Queensland. Initial pilot plant studies focused on the pre-treatment configuration to protect the sensitive reverse osmosis spiral wound membranes. Emphasis was placed upon the removal of fine particulate material, hence a micro-filtration unit supplied by Pall Membranes was evaluated. It was found that the micro-filters required regular air scrubbing and a reverse flush step. The final reverse osmosis plant design had an initial capacity of 9 ML/day but this has since been expanded to 12 ML/day with an option available to further increase to 15 ML/day.

9.6 Problems with RO Operation

Reverse Osmosis like many other technologies for water treatment has to face many operational challenges. Fouling of the membranes is unfortunately all too common and can occur *via* several routes including fouling with organic species (bio-fouling, dissolved organic carbon), blockage with colloidal and particulate matter, scaling caused by sparingly soluble salts and silica precipitation [164]. Reverse Osmosis although highly effective at rejecting most species in solution also has problems with certain elements such as boron.

9.6.1 Bio-Fouling

The membranes that separate the salt and the water in RO are sensitive and prone to biofouling [165]. The microorganisms in the feed water form rigid structures and form a matrix layer on the membrane surface known as a biofilm [166]. Membrane life is reduced as a cause of biofouling thus creating a need for continual membrane chemical cleaning [167]. Biofouling affects the membrane in RO causing decreased permeability, more power consumption and lower rejection rates of contaminants, therefore it is an integral aspect for performance and efficiency [165, 166]. The continual and scheduled chemical cleaning strategies to counteract biofouling can also reduce membrane life and efficiency [167].

There has been membrane modifications implemented to counteract fouling, the most common materials used are oligo (ethylene glycol) or poly (ethylene glycol) PEG [165]. Recent experiments are using adsorption of $Cu(OH)_2$ on the membrane as an anti-biofouling remedy by improving anti-bacterial and anti-adhesion of the membrane [166]. Another study is using semi-permeable polyamide thin-film membranes that have surface nano-structured (SNS) hydrophilic polymer chains [167]. Nano structuring of the membranes has been found to inhibit fouling and is an effective way to customize the top layer of the membrane [167]. Flux decline vs time is the most common way of measuring fouling but by the time this is evident there is already too much damage on the membrane and the full potential of the membrane cannot be restored [164]. Particulate and colloidal particles that are not efficiently removed by pre-treatment cause cake formation on the membrane, thus reducing permeability of the membrane and reducing flux [164].

9.6.2 Scaling by Sparingly Soluble Salts

Scaling is a major problem to RO operation and involves the precipitation and scaling of inorganic compounds [168]. Once super-saturation occurs and the solubility is exceeded the compounds precipitate on the RO membrane. Researchers have found that the inorganic scaling on RO membranes is favored to enhanced concentration polarization within the biofilm layer caused by biofouling [167]. In the water treatment industry the aim of RO is to increase the water recovery, in turn this increases the level of inorganic scaling [169]. Scaling in RO decreases permeate flux through the membrane and damages the semi-membrane by irreversible plugging [169]. The prediction of scale at the design phase and throughout the operation via continuous monitoring is an important tool for RO processes [170]. Concentration of ions in the RO concentrate is a measurement of scale potential [170].

The following variables affect scaling of the RO membrane: concentration of ions; pH; fluid velocity; operating temperature and time [170]. With the intent to reduce scaling problems on the membrane, treatments such as water softening, anti-scalant addition and membrane treatments are employed [151]. The feed water fed to the RO membrane can sometimes be treated using acid to convert the carbonate and bicarbonate (originating from $CaCO_3$) species to carbon dioxide [169]. Nanofiltration (NF) was also used for the softening of the feed water to RO to prevent RO membrane scaling but the NF membranes also exhibit scale [169]. IX softening is another pre-treatment used to prevent scaling in RO membranes as discussed previously [114]. Anti-scalants in RO usually consist of a polyelectrolyte compound containing polyphosphates, polyphosphonates, dendrimeric polymers and poly-acrylates [171]. Anti-scalants play an important role in avoiding scale formation on the membrane reducing downtime for membrane cleaning, operational cost, the use of hazardous acids and recovery rates, however research has shown that anti-scalants induce microbial growth resulting in biofouling of the membrane [171].

9.6.3 Silica Precipitation

Silica scaling on the membrane is another aspect that causes problems to RO operations depending on the concentration that is in the feed water [122]. Kimball [158] postulated that silica precipitation could also be controlled by strict removal of species causing water hardness and multiple-charged ions such as iron and aluminium, as these can co-precipitate with silica. In addition, the author also advocated the removal of particulate matter in the feed as these materials can act as nucleation sites for silica precipitation. By following the latter criteria, Kimball was of the opinion that silica could be kept in a supersaturated or meta-stable state to avoid complications during the reverse osmosis process.

Badruzzaman *et al.* [172] reported pilot plant studies of reverse osmosis treatment of brackish water and emphasized the importance of understanding silica fouling mechanisms which occurred on the spiral wound membranes. Hater *et al*. [173] noted that the presence of calcium and magnesium ions in solution along with silica, resulted in preferred growth of species such as filterable silica. Milne *et al*. [49] stated that three general strategies could be adopted to minimize silica fouling of reverse osmosis membranes during desalination of brackish water: (1) operation at low pH, albeit this can be costly as CS water inherently has high alkalinity [40]; (2) use of high pH following an ion exchange (IX) water softening stage, which may or may not be viable depending upon the chemical costs involved for the IX stage; and, (3) removal of the silica by means of methods such as adsorption using alumina [174], ion exchange with resins [175] and coagulation [176]. Subramani *et al*. [177] described the use of a vibratory shear enhanced process (VSEP) to control silica fouling when a brackish water sample was treated by reverse osmosis. Although colloidal silica fouling of the membrane was limited, it was noted that barium sulphate fouling of the reverse osmosis membranes was not inhibited. The selection of anti-scalants and dosages also plays a role in minimizing silica scaling [122].

9.6.4 Boron

Boron in water is naturally in the form of $B(OH)_3$ and $B(OH)_4^-$ for low concentration solutions of boron, such as those anticipated for coal seam water [178]. Boron rejection rates using brackish water RO membranes is typically in the range 65 to 80 % [149]. The precise rejection rate of boron depends upon several factors such as the pH of the water, boron concentration and membrane type [179]. Farhat *et al*. [180] studied 10 RO membranes, 5 SWRO and 5 BWRO, in regards to boron removal from seawater. It was found that increasing water salinity and temperature decreased boron rejection, whereas higher cross flow velocities and pressures increased the degree of boron removal. Modelling of boron removal by reverse osmosis has recently been presented by Choi and Kim [181] and equations relating to pH and desired target boron concentration in the treated water were provided. Kezia *et al*. [182] found that permeation of boron through reverse osmosis membranes requires consideration of convective flow, not just solution diffusion models. For more in depth appraisal of boron rejection by reverse osmosis, the reader is referred to the excellent review paper by Tu *et al*. [183].

10. Capacitive Deionization (CDI)

Capacitive deionization (CDI) represents a potential alternative means for desalination of brackish water [184, 185]. CDI is essentially a two–stage process wherein the first step involves capture of the ions from solution into porous carbon electrodes by application of an electric potential and the second step releases the ions in a more concentrated solution. Recent advances in the technology have included incorporation of ion exchange membranes in front of both electrode surfaces and this methodology is termed “Membrane Capacitive Deionization” (MCDI) [186-188]. The fundamental processes for CDI and MCDI are shown in Figure 13. According to Długołęcki and van der Wal [189] the cost of desalination when using MCDI can be significantly cheaper than reverse osmosis by application of energy recovery techniques during the regeneration step. Indeed, these authors suggested that the energy usage could be reduced to *ca*. 25 % of the value required for a comparable reverse osmosis process. However, there still appear to be several technical challenges to be overcome before CDI and MCDI become serious commercial options for the coal seam gas industry. For example, Mossad and Zou [190] reported a study of the impact of fouling and scaling during the capacitive deionization process. Of particular concern was the observation that if dissolved organic carbon was present to any significant extent then the electrode performance degraded. Cohen *et al*. [191] also emphasized issues with the stability of the positive electrodes during operation due to oxidation of the carbon.

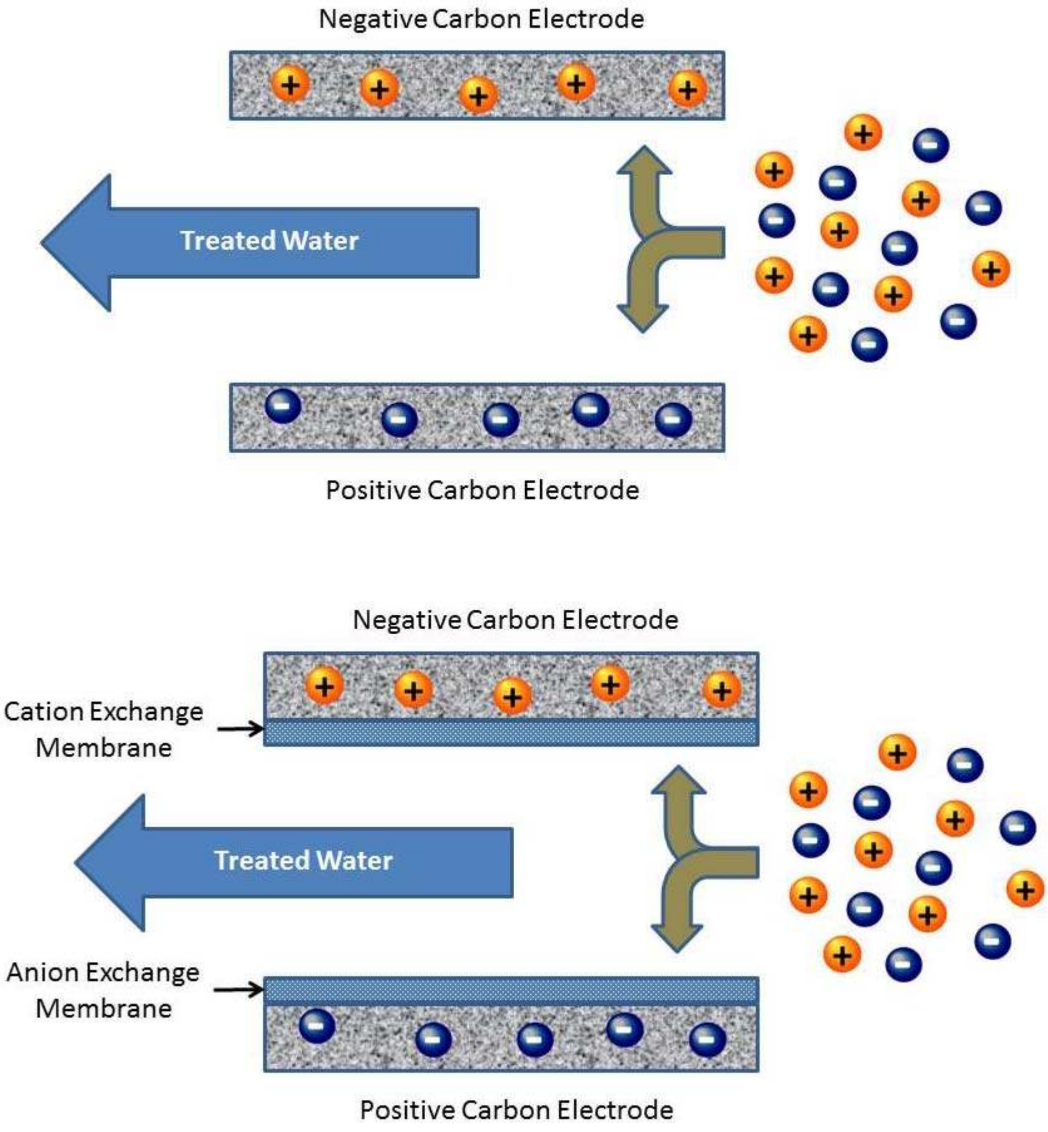


Figure 13: Illustration of Capacitive Deionization (top) and Membrane Capacitive Deionization (bottom)

11. Brine Management

A significant problem concerning the application of membrane technologies such as nanofiltration (NF) and reverse osmosis (RO) is the production of brine. Brine not only comprises of concentrated dissolved salts found in the feed water but also may contain various chemical additives which could be of environmental concern [192]. Research has shown brine and its components has caused severe effects to aquatic organisms when at elevated concentrations [150]. The treatment and disposal of brine is a major challenge for the CSG industry. The brine composition is variable and depends upon feed water quality, permeate quality (relates to recovery rates), pre-treatment methods and addition of chemicals. The aim for the CSG industry is to increase recovery rates in RO plants in order to minimize operational expenditure associated with brine disposal costs [113]. However, as recovery rates are increased the propensity for membrane fouling is usually increased.

In general, brine disposal costs depend on volume produced, quality, pre-treatment, location and method of disposal [150]. Customized systems have been made to recover the salts present in brine [193], and in theory these salts may be purified and used as commercial products [192]. Salt recovery from brine can potentially reduce the cost of the entire water treatment process by minimizing disposal and increasing the water recovery [193].

11.1 Brine Disposal methods

The simplest options for brine disposal have been proposed as: surface water discharge; deep well injection; evaporation ponds and ocean outflows [194].

11.1.1 Surface Water & Ocean Discharge

Surface water or ocean outfall disposal can be the least expensive disposal method but this option may be unavailable due to local regulations and land availability. For instance, Santos GLNG have evaluated the potential for direct discharge of brines to the ocean but the 500 km pipelines required made this option unfeasible [195]. Consideration of the option of filling road tankers with brine and disposing to the ocean was also investigated. However, due to the fact that 200 tankers would be required to be operating continuously each day and covering the 500 km distance, the process was found not to be economically or logistically viable [195]. Therefore, more expensive methods may have to be utilized such as the options outlined below [149]. The key factors to be determined when surface water disposal is applied are: the aquatic species tolerance to salinity levels in the area of disposal; metal and radioactive ion concentrations; compatibility of the brine characteristics with receiving water characteristics; temperature (thermal desalination process); nutrient concentration in brine that may trigger alterations in marine flora and fauna in the receiving waters, and effects of bottom fauna and marine flora in outfall discharge [196].

11.1.2 Reinjection

Deep well injection or Managed Aquifer Recharge (MAR) is a disposal method that comprises injection of the concentrate hundreds to thousands of meters underground below water aquifers, and is potentially the most economical process for inland CSG plants [149]. Deep well injection is a relatively new process and complications exist such as: soluble salt precipitation; damage to seismic activity; site determination; chemical treatment of concentrate; variance in well lifetime; and fresh water aquifer contamination [149]. Arrow Energy is investigating the potential for reinjection of CSG produced water which has either been amended or treated by their reverse osmosis facility [197]. The Precipice Sandstone area has been identified as a prospective site for their Surat Basin site because of the quality and size of the sandstone and comparatively low development of groundwater in this region. Santos GLNG presently operate two brine injection wells at the Timbury Hills Formation and are investigating the feasibility of more aquifer sites [195].

11.1.3 Storage Dams

Evaporation ponds are a relatively simple process to maintain and present minimal operational setbacks [193], albeit this latter approach may be an expensive disposal method [149].

11.2 Membrane Technologies

A range of brine management options have been advanced in recent years which include the use of membrane technologies [198]

11.2.1 Electrodialysis (ED), Electrodialysis Reversal (EDR) and Bipolar Membrane Electrodialysis (BMED):

Electrodialysis [Figure 14] is a cost effective technology that has been evaluated in the water treatment sector and of particular interest for the concentration of brine [199]. The selective movement of ions in the solution forms the basis for ED [200]. ED consists of a number of cells that consist of cation and anion exchange membranes located between cathode and anode electrodes [201]. The current used forces selective ions through the relevant membranes [200]. For example, Zhang *et al.* [202, 203] extensively studied both the technical and economic feasibility of concentrating RO brine from a wastewater treatment facility using electrodialysis. It was shown that the operational costs could be acceptably low if care was taken to decarbonize the solution in order to inhibit scale formation.

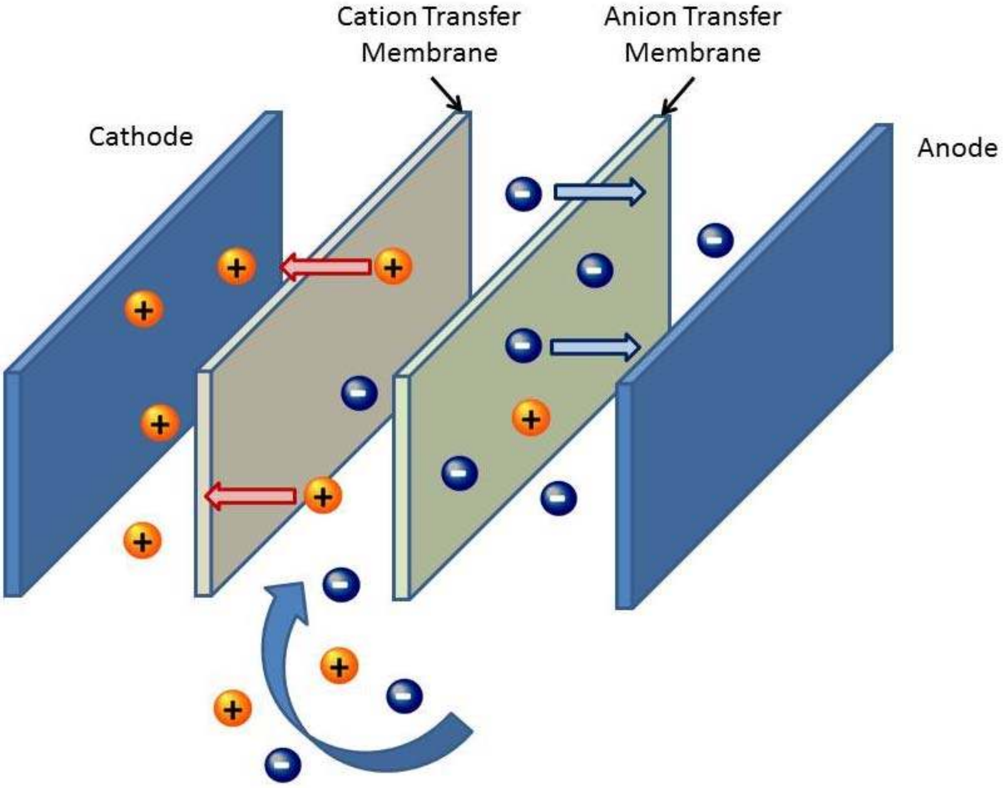


Figure 14: Representation of an Electrodialysis Process

Electrodialysis Reversal (EDR) works on essentially the same principals as ED except for the periodical automated reversal of the cell function and polarity [200]. Approximately every 15 minutes the polarity of the electrodes is reversed and the flows are concomitantly interchanged so that the brine channel now becomes the dilute channel. In theory this latter strategy should minimize scale formation and fouling of the electrodialysis unit [204]. A detailed review of the literature regarding electrodialysis reversal allowed Myint *et al.* [204] to design a system specifically for the treatment of brackish water sources. This unit consisted of four hydraulic stages and four pairs of electrodes and various membranes which were selective to different ions. Overall, the latter design was claimed to be more efficient than other EDR systems and of greater resistance to scaling problems.

Bipolar membrane electrodialysis (BMED) is based on ED using an applied potential with the ionic mobilities of the ions separated using ion selective membranes with a bipolar membrane [205]. The bipolar membrane separates hydroxide and hydrogen ions in the water [205]. Acid and base are produced from BMED by using a membrane electrochemical process by separating the salt [200]. RO brine has a proportion of Na^+ and Cl^- ions that can be used to produce NaOH and HCl respectively, and then concentrate can be passed through the RO again to minimize the brine concentrate further [200].

11.2.2 Forward Osmosis

Forward Osmosis (FO) has gained a resurgence in popularity in recent years with many studies devoted to this research topic [206-208]. The basic premise of forward osmosis operation is the use of a high osmotic pressure draw solutions to desalinate the water of interest [209]. Membrane selection for forward osmosis processes has been shown to be important. For example, Tang and Ng [210] investigated the characteristics of commercial FO membrane material as well as cellulose acetate and polyamide layers from reverse osmosis membranes. Due at least in part to the high hydrophilicity of the cellulose acetate material, it out-performed the FO membrane sample. Martinetti *et al*. [211] evaluated both forward osmosis and membrane distillation for the treatment of brines from a reverse osmosis unit. For brines of relatively low total dissolved solids (TDS) concentration and a high propensity for membrane scaling, forward osmosis performed better than membrane distillation. In contrast, for higher TDS solutions with a lower scaling potential, membrane distillation was superior. Regardless of the technique used to manage the RO brine, membrane fouling was observed. Strategies to enhance membrane performance included cleaning, which proved to be efficient, and also the addition of scale inhibitors.

McGinnis *et al*. [212] reported the application of forward osmosis using an NH_3/CO_2 draw solution to concentrate flow back water with *ca.* 73,000 mg/L total dissolved solids content. With appropriate pre-treatment of the water prior to the FO stage, water recovery rates up to *ca*. 64 % were achieved along with the creation of concentrated brines containing *ca*. 180,000 total dissolved solids. As discussed by Cath [213] forward osmosis can also be coupled to reverse osmosis units when desalinating brackish water samples such as coal seam water.

11.3 Thermal Technologies

11.3.1 Multi-Effect Distillation (MED)

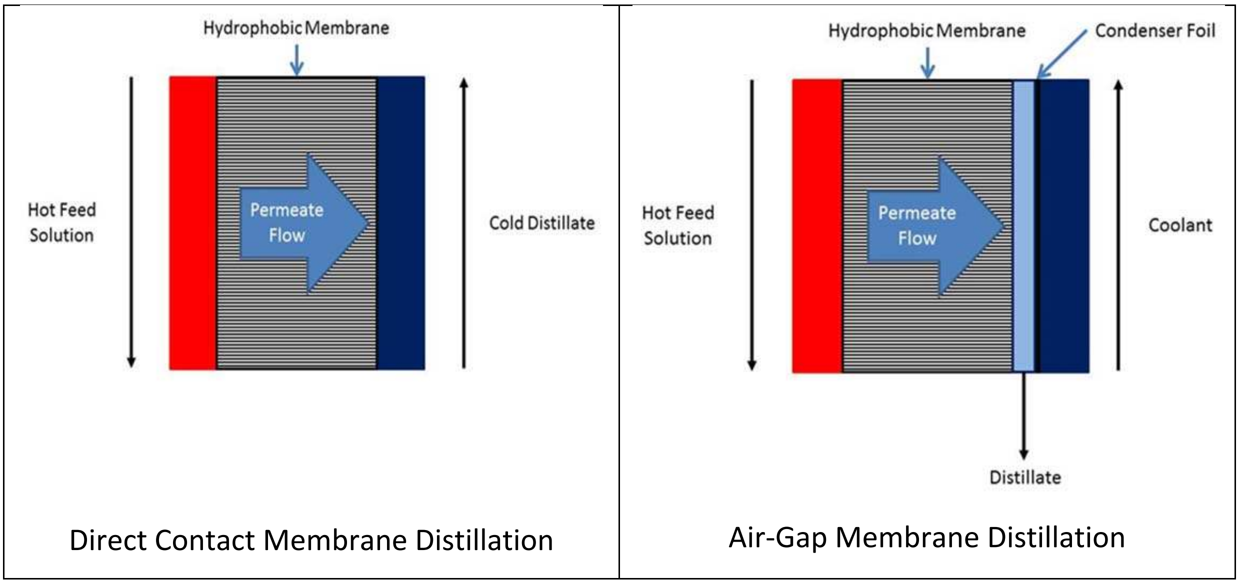
Multi-effect distillation (MED) units have been successfully used primarily in the Middle East for desalination of seawater [214, 215]. The fundamental basis of MED is to recycle the enthalpy of evaporation in successive effects, with many variants of MED in existence. Solar energy can be used as the heat source, with recent publications focusing on the integration of concentrated solar power plants with MED units [216]. Modern variants of the MED process have incorporated other processes such as adsorption desalination in an effort to increase energy efficiency [217, 218]. Rahimi *et al*. [219] have also described boosting MED by a multi-stage flashing process.

11.3.2 Multi-Stage Flash (MSF)

Multi-stage flash (MSF) thermal methods for desalination have been greatly used in areas such as the Middle East for seawater desalination units [220]. MSF involves the evaporation and condensation of water and is usually coupled to power generation facilities in order to source low grade heat [220]. Of primary concern is the need to reduce operational costs as discussed by Alhazmy [221]. Ren [222] evaluated the potential for multi-stage flash desalination of coal seam water in Australia, not only on its own but also in combination with membrane desalination methods such as reverse osmosis. The combination of MSF-RO has received attention as described by authors such as Wu *et al*. [223] and Marcovecchio *et al*. [224].

11.3.3 Membrane Distillation (MD)

Membrane distillation (MD) is a thermal driven desalination process that utilizes a hydrophobic membrane that establishes a physical barrier between the distillate side and the hot feed, where volatile compounds are evaporated [225, 226]. Membrane distillation (MD) can form high quality distillate from brine concentrates [227]. The process includes heating the aqueous feed solution and bringing it to the hydrophobic membrane. The pores of the hydrophobic membrane excludes the aqueous solution and allows vapor to pass and condense (distillate) [193]. The vapor diffuses through the membrane, accomplished by a vapor pressure difference across the hydrophobic membrane [225]. MD has the potential to recover both chemicals and water [228]. However, once the feed solution has a concentration comprising the maximum solute solubility the membrane can exhibit scaling and wetting reducing membrane flux [229]. There are several configurations available: DCMD - Direct contact membrane distillation; AGMD - Air gap membrane distillation; SGMD – Sweeping gas membrane distillation; and, VMD – Vacuum membrane distillation [228], two of which are illustrated in Figure 15.



Direct Contact Membrane Distillation

Air-Gap Membrane Distillation

Figure 15: Illustration of the Direct Contact and Air-Gap Membrane Distillation Processes

Alkhudhiri *et al*. [230] examined the use of air gap membrane distillation to treat highly saline water samples comprising of salts similar to those found in CSG brines. Water flux rates were found to decrease when the brine concentration was elevated and enhanced when membrane pore sizes were increased. Likewise, Singh and Sirkar [231] studied both concentrated brines and produced water by direct contact membrane distillation. Alkhudhiri *et al*. [232] applied air gap membrane distillation to produced water from the oil industry which was characterized by very high dissolved salt concentrations. Both feed temperature and flow rate promoted the flux rates over the membrane. With regards to process economics, if waste heat is available and carbon taxes applied, membrane distillation has been shown to be a viable option [233]. Pilot plant studies of membrane distillation using waste heat have similarly concluded the economic attractiveness of this method for desalination compared to conventional techniques such as reverse osmosis [234]. Integration of solar energy as the heat source is attractive [Figure 16], especially for smaller scale operations [235].

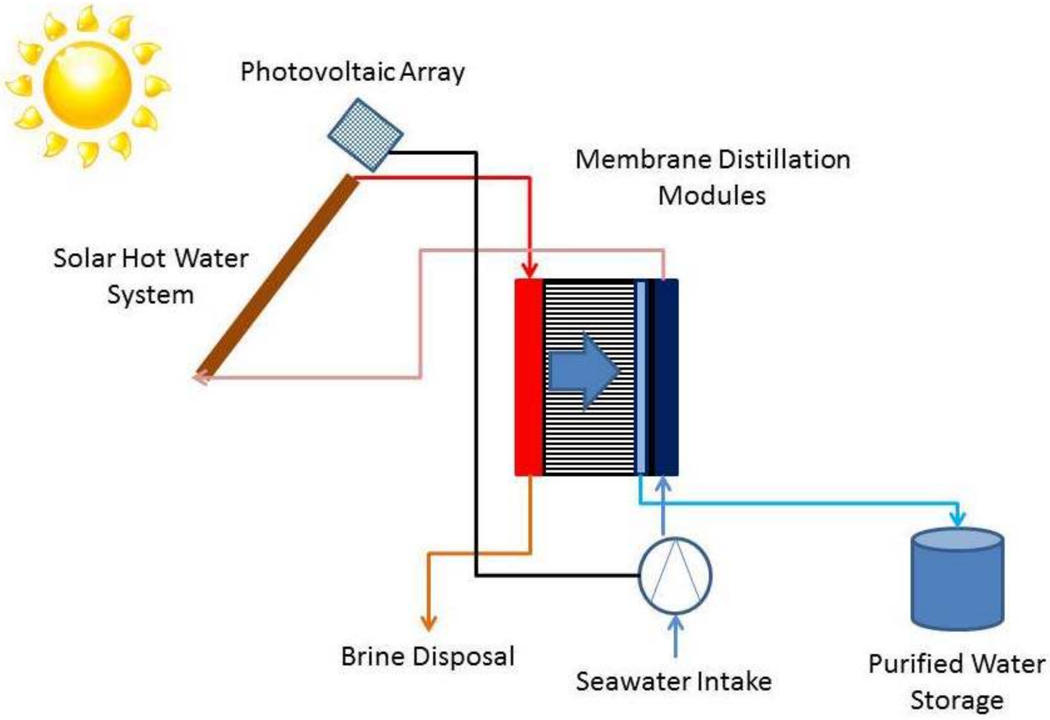


Figure 16: Schematic of Membrane Distillation Unit Operated by Queensland University of Technology for Solar Purification of Seawater and Brackish Water

Duong *et al*. [236] recently conducted pilot plant trials using air gap membrane distillation to treat brines from reverse osmosis treated coal seam water. High water recovery rates were obtained and performance was apparently stable over a reasonable time period. Concerns were expressed concerning the possibility that membrane fouling due to silica and calcium scaling may restrict efficiency during long term operation. Estimates suggested that 1 hectare of solar collectors was sufficient to supply enough heat to treat 118 kL per day of CSG brine.

11.3.4 Wind Aided Intensive Evaporation (WAIV)

Brine evaporation ponds although allowed according to regulations are problematic in that they require a large land area and thus can be a costly option for brine treatment. Gilron *et* *al*. [237] have advocated the use of vertically mounted evaporation surfaces comprised of preferably woven netting. Katzir *et al*. [238] used a bench-pilot scale WAIV system to evaluate the concentration of reverse osmosis brine. These authors confirmed that a substantial increase in evaporation rate for a WAIV unit compared to conventional pan evaporation. Techno-economic analysis suggested that brine removal costs using WAIV were only *ca*. 5.5 % of overall processing costs. When using RO brine, some precipitation of calcium sulphate was noted on the screens. Macedonio *et al*. [239] installed a WAIV system and then a membrane crystallizer unit in order to treat brine from a reverse osmosis plant. Economic analysis again confirmed the viability of WAIV technology with capital cost less than half that of evaporation ponds. When coupled with the membrane crystallizer the cost of salt recovery was further diminished. Such outlined benefits indicate that the application of WAIV technology for the CSG industry is worthy of consideration.

11.3.5 Membrane Crystallization

Membrane crystallization is an innovative technique that encompasses separation and purification [194]. Membrane crystallization is a technology that is based on membrane distillation (MD) which has been discussed previously [200]. The process is based on the evaporative mass transfer of volatile solvents where micro-porous hydrophobic membranes are used in order to concentrate the feed solution above their saturation limit where crystals may nucleate and grow in a saturated medium [194].

11.4 Eutectic Freeze Crystallization (EFC)

EFC is a relatively new technology that has the potential for lower cost treatment of brines compared to thermal methods [200]. EFC technology utilizes the change in density between the salt and ice produced allowing adequate separation [200]. At the eutectic point for the solution, salts are recovered as solids and pure water turns to ice. Ice has a density that is lower than the feed solution, this allows the ice to float and the salt to sink to be further recovered [240]. These salts may be washed further to produce the desired level of purity [240]. Rahman [241] outlined the conditions to separate a solution of sodium chloride and water and noted that at -20^{o}C both ice and sodium chloride precipitated. The use of EFC has been found to operate under lower energy consumption than evaporation separation processes [240]. For example, van der Ham *et al*. [242] studied eutectic freezing of sodium nitrate solutions and concluded that energy reductions of *ca*. 70 % were obtained relative to standard evaporation methods.

Lewis *et al*. [243] examined complex multicomponent mixtures which were more realistic for practical application of the eutectic freezing technology. They demonstrated that sodium could be selectively recovered and that thermodynamic modelling could predict when different salts would crystallize out of solution. More recently Randall [244] described a case study where brine from a reverse osmosis plant operating in high recovery mode was treated using eutectic freezing. The overall water recovery of the RO plant was increased to 99.9% and both sodium sulphate and calcium sulphate were recovered at high purity levels. Fernández-Torres *et al*. [245] conducted a life cycle analysis for eutectic freezing compared to evaporative crystallization and discovered that no matter what the scenario was, the energy consumption was 6 to 7 times less for eutectic freezing than evaporative crystallization and that the eutectic method produced substantially less greenhouse gas emissions.

11.5 Mechanical Vapor Compression

Mechanical vapor compression (MVC) comprises of a vapor compressor that pressurizes the vapor from an evaporator [246]. The system consists of an evaporator, vapor compressor, gas injector, venting system, pumping units and feed heaters [247]. MVC essentially starts with low temperature vapor that is compressed to increase the temperature and enthalpy [248]. This heated vapor is then used for separation, cost savings and evaporation [248]. This compressed vapor transfers its energy to the evaporating brine concentrate that is located inside a separate evaporator followed by condensation forming pure distillate [246]. The brine is sprayed on the outside of the evaporator tubes and as the compressed vapor condenses it releases its super and latent heat to the brine concentrate [248] and the compressed vapor flows up the evaporator tubes. The advantage of MVC consists of low pre-treatment, no external heat source, high product purity and compact structure [248]. However, there are reported scaling problems on the evaporator tubes, which needs to be considered [248].

12. Salt Disposal Options

Once the brine has been concentrated and treated the question of how to dispose of the acquired salts needs to be considered. Estimates by QGC suggest that by the year 2040 a total of 4 million tonnes of salt will have been collected from its CSG operations in Queensland [249]. According to Santos GLNG [195] there are five options for salt disposal or reuse. The first is road transport to a purpose built salt repository. The second option is road transport to an ocean outfall which in the Queensland context is not considered viable. Thirdly, the salt could be sent to a commercial waste disposal facility such as a landfill site, however, there is clear opposition to this possibility with local mayors vowing not to allow dumping of salt in their area [250]. Another option is to close evaporation ponds and leave the salt *in situ* by construction of a fit for purpose salt repository. Finally, commercial salt production could be considered as the CS water can provide sodium chloride, sodium bicarbonate, calcium carbonate, sodium carbonate and sodium sulphate.

Queensland Gas Corporation are working in association with APLNG and Arrow Energy in relation to the development of a selective salt recovery technology [251]. Several international trials have been completed and the outcome has been that a technical process has been successfully demonstrated to produce commercial grade salts. Whether this latter option is commercially viable is still debatable. The Chlor-alkali industry is potentially the most suitable candidate for use of salts recovered from reverse osmosis treatment/brine management of coal seam gas associated water. Chlor-alkali plants involve the conversion of salt (sodium chloride) to sodium hydroxide and chlorine gas [252]. World chlor-alkali production is in excess of 68 million tonnes per annum and involves mainly the use of electrolysis in a membrane cell [252]. Researchers have previously considered using concentrated brine from saltwater reverse osmosis desalination units as a feed for chlor-alkali plants [253]. However, as yet to the best of our knowledge there is no published data concerning the application of brines from the coal seam gas industry.

13. Conclusions

The extraction of coal seam gas and treatment of associated water is not a trivial exercise. The composition of coal seam water is extremely variable and changes depending not only between Basins but also within wells located in the same Basin. Beneficial reuse options depend upon the local environment, regulations and neighboring industries. The choice of water treatment technologies is varied, with the most popular method in Australia being reverse osmosis. Due to the propensity for membrane fouling, extensive pre-treatment of the coal seam water is required to remove species responsible for scaling and biofouling. However, the optimal configuration of technologies to use prior to the central desalination stage has not yet been determined and several innovative technologies for CS water pre-treatment such as electrocoagulation are worthy of consideration. Indeed, even the use of reverse osmosis is not a foregone conclusion, as ion exchange may offer advantages for certain water types. Brine management is a topic of particular concern as disposal of the salts is not easy due to their low inherent value. The need to concentrate the brines to very high TDS values and concomitantly low volumes is not in dispute, the technology to achieve the latter goal is as yet not confirmed. The field of coal seam water treatment is one which is expected to see tremendous research and development efforts in forthcoming years.

14. Acknowledgements

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List of Figures