# Produced water treatment technologies

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## Abstract

Produced water is a complex mixture of organic and inorganic compounds and the largest volume of by-product generated during oil and gas recovery operations. The potential of oilfield produced water to be a source of fresh water for water-stressed oil-producing countries and the increasing environmental concerns in addition to stringent legislations on produced water discharge into the environment have made produced water management a significant part of the oil and gas business. This article reviews current technologies for the management of produced water, examines how electrochemical techniques may be used in these areas and compares the prospects for future development. It suggests that treatment technologies based on electrochemistry could be the future of produced water management, since produced water is a potential electrolyte because it has a relatively good conductivity. It also explains that by applying photoelectrochemistry, water electrolysis, fuel cell and electrodeposition, electrochemical engineering could achieve energy storage, production of clean water and recovery of valuable metals from produced water with minimal or no negative impact on the environment.

*Keywords:* produced water; treatment technology; electrochemistry; electrodeposition; photoelectrochemistry; water electrolysis; legislation; management

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## 1 INTRODUCTION

Petroleum is a major source of energy and revenue for many countries today, and its production has been described as one of the most important industrial activities in the twenty-first century [1]. Since late 1850s when Edwin Drake drilled the first oil well, demand for petroleum has continued to rise. It is estimated that world daily petroleum consumption would increase from 85 million barrels in 2006 to 106.6 million barrels by 2030 [2]. Despite its significance, petroleum is produced with large volumes of waste, with wastewater accounting for more than 80% of liquid waste [3] and as high as 95% in ageing oilfields [4]. Generally, the oil/water volume ratio is 1:3 [5].

Produced water has a complex composition, but its constituents can be broadly classified into organic and inorganic compounds [6], including dissolved and dispersed oils, grease, heavy metals, radionuclides, treating chemicals, formation solids, salts, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen [5–8]. Globally, ∼250 million barrels of water are produced daily from both oil and gas fields, and more than 40% of this is discharged into the environment. Currently, oil and gas operators treat produced water via one or more of the following options [9]:

- Avoid production of water: water fractures are blocked by polymer gel or downhole water separators, but this option is not always possible.
- Inject into formations: produced water may be injected back to its formation or into other formations. This option often requires transportation of water, and treatment to reduce fouling and bacterial growth. In the long term, the stored produced water may pollute the underground waters.
- Discharge to the environment: produced water may be discharged to the environment as long as it meets onshore and offshore discharge regulations.
- Reuse in petroleum industry operations: minimally treated produced water may be used for drilling and workover operations within the petroleum industry.
- Apply in beneficial uses: produced water may be consumed for irrigation, wildlife consumption and habitat, industrial water and even drinking water. However, beneficial uses of produced water may involve significant treatment [5, 9].

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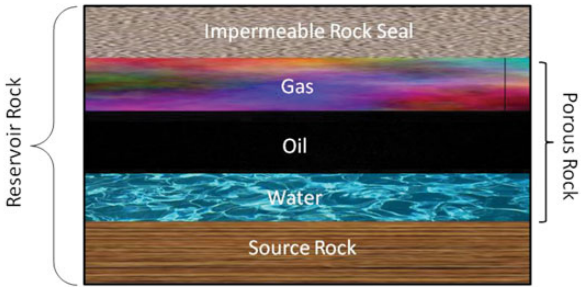



**Figure 1.** *Sketch of a typical reservoir.*

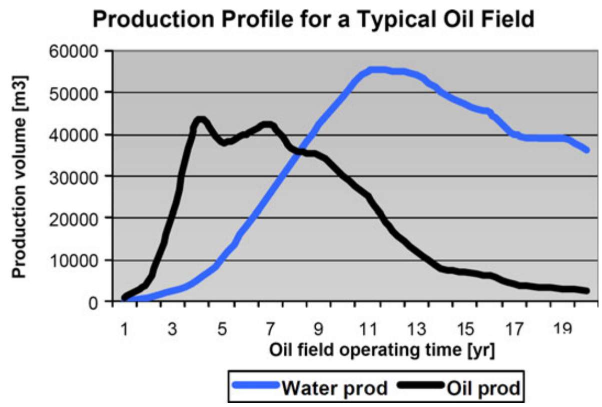



**Figure 2.** *Typical production profile for an oilfield [17].*

Environmental concerns and the prospect of beneficial uses have driven research into the treatment of produced water. Current conventional treatment technologies are targeted at removal of heavy metals, oil and grease, suspended solids and desalination, which often lead to the generation of large volumes of secondary waste. For instance, heavy metals are removed as sludge using current treatment technologies [10]. This article reviews current produced water treatment technologies and examines the ability of electrochemically driven technology to store energy, produce clean water and recover valuable materials from produced water with minimal negative impact on the environment.

## 2 WHAT IS PRODUCED WATER?

Natural water or formation water is always found together with petroleum in reservoirs. It is slightly acidic and sits below the hydrocarbons in porous reservoir media (Figure 1). Extraction of oil and gas leads to a reduction in reservoir pressure, and additional water is usually injected into the reservoir water layer to maintain hydraulic pressure and enhance oil recovery.

In addition to injected water, there can be water breakthrough from outside the reservoir area, and as oil and gas production continues, the time comes when formation water reaches production well, and production of water begins alongside the hydrocarbons. This water is known as produced water or oilfield brine, accounting for the largest volume of by-product generated during oil and gas recovery operations [11, 12]. It is a mixture of injected water, formation water, hydrocarbons and treating chemicals [13], generally classified as oilfield produced water, natural gas produced water and coal bed methane (CBM) produced water depending on the source.

Oilfields are responsible for more than 60% of daily produced water generated worldwide [5]. The rate of oilfield produced water production is expected to increase as oilfield ages (Figure 2). Other factors have been reported to affect the quantity of produced water generated in an oilfield [11].

Generally, produced water is composed of dissolved and dispersed oil components, dissolved formation minerals, production chemicals, dissolved gases (including $CO_2$ and $H_2S$) and produced solids [14]. There is a wide variation in the level of its organic and inorganic composition due to geological formation, lifetime of the reservoir and the type of hydrocarbon produced.

### 2.1 Dissolved and dispersed oil components

Dispersed and dissolved oil components are a mixture of hydrocarbons including BTEX (benzene, toluene, ethylbenzene and xylene), PAHs (polyaromatic hydrocarbons) and phenols. Dissolved oils are the polar constituent organic compounds in produced water, while small droplets of oil suspended in the aqueous phase are called dispersed oil [6, 10, 15]. BTEX, phenols, aliphatic hydrocarbons, carboxylic acid and low molecular weight aromatic compound are classified as dissolved oil, while less-soluble PAHs and heavy alkyl phenols are present in produced water as dispersed oil [16]. Dissolved and dispersed oil content in produced water is dangerous to the environment and their concentration can be very high at some oil fields [6, 16–18]. The quantity of oil present in produced water is governed by a number of complex but interrelated factors [6, 14, 17].

### 2.2 Dissolved mineral

Dissolved inorganic compounds or minerals are usually high in concentration, and classified as cations and anions, naturally occurring radioactive materials and heavy metals. Cations and anions play a significant role in the chemistry of produced water. $Na^+$ and $Cl^-$ are responsible for salinity, ranging from a few milligrams per litre to ~300 000 mg/l [19]. $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$, $HCO_3^-$, $Na^+$, $K^+$, $Ca^{2+}$, $Ba^{2+}$, $Mg^{2+}$, $Fe^{2+}$ and $Sr^{2+}$ affect conductivity and scale-forming potential. Typical oilfield produced water contains heavy metals in varied concentrations, depending on the formation geology and the age of oil well [5, 20]. Heavy metal concentrations in produced water are usually higher than those of receiving water (for enhanced oil recovery) and those found in sea water [19].

$^{226}Ra$ and $^{228}Ra$ are the most abundant naturally occurring radioactive elements present in oilfield produced water [20]. Radioactivity of produced water results primarily from radium that is co-precipitated with barium sulphate (scale) or other types of scales. The concentration of barium ions

**Table 1.** *Composition of oilfield produced water [5].*

| Parameter | Minimum value | Maximum value | Heavy metal | Minimum value (mg/l) | Maximum value (mg/l) |
|---|---|---|---|---|---|
| Density (kg/m$^3$) | 1014 | 1140 | Calcium | 13 | 25 800 |
| Conductivity (μS/cm) | 4200 | 58 600 | Sodium | 132 | 97 000 |
| Surface tension (dyn/cm) | 43 | 78 | Potassium | 24 | 4300 |
| pH | 4.3 | 10 | Magnesium | 8 | 6000 |
| TOC (mg/l) | 0 | 1500 | Iron | <0.1 | 100 |
| TSS (mg/l) | 1.2 | 1000 | Aluminium | 310 | 410 |
| Total oil (IR; mg/l) | 2 | 565 | Boron | 5 | 95 |
| Volatile (BTX; mg/l) | 0.39 | 35 | Barium | 1.3 | 650 |
| Base/neutrals (mg/l) | — | <140 | Cadmium | <0.005 | 0.2 |
| Chloride (mg/l) | 80 | 200 000 | Copper | <0.02 | 1.5 |
| Bicarbonate (mg/l) | 77 | 3990 | Chromium | 0.02 | 1.1 |
| Sulphate (mg/l) | <2 | 1650 | Lithium | 3 | 50 |
| Ammoniacal nitrogen (mg/l) | 10 | 300 | Manganese | <0.004 | 175 |
| Sulphite (mg/l) | — | 10 | Lead | 0.002 | 8.8 |
| Total polar (mg/L) | 9.7 | 600 | Strontium | 0.02 | 1000 |
| Higher acids (mg/l) | <1 | 63 | Titanium | <0.01 | 0.7 |
| Phenol (mg/l) | 0.009 | 23 | Zinc | 0.01 | 35 |
| Volatile fatty acids (mg/l) | 2 | 4900 | Arsenic | <0.005 | 0.3 |
| | | | Mercury | <0.005 | 0.3 |
| | | | Silver | <0.001 | 0.15 |
| | | | Beryllium | <0.001 | 0.004 |

**Table 2.** *Production chemicals in oil and gas fields produced water [14].*

| Chemical | Concentration: oil field | | Concentration: gas field | |
|---|---|---|---|---|
| | Typical (mg/l) | Range (mg/l) | Typical (mg/l) | Range (mg/l) |
| Corrosion inhibitor[a] | 4 | 2–10 | 4 | 2–10 |
| Scale inhibitor[b] | 10 | 4–30 | – | – |
| Demulsifier[c] | 1 | 1–2 | – | – |
| Polyelectrolyte[d] | 2 | 0–10 | – | – |
| Methanol | | | 2000 | 1000–15 000 |
| Glycol (DEG) | | | 1000 | 500–2000 |

[a]Typically containing amide/imidazoline compounds.
[b]Typically containing phosphate ester/phosphate compounds.
[c]Typically containing oxylated resins/polyglycol ester/alkyl aryl sulphonates.
[d]For example, polyamine compounds.

in produced water could give a strong indication of radium isotopes present in it [21]. In some oilfields, up to 21 Bq/l of $^{228}$Ra have been detected in produced water samples [5]. Table 1 lists typical composition and properties of oilfield produced water [5].

### 2.3 Production chemicals

Production chemicals (Table 2) can be pure compounds or compounds containing active ingredients dissolved in a solvent or a co-solvent, and used for inhibition of corrosion, hydrate formation, scale deposition, foam production, wax deposition, bacterial growth, gas dehydration and emulsion breaking in order to improve the separation of oil and water [14]. These chemicals enter produced water in traces and sometimes significant amounts [18] and vary from platform to platform. Active ingredients partition themselves into all phases present depending on their relative solubilities in oil, gas or water. The fate of these chemicals is difficult to determine because some active ingredients are consumed within the process [18].

### 2.4 Produced solids

Produced solids include clays, precipitated solids, waxes, bacteria, carbonates, sand and silt, corrosion and scale products, proppant, formation solids and other suspended solids [5]. Their concentrations vary from one platform to another. Produced solids could cause serious problems during oil production. For example, common scales and bacterial can clog flow lines, form oily sludge and emulsions which must be removed [22].

### 2.5 Dissolved gases

The major dissolved gases in produced water are carbon dioxide, oxygen and hydrogen sulphide. They are formed naturally, by the activities of bacterial or by chemical reactions in the water.

## 3 ENVIRONMENTAL IMPACT AND LEGISLATION

The general practice in use for produced water treatment is gravity-based separation and discharge into the environment, which can pollute soil, surface water and underground water [5]. For a long time, only non-polar oil in water (OIW) was regulated by government, while little attention was given to dissolved organics in produced water [17]. Current researches are paying more attention to the consequence of dissolved organic components, heavy metals and production chemicals on living organisms, since their long-term effects on the environment are not fully documented and understood. It has been reported that metals and hydrocarbons from oil platforms are very toxic to the ecosystem and fish exposed to alkyl phenols have disturbances in both organs and fertility [17, 23].

A general legislation for discharging produced water into sea has been 40 ppm OIW, but an increase in environmental concerns has made many countries to implement more stringent regulatory standards. The Oslo Paris Convention (OSPAR) agreed that the maximum discharge be reduced to 30 ppm OIW and the overall oil discharges in produced water be reduced by 15% from what they were in 1999 [17]. The United States Environmental Protection Agency (USEPA) sets a daily maximum for oil and grease at 42 ppm. In Australia, permitted offshore discharge of oil and grease in produced water is 30 ppm and the People's Republic of China now sets the monthly average limits of 'oil and grease' and 'chemical oxygen demand' at 10 and 100 ppm, respectively [5]. The Convention for the Protection of the Marine Environment of the North–East Atlantic sets the annual average limit for discharge into the sea at 40 ppm [16].

The EU Water Framework Directive (WFD) adopted in 2000 is committed to 'zero discharge' in response to the need for a more protective system to tackle aquatic pollution [24]. Since 2005, oil operators in Norway agreed to implement a zero environmental harmful discharge. To achieve this, the Norwegian Oil Industries Associations developed the Environmental impact factor (EIF), which considers all the contaminants in produced water [17]. Similarly, OSPAR commission has agreed on zero discharge of pollutants into the sea [25]. Most oil and gas companies around the world are now working towards the implementation of 'zero-discharge' of contaminants in produced water [26]. In addition to legislation, many water-stressed countries with oilfields are looking for ways to supplement their limited fresh water resources by focusing on efficient and economical methods to treat produced water, so that it can be channelled to agricultural and industrial uses [16].

# 4 PRODUCED WATER MANAGEMENT TECHNOLOGIES

The general objectives for operators treating produced water are: de-oiling (removal of dispersed oil and grease), desalination, removal of suspended particles and sand, removal of soluble organics, removal of dissolved gases, removal of naturally occurring radioactive materials (NORM), disinfection and softening (to remove excess water hardness) [9]. To meet up with these objectives, operators have applied many standalone and combined physical, biological and chemical treatment processes for produced water management. Some of these technologies are reviewed in this section.

## 4.1 Membrane filtration technology

Membranes are microporous films with specific pore ratings, which selectively separate a fluid from its components. There are four established membrane separation processes, including microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) [27]. RO separates dissolved and ionic components, MF separates suspended particles, UF separates macromolecules [28] and NF is selective for multivalent ions [29]. MF and UF can be used as a standalone technology for treating industrial wastewater, but RO and NF are usually employed in water desalination. Membrane technology operates two types of filtration processes, cross-flow filtration or dead-end filtration (Figure 3), that can be a pressure (or vacuum)-driven system [30].

### 4.1.1 *Microfiltration/ultrafiltration*

MF has the largest pore size (0.1–3 μm) and is typically used for the removal of suspended solids and turbidity reduction. It can operate in either cross-flow or dead-end filtration. UF pore sizes are between 0.01 and 0.1 μm. They are employed in the removal of colour, odour, viruses and colloidal organic matter [30, 31]. UF is the most effective method for oil removal from produced water in comparison with traditional separation methods [32],

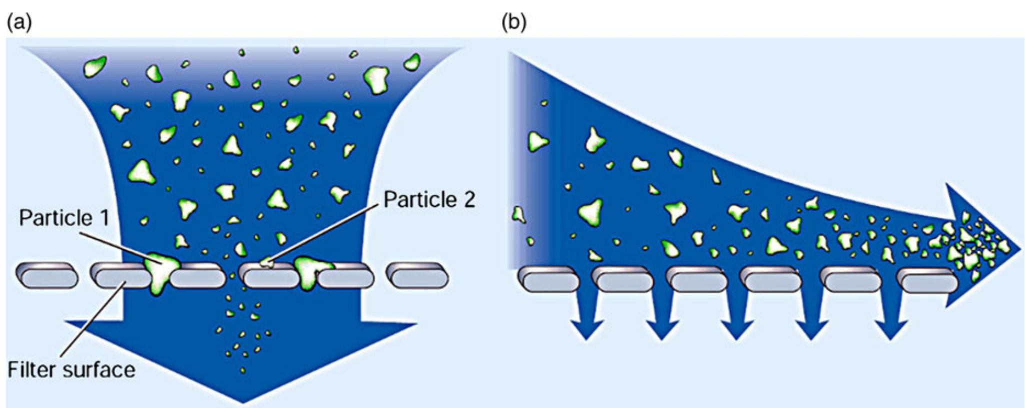



**Figure 3.** *Comparison of dead-end filtration and cross-flow filtration [107].*

and it is more efficient than MF for the removal of hydrocarbons, suspended solids and dissolved constituents from oilfield produced water [33]. Both MF and UF operate at low transmembrane pressure (1–30 psi) and can serve as a pre-treatment to desalination but cannot remove salt from water [30].

#### 4.1.2 *Polymeric/ceramic membranes*

Polymeric and ceramic membranes are used for UF/MF treatment of water. Polymeric MF/UF membranes are made from polyacrylonitrile and polyvinylidene and ceramic membranes from clays of nitrides, carbides and oxides of metals [34]. Ceramic UF/MF membranes have been used in a full-scale facility for the treatment of produced water [30]. Product water from this treatment was reported to be free of suspended solids and nearly all non-dissolved organic carbon [35–39]. Ceramic UF/MF membranes can operate in both cross-flow filtration and dead-end filtration modes and have a lifespan of >10 years. Chemicals are not required for this process except during periodic cleaning of membranes and pre-coagulation (used to enhance contaminants removal).

#### 4.1.3 *Reverse osmosis and nanofiltration*

RO and NF are pressure-driven membrane processes. Osmotic pressure of the feed solution is suppressed by applying hydraulic pressure which forces permeate (clean water) to diffuse through a dense, non-porous membrane [40]. Seawater RO can remove contaminants as small as 0.0001 μm, but its major disadvantage is membrane fouling and scaling [30, 41]. Early studies on using RO to treat produced water failed due to insufficient process integration and poor treatment [42–46]. Nicolaisen and Lien [46] however reported a successful RO treatment of oilfield produced water in Bakersfield, California. The pilot system which was operated for over 1700 h in 6 months produced 20 gpm of clean water. Bench-scale studies have shown the potential of brackish water RO membranes to successfully treat oil and gas produced water. Experiments indicated that RO membrane technology would be excellent for oilfield produced water treatment with appropriate pre-treatment technology [27, 47].

Capital costs of RO membrane systems vary depending on the size of rejection required, materials of construction and site location. Operating costs depend on energy price and total dissolved solid (TDS) level in the feed water. RO membrane systems generally have a life expectancy of 3–7 years [30]. NF is a robust technology for water softening and metals removal and is designed to remove contaminants as small as 0.001 μm [30]. It is applicable for treating water containing TDS in the range of 500–25 000 ppm. This technology is similar to RO [30]. NF membranes were employed for produced water treatment on both bench and pilot scales [27, 46]. Mondal and Wickramasinghe [47] studied the effectiveness of NF membranes for the treatment of oilfield produced water. Results showed a minimal improvement when compared with the effectiveness of brackish water RO treatment of the same feed water. A comparison of various membrane treatment technologies is shown in Table 3.

### 4.2 Thermal technologies

Thermal treatment technologies of water are employed in regions where the cost of energy is relatively cheap. Thermal separation process was the technology of choice for water desalination before the development of membrane technology. Multistage flash (MSF) distillation, vapour compression distillation (VCD) and multieffect distillation (MED) are the major thermal desalination technologies [48]. Hybrid thermal desalination plants, such as MED–VCD, have been used to achieve higher efficiency [49]. Although membrane technologies are typically preferred to thermal technologies, recent innovations in thermal process engineering make thermal process more attractive and competitive in treating highly contaminated water [30, 50].

#### 4.2.1 *Multistage flash*

MSF distillation process is a mature and robust technology for brackish and sea water desalination. Its operation is based on evaporation of water by reducing the pressure instead of raising the temperature. Feed water is pre-heated and flows into a chamber with lower pressure where it immediately flashes into steam [48]. Water recovery from MSF treatment is ~20% and often requires post-treatment because it typically contains 2–10 mg/l of TDS [30]. A major setback in operating MSF is scale formation on heat transfer surfaces which often makes this process require the use of scale inhibitors and acids. Overall costs vary depending on the size, site location and materials of construction [51]. Its energy requirement is between 3.35 and 4.70 kWh/bbl [52].

Globally, MSF market share has significantly decreased due to competition of membrane technologies, but it is a relatively cost-effective treatment method with plant life expectancy of more than 20 years, and can be employed for produced water treatment [50].

#### 4.2.2 *Multieffect distillation*

MED process involves application of sufficient energy that converts saline water to steam, which is condensed and recovered as pure water. Multiple effects are employed in order to improve the efficiency and minimize energy consumption (Figure 4). A major advantage of this system is the energy efficiency gained through the combination of several evaporator systems. Product water recovery from MED systems are in the range of 20–67% depending on the type of the evaporator design employed [48]. Despite the high water recovery from MED systems, it has not been extensively used for water production like MSF because of scaling problem associated with old designs. Recently, falling film evaporators have been introduced to improve heat transfer rates and reduce the rate of scale formation [49].

MED has a life cycle of 20 years and can be applied to a wide range of feed water quality like MSF. It is good for high TDS produced water treatment [30, 49]. Scale inhibitors and acids may be required to prevent scaling and pH control is

**Table 3.** *Comparison of produced water membrane treatment technologies.*

| Technology | Ceramic MF/UF membrane | Polymeric MF/UF membrane | NF | RO |
|---|---|---|---|---|
| Feasibility | Ceramic membranes have been used to treat oilfield produced water and extensively used in other industrial water treatments. They are applicable to all types of produced water irrespective of their TDS and salt concentrations, but produced water with high concentrations may be problematic | Applicable to water with high TDS and salt concentrations and also has the potential to treat produced water however it is extensively used in the municipal water treatment | This technology is used for water softening and removal of metals from wastewater. It is specifically efficient for feed water containing TDS ranging from 500 to 25 000 mg/l. NF is a poor technology for produced water treatment and is inappropriate as a standalone technology | This is a robust technology for seawater desalination and has been employed in produced water treatment. For this technology to be effective in produced water treatment, extensive pre-treatment of feed water is necessary. Several pilot studies failed due to poor pre-treatment and insufficient system integration |
| Energy consumption | Not available | Not available | It uses electrical energy and its energy requirement is less than what is required in RO systems. Approximately NF system requires 0.08 Kwh/bbl to power its high-pressure pumps [112] | RO use electrical energy for its operation. SWRO requires 0.46–0.67 KWh/bbl if energy recovery device is integrated [113]. BWRO require less energy than equivalent SWRO system. BWRO requires ~0.02–0.13 KWh/bbl of energy to power the system's pumps |
| Chemical use | Ferric chloride, polyaluminium chloride and aluminium sulphate are common coagulants used for pre-coagulation. Acids, bases and surfactants are used in cleaning process | Ferric chloride, polyaluminium chloride and aluminium sulphate are common coagulants used for pre-coagulation. Acids, bases and surfactants are used in cleaning process | Caustic and scale inhibitors are required to prevent fouling. NaOH, $H_2O_2$, $Na_2SO_4$, HCl, or $Na_4$EDTA are required for cleaning the system. | Caustic and scale inhibitors are required to prevent fouling. NaOH, $H_2O_2$, $Na_2SO_4$, $H_3PO_4$, HCl, or $Na_4$EDTA are required for cleaning the system |
| Pre/post-treatment | Cartridge filtration and coagulation are usually used as a pre-treatment. Post-treatment may be required for polishing depending on the product water | Cartridge filtration and coagulation are usually used as a pre-treatment. Post-treatment may be required for polishing depending on the product water | Extensive pre-treatment is required to prevent fouling of membrane. Product water may require remineralization to restore SAR values | Extensive pre-treatment is required to prevent fouling of membrane. Product water may require remineralization or pH stabilization to restore SAR values |
| Overall cost | Not available | Capital costs depend on feed water quality and size of the polymeric membrane system. Approximate capital cost is \$0.02–\$0.05/bpd. Approximate Operation and Maintenance costs \$0.02–\$0.05/bpd [30] | Capital cost range from \$35 to \$170/bpd. Operating cost is ~\$0.03/bbl. | Capital costs of BWRO vary from \$35 to \$170/bpd and operating costs are ~\$0.03/bbl. Capital costs of SWRO vary from \$125 to \$295/bpd and operating costs are ~\$0.08/bbl |
| Life cycle | >10 years | 7 years or more | 3–7 years | 3–7 years |
| Advantages | (1) Product water is totally free of suspended solids<br>(2) It can be operated in cross-flow or dead-end filtration mode<br>(3) Product water recovery range from 90% to 100%<br>(4) Ceramic membranes have a longer lifespan than polymeric membranes | (1) Product water is free of suspended solids<br>(2) Product water recovery range from 85% to 100% | (1) It has high pH tolerance<br>(2) System can be operated automatically leading to less demand of skilled workers<br>(3) Energy costs can be reduced by implementing energy recovery subsystems<br>(4) It does not require solid waste disposal<br>(5) Water recovery between 75% and 90% | (1) It has high pH tolerance<br>(2) System can be operated automatically leading to less demand of skilled workers<br>(3) Energy costs can be reduced by implementing energy recovery subsystems<br>(4) It performs excellently for produced water treatment with appropriate pre-treatment<br>(5) It does not require concentrate treatment as brine generated is usually disposed into sea<br>(6) Product water recovery in SWRO is between 30% and 60%, and between 60% and 85% in BWRO |
| Disadvantages | (1) Irreversible membrane fouling can occur with significant amount of iron concentration in feed water<br>(2) Membrane requires periodic cleaning<br>(3) Waste generated during backwash and cleaning processes require disposal/recycling or further treatment | (1) Membrane requires periodic cleaning<br>(2) Waste generated during backwash and cleaning processes require disposal/recycling or further treatment | (1) It is highly sensitive to organic and inorganic constituents in the feed water<br>(2) Membranes cannot withstand feed temperatures in excess of 45°C<br>(3) It requires several backwashing cycles | (1) It is highly sensitive to organic and inorganic constituents in the feed water<br>(2) Membranes cannot withstand feed temperatures in excess of 45°C |

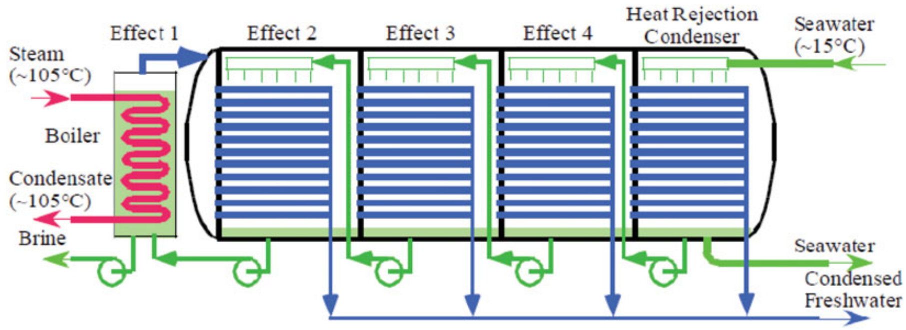



**Figure 4.** *Schematic diagram of a conventional MED system [108].*

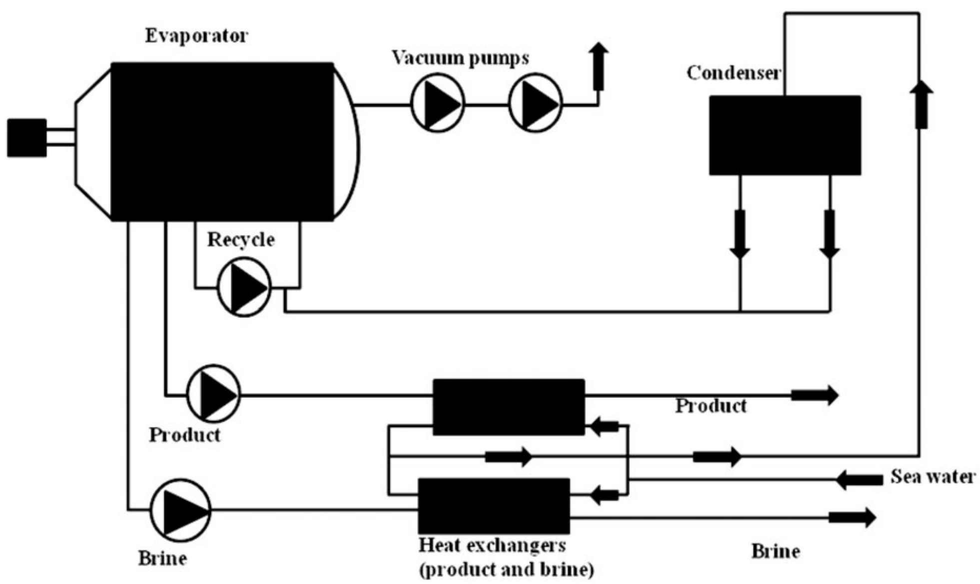



**Figure 5.** *Flow diagram of a vapour compression process (redrawn) [109].*

essential to prevent corrosion. Power energy consumption is in the range of 1.3–1.9 kWh/bbl [52], operating cost is ∼$0.11/bbl and total unit cost is $0.16/bbl [51].

### 4.2.3 *Vapour compression distillation*

VCD process is an established desalination technology for treating seawater and RO concentrate [30]. Vapour generated in the evaporation chamber is compressed thermally or mechanically, which raises the temperature and pressure of the vapour. The heat of condensation is returned to the evaporator and utilized as a heat source (Figure 5). VCD is a reliable and efficient desalination process and can operate at temperatures below 70°C, which reduces scale formation problems [53].

Energy consumption of a VCD plant is significantly lower than that of MED and MSF. The overall cost of operation depends on various factors, including purpose of plant, zero liquid discharge target, size of plant, materials of construction and site location. Cogeneration of low-pressure steam can significantly reduce the overall cost. Although this technology is mainly associated with sea water desalination, various enhanced vapour compression technologies have been employed for produced water treatment [30].

### 4.2.4 *Multieffect distillation–vapour compression hybrid*

Hybrid MED–VCD has been recently used to treat produced water. Increased production and enhanced energy efficiency are the major advantages of this system. It is believed that this new technology would replace the older MSF plants [30]. GE has developed produced water evaporators which uses mechanical vapour compression. These evaporators exhibit a number of advantages over conventional produced water treatment methods, including reduction in chemical use, overall cost, storage, fouling severity, handling, softer sludge and other waste stream [54]. More than 16 produced water evaporators have been installed in Canada, and more are expected to be installed in other regions of the world [55]. The life expectancy of produced water evaporators is 30 years [30]. A comparison of various thermal treatment technologies is shown in Table 4.

**Table 4.** *Comparison of produced water thermal treatment technologies.*

| Technology | MSF | MED | VCD technology | MED–vapour compression hybrid | Freeze thaw evaporation |
|---|---|---|---|---|---|
| Feasibility | This is a mature and robust desalination technology that can be employed for produced water treatment. MSF is applicable to all types of water with high TDS range up to 40 000 mg/l | This is a mature and robust desalination technology that can be employed for produced water treatment. MED is applicable to all types of water and a wide range of TDS | This is a mature and robust seawater desalination technology. It is applicable to all types of waste water with TDS level greater than 40 000 mg/l. Various enhanced VCD have been applied in produced water treatment | A mature desalination technology that has been employed in produced water treatment. It is usually employed for treating water with high TDS. In future product, water quality may be increased. For example, product water recovery of ~75% was achieved by GE using brine concentrator and analyser [114] | This is a mature and robust technology for produced water treatment. It does not require infrastructure. This process requires favourable soil conditions, a significant amount of land and a substantial number of days with temperatures below freezing |
| Energy consumption | Electrical energy required ranges from 0.45 kWh/bbl to 0.9 kWh/bbl. Thermal energy required is estimated at 3.35 kWh/bbl [30]. Overall energy required for MSF ranges from 3.35 to 4.70 kWh/bbl [52] | MED requires both thermal and electrical energy types. Electrical energy consumed is approximately 0.48 kWh/h/bbl [51] and power consumption is 1.3–1.9 kWh/bbl [52] | VCD requires both thermal and electrical energy. For desalination, power energy consumption is ~1.3 kWh/bbl [53]. Electricity consumption is 1.1 kWh/bbl for mechanical vapour compression (MVC) and to achieve zero-liquid discharge energy demand is ~4.2–10.5 kWh/bbl [30, 51] | It uses both thermal and electrical energy. Power consumption for desalination is ~0.32 kWh/bbl [49]. To achieve zero-liquid discharge energy consumption is around 4.2–10.5 kWh/bbl [30] | It uses electrical energy, but data are not available |
| Chemical use | EDTA, acids and other antiscaling chemicals are used to prevent scaling. pH control is also necessary to prevent corrosion | Scale inhibitors are required to prevent scaling. Acid, EDTA and other antiscaling chemicals are required for cleaning and process control | Scale inhibitors and acids are required to prevent scaling. EDTA and other antiscaling chemicals are required for cleaning and process control. Corrosion is prevented by pH control | Scale inhibitors are required to prevent scaling. Acids, EDTA and other antiscaling chemicals are required for cleaning and process control. Corrosion is prevented by pH control | None |
| Pre/ post-treatment | Pre-treatment is done to remove large suspended solids. This requires screens and rough filtration. Product water stabilization is required because of its low TDS | Pre-treatment is done to remove large suspended solids similar to MSF. This requires screens and rough filtration. Product water stabilization is required because of its low TDS | Pre-treatment and post-treatments are required in order to avoid fouling and because of low TDS level in product water, respectively | It requires a less rigorous pre-treatment compared with membrane technologies. Lime bed contact post-treatment is required because of low TDS of product water | It requires minimal pre- and post-treatment depending on product water quality and discharge standards |
| Overall cost | Capital costs vary between $250 and $360 per bpd. Operating costs are ~$0.12/bbl and total unit costs are $0.19/bbl [51] | Overall cost is lesser than in MSF. Capital costs ranges from $ 250 to $330 per bpd. Operating costs are ~0.11/bbl and total unit costs are $ 0.16/bbl [51] | Capital costs of vapour compression for sea water desalination ranges from $140 to 250 per bpd depending on various factors. Operating costs are ~0.075/bbl and total unit costs are $0.08/bbl for seawater desalination [51] | Capital cost is ~$250 per bbl per day [51]. Operation costs depend on the amount of energy consumed | It depends on location |
| Life cycle | Typically 20 years but most plants operate for more than 30 years | Typically 20 years | Typically 20 years but may operate for more years | Typically 20 years but may be longer if made of materials with high corrosion resistance | Expected lifespan is 20 years |

| | | | | | |
|---|---|---|---|---|---|
| Advantages | (1) It requires less rigorous pre-treatment and feed condition compared with membrane technologies<br>(2) It has a significantly long lifespan.<br>(3) MSF system can withstand harsh conditions<br>(4) It can easily be adapted to highly varying water quality<br>(5) Cost of labour is cheaper than using membrane technology<br>(6) Good for high TDS produced water treatment<br>(7) Product water quality is high with TDS levels between 2 mg/l and 10 mg/l. | (1) It requires less rigorous pre-treatment and feed condition compared with membrane technologies<br>(2) It has a long lifespan.<br>(3) Energy requirement is cheaper than using MSF.<br>(4) It can easily be adapted to highly varying water quality<br>(5) Cost of labour is cheaper than using MSF or membrane technology<br>(6) Good for high TDS produced water treatment<br>(7) Product water quality is high<br>(8) It does not require special concentrate treatment<br>(9) Product water recovery of up to 67% can be achieved using stacked vertical tube design [30] | (1) Applicable to all types of water and water with high TDS $>$ 40 000 mg/l.<br>(2) It is a smaller unit compared with MS F and MED<br>(3) It has high ability to withstand harsh conditions<br>(4) It does not require special concentrate treatment<br>(5) Pre -treatment is less rigorous compared with membrane treatment | (1) It has high product water quality<br>(2) Excellent treatment technology for produced water with high TDS and zero liquid discharge<br>(3) System can withstand harsh condition | (1) Excellent for zero liquid discharge<br>(2) It requires low skilled labour, monitoring and control<br>(3) It is highly reliable and can be easily adapted to varying water quality and quantity |
| Disadvantages | (1) Low product water recovery usually between 10 and 20% [88]<br>(2) It is not flexible for varying water flow rates<br>(3) Scaling and corrosion can be a problem | (1) Typically low product water recovery usually between 20% and 35% [30]<br>(2) It is not flexible for varying water flow rates<br>(3) Scaling and corrosion can be a problem<br>(4) High level of skilled labour required | (1) Typically low product water recovery is usually around 40%<br>(2) It is not flexible for varying water flow rates<br>(3) Scaling and corrosion can be a problem<br>(4) High level of skills are required to operate system | (1) Not applicable to produced water wells point source<br>(2) Being a hybrid design, it requires very highly skilled labour | (1) Cannot treat produced water with high methanol concentration<br>(2) Moderate product water quality containing $\sim$1000 mg/l TDS [72]<br>(3) Can only work in winter time and in places with below freezing temperatures<br>(4) A significant amount of land is required<br>(5) It generates secondary waste streams |

## 4.3 Biological aerated filters

Biological aerated filter (BAF) is a class of biological technologies which consists of permeable media that uses aerobic conditions to facilitate biochemical oxidation and removal of organic constituents in polluted water. Media is not more than 4 in in diameter to prevent clogging of pore spaces when sloughing occur [56]. BAF can remove oil, ammonia, suspended solids, nitrogen, chemical oxygen demand (COD), biological oxygen demand (BOD), heavy metals, iron, soluble organics, trace organics and hydrogen sulphide from produced water [30, 57]. It is most effective for produced water with chloride levels below 6600 mg/l [30].

This process requires upstream and downstream sedimentation to allow the full bed of the filter to be used. Removal efficiencies of up to 70% nitrogen, 80% oil, 60% COD, 95% BOD and 85% suspended solids have been achieved with BAF treatment [57].

Water recovery from this process is nearly 100% since waste generated is removed in solid form [58]. BAF usually have a long lifespan. It does not require any chemicals or cleaning during normal operations. Its power requirement is 1–4 kWh/day, and capital accounts for the biggest cost of this technology. Solids disposal is required for accumulated sludge in sedimentation basins and can account for up to 40% of the total cost of this technology [56].

## 4.4 Hydrocyclones

Hydrocyclones use physical method to separate solids from liquids based on the density of the solids to be separated. They are made from metals, plastics or ceramic, and usually have a cylindrical top and a conical base with no moving parts (Figure 6). The performance of the hydrocyclone is determined by the angle of its conical section [30]. Hydrocyclones can remove particles in the range of 5–15 μm and have been widely used for the treatment of produced water [30, 59].

Nearly 8 million barrels per day of produced water can be treated with hydrocyclones [60]. They are used in combination with other technologies as a pre-treatment process. They have a long lifespan and do not require chemical use or pre-treatment of feed water. A major disadvantage of this technology is the generation of large slurry of concentrated solid waste.

## 4.5 Gas flotation

Flotation technology is widely used for the treatment of conventional oilfield produced water. This process uses fine gas bubbles to separate suspended particles that are not easily separated by sedimentation. When gas is injected into produced water, suspended particulates and oil droplets are attached to the air bubbles as it rises. This results into the formation of foam on the surface of the water which is skimmed off as froth [61].

There are two types of gas flotation technology (dissolved gas flotation and induced gas flotation) based on the method of gas bubble generation and resultant bubble sizes. In dissolved gas floatation units, gas is introduced into the flotation chamber by a vacuum or by creating a pressure drop, but mechanical shear or propellers are used to create bubbles in induced gas flotation units [62]. Gas floatation can remove particles as small as 25 μm and can even remove contaminants up to 3 μm in size if coagulation is added as pre-treatment, but it cannot remove soluble oil constituents from water [30]. Flotation is most effective when gas bubbles size is less than oil droplet size and it is expected to work best at low temperature since it involves dissolving gas into water stream.

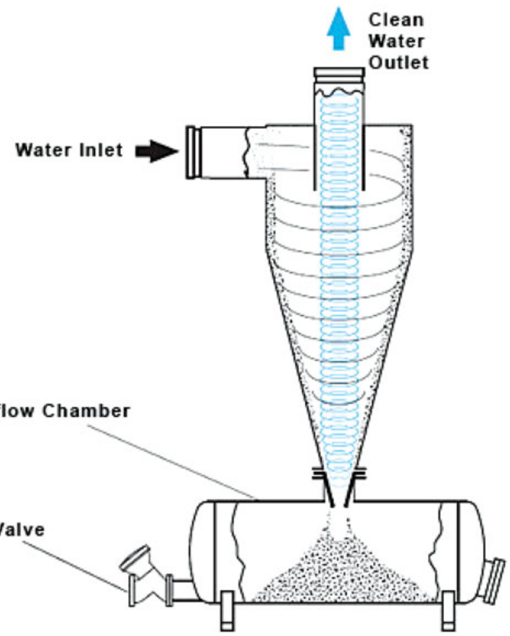



**Figure 6.** *Hydrocyclone flow scheme and mode of operation [110].*

Flotation can be used to remove grease and oil, natural organic matter, volatile organics and small particles from produced water [6, 30, 61, 62]. It does not require chemical use, except coagulation chemicals are added to enhance removal of target contaminants. Solid disposal will be necessary for the sludge generated from this process and the estimated cost for flotation treatment is \$0.60/m$^3$ of produced water [62].

## 4.6 Evaporation pond

Evaporation pond is an artificial pond that requires a relatively large space of land designed to efficiently evaporate water by solar energy [63]. They are designed either to prevent subsurface infiltration of water or the downward migration of water depending on produced water quality [64]. It is a favourable technology for warm and dry climates because of the potential for high evaporation rates. Evaporation ponds are typically economical and have been employed for the treatment of produced water onsite and offsite. Ponds are usually covered with nettings to prevent potential problems to migratory waterfowl caused by contaminants in produced water [30]. All water is lost to the environment when using this technology which is a major setback when water recovery is an objective for water treatment.

## 4.7 Adsorption

Adsorption is generally utilized as a polishing step in a treatment process rather than as a standalone technology since adsorbents can be easily overloaded with organics. It has been used to remove manganese, iron, total organic carbon (TOC), BTEX, oil and more than 80% of heavy metals present in produced water [30]. There are a variety of adsorbents, such as activated carbon, organoclays, activated alumina and zeolites [65]. Adsorption process is applicable to water treatment irrespective of salinity. It requires a vessel to contain the media and pumps to implement backwashes which happen periodically to remove particulates trapped in the voids of the media. Replacement or regeneration of the media may be required depending on feed water quality and media type. The rate of media usage is one of the main operational costs of adsorption technology [30, 65]. Chemicals are used to regenerate media when all active sites are blocked which often results in liquid waste disposal, and media replacement results in solid waste management.

## 4.8 Media filtration

Filtration technology is extensively used for the removal of oil and grease and TOC from produced water [30]. Filtration can be accomplished by the use of various types of media such as sand, gravel, anthracite, walnut shell and others. Walnut shell filters are commonly used for produced water treatment. This process is not affected by water salinity and may be applied to any type of produced water. Media filtration technology is highly efficient for the removal of oil and grease, and efficiency of more than 90% has been reported [30]. Efficiency can be further enhanced if coagulants are added to the feed water prior to filtration. Media regeneration and solid waste disposal are setbacks to this process.

## 4.9 Ion exchange technology

Ion exchange is a widely applied technology in industrial operations for various purposes, including utilization for the treatment of CBM produced water. It is especially useful in the removal of monovalent and divalent ions and metals by resins from produced water [66]. Nadav [67] suggested that ion exchange has the potential to remove boron from RO permeate of produced water. Ion exchange technology has a lifespan of ~8 years and will require pre-treatment options for solid removal. It also requires the use of chemicals for resin regeneration and disinfection. The operating cost accounts for more than 70% of the overall cost of this technology [30].

## 4.10 Chemical oxidation

Chemical oxidation is an established and reliable technology for the removal of colour, odour, COD, BOD, organics and some inorganic compounds from produced water [68]. Chemical oxidation treatment depends on oxidation/reduction reactions occurring together in produced water because free electrons cannot exist in solution [64]. Oxidants commonly used include ozone, peroxide, permanganate, oxygen and chlorine. The oxidant mixes with contaminants and causes them to break down. The oxidation rate of this technology depends on chemical dose, type of the oxidant used, raw water quality and contact time between oxidants and water [30]. Chemical cost during this process may be high [69].

Energy consumption accounts for ~18% of the total cost of operations and maintenance [30]. It requires minimal equipment and has a life expectancy of 10 years or greater and solid separation post-treatment may be employed to remove oxidized particles [30].

## 4.11 Electrodialysis/electrodialysis reversal

Electrodialysis (ED) and ED reversal (EDR) are mature electrochemically driven desalination technologies. These processes involve separation of dissolved ions from water through ion exchange membranes. They use a series of ion exchange membranes containing electrically charged functional sites arranged in an alternating mode between the anode and the cathode to remove charge substances from the feed water (Figure 7). If the membrane is positively charged, only anions are allowed to pass through it. Similarly, negatively charged membranes allow only cations to pass through them. EDR uses periodic reversal of polarity to optimize its operation [30].

EDR and ED technologies have only been tested on a laboratory scale for the treatment of produced water. Sirivedhin *et al.* [8] reported that ED is an excellent produced water treatment technology, but it works best for treating relatively low saline produced water. ED/EDR membrane lifetime is between 4 and 5 years, but major limitations of this technology are regular membrane fouling and high treatment cost [30].

## 4.12 Freeze thaw evaporation

Freeze thaw evaporation (FTE®) process developed in 1992 by Energy & Environmental Research Centre (EERC) and B.C. Technologies Ltd (BCT) is a mature and robust technology for produced water treatment and disposal [70]. FTE® process employs freezing, thawing and conventional evaporation for produced water management. Naturally, salts and other

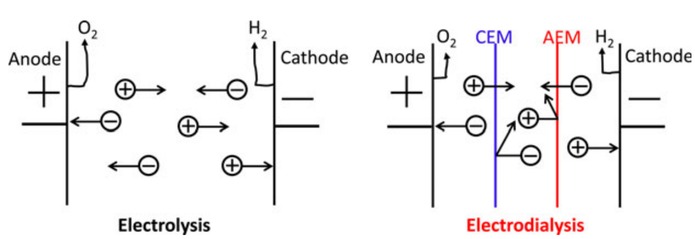



**Figure 7.** *Comparison of electrolysis and electrodialysis (CEM, cation exchange membrane; AEM, anion exchange membrane) [111].*

dissolved constituents in produced water lower its freezing point below 32 F. When produced water is cooled below 32 F but not below its freezing point, relatively pure ice crystals and an unfrozen solution are formed. The unfrozen solution contains high concentration of dissolved constituents in the produced water and it is drained from the ice. The ice can be collected and melted to obtain clean water. About 50% of water can be recovered from this process during winter, but at other seasons, no water is recovered because FTE® works as a conventional evaporation pond. FTE® can remove over 90% of heavy metals, TDS, volatile and semi-volatile organics, total suspended solids and total recoverable petroleum hydrocarbons in produced water [71, 72].

FTE® does not require chemicals, infrastructure or supplies that limit its use. It is easy to operate and monitor, and has a life expectancy of ~20 years [30]. However, it can only work in a climate that has substantial number of days with temperatures below freezing and usually requires a significant amount of land. Waste disposal is essential when using FTE technology because it generates a significant amount of concentrated brine and oil.

## 4.13 Dewvaporation: AltelaRain$^{SM}$ process

Dewvaporation is a desalination technology. A prototype system based on dewvaporation process, AltelaRain$^{SM}$, was developed by Altela Inc. and is already applied in full-scale commercial treatment of produced water. Its principle of operation is based on counter current heat exchange to produce distilled water [73]. Feed water is evaporated in one chamber and condenses on the opposite chamber of a heat transfer wall as distilled water (Figure 8).

Approximately 100 bbl/day of produced water with salt concentration in excess of 60 000 mg/l TDS can be processed by this system [70]. High removal rates of heavy metals, organics and radionuclides from produced water have also been reported for this technology. In one plant, chloride concentration was reduced from 25 300 to 59 mg/l, TDS from 41 700 to 106 mg/l and benzene concentration from 450 μg/l to non-detectable after treatment with AlterRain$^{SM}$ [74].

According to Altela Inc., energy requirements of this system are low because it operates at ambient pressures and low temperatures. This makes it a viable alternative water treatment at remote oil wells where there is no high power grid [74], but there is no information on the overall cost of the system which is likely to be its major disadvantage.

## 4.14 Macro-porous polymer extraction technology

Macro-porous polymer extraction (MPPE) is one of the best available technologies and best environmental practices for produced water management on offshore oil and gas platforms [75]. It is a liquid–liquid extraction technology where the extraction liquid is immobilized in the macro-porous polymer particles. These particles have a diameter of ~1000 μm, pore sizes of 0.1–10 μm and porosity of 60–70%. Polymers were initially designed for absorbing oil from water but later applied to produced water treatment in 1991 [76]. In 2002, the first

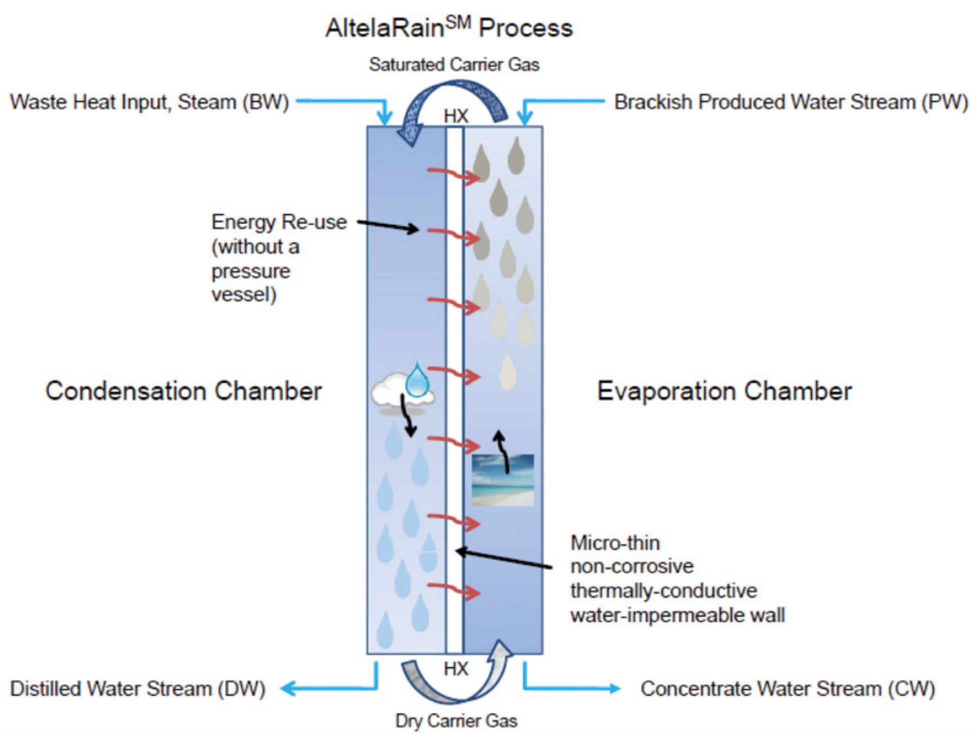



**Figure 8.** *Schematic diagram of AltelaRain$^{SM}$ process [73].*

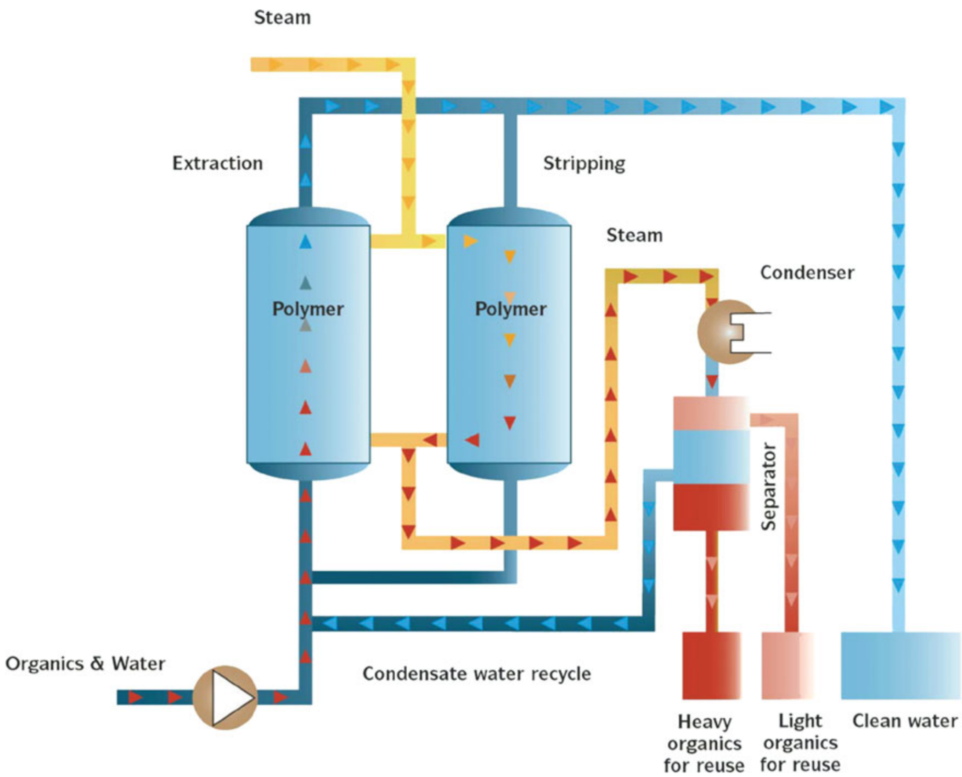



**Figure 9.** *MPPE process [76].*

commercial MPPE unit offshore was successfully installed on platforms in the Dutch part of the North Sea. MPPE was used for the removal of dissolved and dispersed hydrocarbons, achieving >99% removal of BTEX, PAHs and aliphatic hydrocarbons at 300–800 ppm influent concentration. It was also reported that removal efficiency of 95–99% for aliphatics below $C_{20}$ and total aliphatic removal efficiency of 91–95% was possible [77].

In the MPPE unit, produced water is passed through a column packed with MPPE particles containing specific extraction liquid. The immobilized extraction liquid removes hydrocarbons from the produced water as shown in Figure 9. The two columns allow for continuous operation with simultaneous extraction and regeneration [75].

Almost all hydrocarbons present in produced water can be recovered from this process which can in turn be disposed or recycled. Stripped hydrocarbons can be condensed and separated from feed water by gravity, and product water is either discharged or reused.

This technology is essentially used to reduce the toxic content of produced water and can withstand produced water containing salt, methanol, glycols, corrosion inhibitors, scale inhibitors, $H_2S$ scavengers, demulsifiers, defoamers and dissolved heavy metals. Pre-treatment through hydrocyclones or other flotation methods is however necessary before letting produced water from oilfields flow into the MPPE unit. Studies have shown that in gas/condensate produced water streams pre-treatment is not required and MPPE can remove the whole spectrum of aliphatics, as well as BTEX and PAHs [78].

As international legislations seek ‘zero discharge’ of contaminants into the environment and focus on the EIF of contaminants, MPPE will be a major produced water treatment technology in the future. A study carried out by Statoil to compare the effect of different treatment technologies of oilfield produced water on EIF found that the MPPE technology had the highest EIF reduction of ~84% [79, 80]. A relatively high cost of unit is a major disadvantage of this technology. Tables 5 and 6 compare produced water treatment technologies discussed in this section.

## 5 ELECTROCHEMISTRY AND PRODUCED WATER TREATMENT

Electrochemistry is rarely employed in produced water treatment, even though it has been widely used in the treatment of other wastewaters. So far, only ED and EDR are established electrochemical treatment technologies of produced water and are mainly useful when removing salts from produced water for irrigation use. However, heavy metals, oil, produced solids and other contaminants present in produced water can be as harmful to the soil as its salt content. Progress in electrochemistry knowledge and research suggests that electrochemistry

**Table 5.** *Comparison of produced water treatment technologies I.*

| Technology | BAF | Media filtration | Gas flotation | Evaporation pond | MPPE technology |
|---|---|---|---|---|---|
| Feasibility | This is a well-established technology that has been used for produced water treatment [30]. It is mostly effective for feed water with chloride levels below 6600 mg/l [115] | This technology has been extensively used for produced water treatment. It is applicable for all TDS and independent of salt concentration | This technology is widely used in the petroleum industry, primarily used for conventional oil and gas produced water treatment [6, 30]. It is applicable for produced water with high TO and particulate $<$7% solids [30] | This technology is often employed for produced water at full scale. It is applicable to any kind of produced water and its efficiency depends on system design | It is a robust technology applicable for treating both oil and gas produced water. MPPE unit are easy to operate, reliable, fully automated and ideal for process integrated applications |
| Energy consumption | 1–4 KWh | Minimal energy required. Energy is required for backwashing filters | Energy required to dissolve gas in the feed stream | None, except pumping is required to get water to/from the pond | Low energy consumption |
| Chemical use | None | Chemicals required for media regeneration. Coagulants may also be required | Coagulants may be required to remove target contaminants | No chemicals required | None |
| Pre/ post-treatment | Sedimentation may be required as a pre-treatment process. Typically, post-treatment is not required | None required | No post-treatment required, but coagulation may be required as a pre-treatment process | Typically no pre- or post-treatment is required. But post-treatment may be required depending on product water quality | Pre-treatment is required for oilfield produced water but not necessary for gas field produced water |
| Overall cost | Not available but capital accounts for majority of overall cost. | Not available | No information available | Not available | Not available |
| Life cycle | Long lifetime expected | It depends on media type | No information available | Long lifespan | Long |
| Advantages | (1) Water recovery is almost 100% (2) Easy to adapt to wide range of water quality and quantity (3) Little need for maintenance. (4) Does not require post-treatment (5) Some BAF does not require any equipment | (1) $>$90% oil and grease removal efficiency (2) Can achieve nearly 100% water recovery | (1) Product water recovery is almost 100% (2) No post-treatment required | (1) It is very cheap (2) Does not require the use of chemicals and energy | (1) No sludge formation (2) No emission to air (3) Separated hydrocarbons can be reused (4) It is flexible and ideal for process integrated applications and can be used offshore (5) Hydrocarbon removal efficiency is about $>$99% (6) Fully automated and can be remotely controlled (7) No biological fouling because of periodic *in situ* regeneration steam |
| Disadvantages | Solid disposal required for sludge that accumulates in the sedimentation basin can cost up to 40% of the overall cost [30] | Waste disposal system required for spent media or waste produced during media regeneration | (1) Not ideal for high-temperature feed water (2) Solid disposal is required for sludge generated | (1) Water volume may be lost due to evaporation (2) Waste disposal is required for materials that settle out of feed water | (1) High cost of unit (2) Energy consumption is relatively high compared with other technologies (3) Pre-treatment of oilfield produced water increases the cost of processing |

**Table 6.** *Comparison of produced water treatment technologies II.*

| Technology | Adsorption | Hydrocyclone | Ion exchange process | Chemical oxidation | ED/EDR |
|---|---|---|---|---|---|
| Feasibility | This technology is commonly used for produced water treatment. Applicable to all types of produced water irrespective of TDS and salt concentrations. It can significantly reduce heavy metals, TOC, BTEX and oil concentrations. It is best used as a polishing step rather than a major treatment process in order to avoid rapid consumption of adsorbent material | It is applicable for the treatment to all types of produced water irrespective of TDS, organic and salt concentrations. It can reduce oil and grease concentration to 10 ppm | This is a large industrial operation applicable to produced water treatment. It is applicable to produced water with TDS range of 500–7000 mg/l. Efficiency of this technology depends on the quality of feed water and IX resin | This is a well-established and reliable technology for the removal of COD, BOD, organic and some inorganic compounds present in produced water. It is applicable to all types of produced water irrespective of TDS and salt concentration | This technology is robust for seawater desalination and waste water reclamation. Although it is excellent for produced water application it has only been tested for produced water treatment on laboratory scale |
| Energy consumption | Minimal | Does not require energy except to pump water to/from the hydrocyclone | Uses electrical energy. Energy requirements only include pumping costs. Typically 0.07 KWh/bbl assuming a 200 gpm flow rate, 5 m pumping head [30] | Energy consumption accounts for ~18% of the total operation and maintenance of the oxidation process | Energy type: electricity. 0.14–0.20 KWh/lb NaCl equivalent removed [30] |
| Chemical use | Chemicals required for media regeneration | None | Regenerant solution may be $H_2SO_4$, NaOH, HCl, NaCl or $Na_2CO_3$. $H_2O_2$ or NaOCl cleaning solutions may be used to limit fouling | Chemicals such as chlorine, chlorine dioxide, permanganate, oxygen and ozone are required as oxidants | Scale inhibitor required to prevent scaling. Acid, caustic, disinfectant, EDTA and other antiscaling chemicals are required for cleaning and process control |
| Pre/post-treatment | Not relevant because adsorption is usually a polishing stage in produced water treatment | Pre-treatment is not required. Post-treatment may be required to remove other contaminants from feed water | Pre-treatment is essential to remove suspended solids, scaling mineral and oxidized metals. Product water may require remineralization of pH stabilization | No pre- or post-treatment is required | Filtration of fouling and scaling substances in addition to solid particles is a necessary pre-treatment process. Remineralization of product water is also necessary for SAR adjustment and disinfection |
| Overall cost | Not available | Not available | Cost for IX resin varies between \$0.08 and \$0.11/bbl at 5bbl per minute and \$0.04–\$0.07/bbl at 21bbl per minute. Operating costs account for ~70% of the total cost at lower flow rate. At 21 bbl per minute, operating costs increase to ~80% [30] | Capital cost is about \$0.01/gpd. Operation and maintenance cost is about \$0.01/bbl [30]. | Total costs depend on feed water TDS and site location. 8000 bbl/day treatment train of CBM produced water is estimated to cost 15 cents per barrel [116] |
| Life cycle | It depends on media type | Long lifespan | Average lifecycle of anion resins is 4–8 years. Average lifecycle of cation resins is 10–15 years [30] | Expected life of chemical metering is 10 years | ED membrane lifetime is estimated to be 4–5 years [30] |

*Continued*

**Table 6.** *Continued*

| Technology | Adsorption | Hydrocyclone | Ion exchange process | Chemical oxidation | ED/EDR |
|---|---|---|---|---|---|
| Advantages | (1) >80% removal of heavy metals [65]<br>(2) Can achieve nearly 100% water recovery | (1) Does not require the use of chemicals and energy<br>(2) High product water recovery<br>(3) Can reduce oil and grease concentrations to 10 ppm<br>(4) Can be used for treating any kind of produced water<br>(5) Does not require pre-treatment | (1) It requires minimal supervisory oversight<br>(2) May operate continuously for 10–20 h<br>(3) Energy requirements are minimal | (1) It requires minimal equipment<br>(2) No waste is generated from this process<br>(3) It does not require pre- and post-treatment<br>(4) It has 100% water recovery rate | (1) It does not require special infrastructure<br>(2) Modest to withstand harsh conditions<br>(3) Excellent for produced water application |
| Disadvantages | Waste disposal system required for spent media or waste produced during media regeneration | (1) Solids can block inlet and scales formation can lead to extra cost in cleaning<br>(2) Disposal is required for secondary waste generated | (1) High operating and chemical costs<br>(2) High sensitive to fouling | (1) Chemical cost may be high<br>(2) Periodic calibration and maintenance of chemical pump is required<br>(3) Chemical metering equipment is critical for this process | (1) This technology has only been tested on a laboratory scale for produced water treatment<br>(2) Fairly flexible to varying water quality<br>(3) Operation requires highly skilled labour<br>(4) Process requires periodic maintenance and chemical cleaning<br>(5) Concentrate disposal is required |

could be the future treatment technology of produced water. Although current treatment technologies have been used to carry out desalination, de-oiling, removal of suspended solids and in some cases NORM removal from produced water, they are accompanied by many setbacks. High treatment cost, production and discharge of secondary waste, high energy requirement and use of chemicals in some cases are common problems facing these technologies.

Electrochemistry on the other hand is a relatively cheap green technology. It does not generate secondary waste nor involve the use of additional chemicals, and offers improved beneficial uses of produced water. It can generate and store energy, remove organics, produce clean water and recover valuable materials from produced water with little or no negative impact on the environment. This is achievable by harmonizing photoelectrochemistry (photoelectrolysis, photocatalysis and photoelectrocatalysis), water electrolysis, fuel cell, electrodeposition and other electrochemical techniques into a single electrochemical process technology.

Photoelectrolysis is a chemical process of breaking down molecules into smaller units by light [81]. This process has played significant roles in hydrogen production and removal of organics from wastewater [81–86]. Fujishima and Honda [87] first reported the photocatalytic decomposition of water on $TiO_2$ electrodes. This method has been investigated for the removal of organics from produced water and used successfully for a variety of organic pollutant treatment. [5]. Photodegradation of organics has been enhanced by the addition of oxidants such as hydrogen peroxide, peroxymonosulphate (oxone) and peroxydisulphate, but the presence of hydrogen peroxide may induce corrosion process [88, 89]. Semiconductor photocatalysis has been reported to effectively reduce hydrocarbon content in produced water by 90% in 10 min [90].

Photoelectrocatalysis is reported to be a more efficient process for the removal of organics from waste water. Li *et al.* [91] reported that COD removal efficiencies by photoelectrocatalysis from synthetic produced water are much higher than removal by photocatalysis and electrochemical oxidation. Results showed that photoelectrocatalytic degradation of organic pollutants is much favoured in acidic solution than in neutral and/or alkaline solutions. In another experiment, Li *et al.* [92] found that photoelectrocatalysis exhibited a superior capability to reduce genotoxicity to photocatalysis, while photocatalysis did not cause appreciable change in mutagenicity.

Ma and Wang [93] set up a catalytic electrochemical pilot-scale plant for the removal of organics from oilfield produced water, using double anodes with active metal and graphite, and iron as the cathode and a noble metal catalyst with big surface (Figure 10). They found that COD and BOD were reduced by over 90% in 6 min, suspended solids by 99%, $Ca^{2+}$ content by 22%, corrosion rate by 98% and bacteria (sulphate reducing bacteria and iron bacteria) by 99% in 3 min under 15V/120A.

Photoelectrolysis also offers a great promise for inexpensive production of hydrogen and has widely been reported for the generation of hydrogen through water splitting [94–100].

Although not yet competitive on a commercial scale, photoelectrolysis has the potential to become a major hydrogen production process. Powder semiconductor photocatalysts, nano-photocatalysts, photoanodes and several metal oxides are being investigated for improved hydrogen production from water [94, 101]. As these technologies develop, generation of hydrogen from produced water would become a reality. Thus, it may be possible to reduce the energy cost of produced water treatment significantly if removal of organics and generation of hydrogen from produced water is efficiently carried out by photoelectrolysis.

Fuel cell is another major electrochemical technology that is important in the future of produced water treatment technology. Fuel cell converts chemical energy contained in, for example, $H_2$ gas into electricity and generates water and heat as by-products (Figure 11) [102, 103].

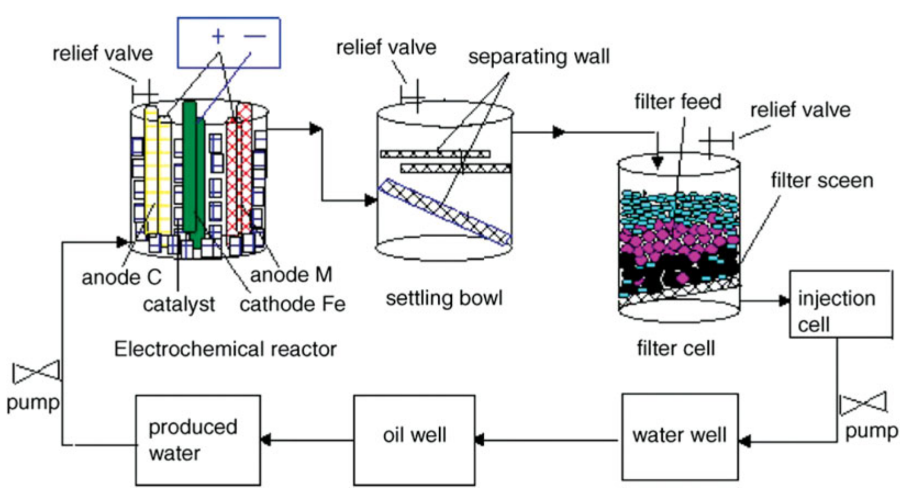



**Figure 10.** *Flow diagram of an electrochemical pilot-scale plant [93].*

This technology is important in converting produced water into drinking water. Hydrogen generated from photoelectrolysis of produced water can be fed into a fuel cell to produce clean water which upon further treatment can be converted into drinking water.

Fuel cell is a particular choice technology for converting produced water into drinking water because it also generates electricity and heat which can be recycled into the treatment process. The application of fuel cell technology to future produced water treatment depends on successful research into its cost reduction, efficiency improvement and increased life span [102].

Electrodeposition is a mature technology that is widely applied in various fields of electrochemistry, particularly in material coating, fabrication of magnetic films and metal recovery [104–106]. It is a cathodic reaction where a metal ion gains electrons to become metal.

$$M^{n+} + ne^- \rightarrow M_{(s)}$$

Some established produced water treatment technologies have reported the removal of heavy metals, but so far, there is no established technology for recovery of metals from produced water and electrodeposition may be used for this purpose. In a recent experiment, we demonstrated that electrodeposition can be used for Cu recovery from produced water. Figure 12 shows the SEM/EDX image of Cu deposits recovered from synthetic produced water in an experiment carried out in our laboratory.

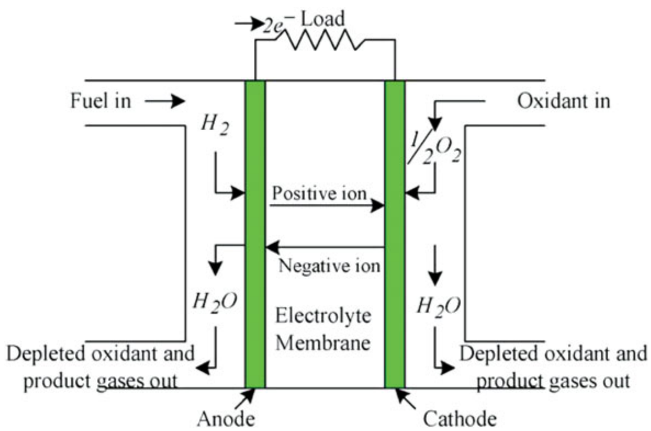


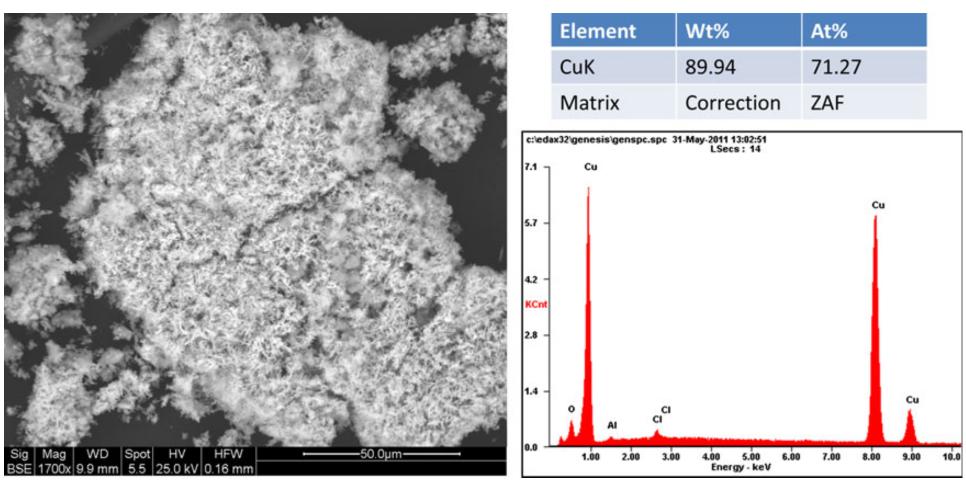

**Figure 11.** *A fuel cell [102].*

Copper was electrodeposited at −0.7 V on a titanium working electrode for 15 min using the chronoamperometry method. The synthetic produced water used in this experiment contained 1000 mmol/mol $Cu^{2+}$ at pH 4. Ag/AgCl and graphite were employed as the reference and counter electrodes, respectively. Full details of this experiment and deposition of other metals from synthetic produced water would be published in another article. Electrodeposition can potentially recover metals that would be otherwise lost in metal removal processes from produced water.

In the future, an electrochemical process unit for produced water treatment would integrate photoelectrochemistry, water electrolysis, fuel cell and electrodeposition technologies to achieve production of clean water, storage of energy and recovery of valuable metals from oilfield produced water.

# 6 CONCLUSION

Raw produced water is commonly regarded as a high-volume toxic waste but can be beneficial to humans if properly managed. The treatment of produced water is very important due to legislation and environmental concerns. In the future, demand for the treatment of produced water as a source of fresh water is very likely with the world population now above 7 billion and the demand for freshwater on the increase. In this article, we have reviewed major produced water treatment technologies and their application in future management. Current thermal produced water treatment technologies are mature but may not be relevant in future management unless



| Element | Wt% | At% |
|---|---|---|
| CuK | 89.94 | 71.27 |
| Matrix | Correction | ZAF |



**Figure 12.** *SEM/EDX of Cu deposit from synthetic produced water.*

significant reductions are made in energy costs. This may be achieved if low-pressure steam is available through cogeneration arrangements. Membrane technologies are some of the finest for produced water treatment today; however, significant progress must be made to reduce membrane fouling and secondary waste generation for them to compete well in the future management of produced water. High costs of rigorous pre-treatment, fouling, and regular backwashing are major setbacks of these technologies for future application. MPPE technology is a fairly new produced water treatment technology that may well compete in the future management of produced water. Its potential to achieve a zero pollutant discharge and a significant reduction in energy consumption compared with thermal technologies are very promising, but advancement is needed to bring down its relatively high cost. It has been reported that to optimize produced water treatment, two or more technologies must be combined or employed in a hybrid system [5], but a cost-effective technology with zero pollutant discharge will be the technology of choice for the future management of produced water and this can be potentially achieved by electrochemistry. The application of electrochemically driven treatment technologies can lead to the production of clean water, production/storage of energy and recovery of valuable materials from produced water by integrating photo-electrochemistry, electrodeposition, fuel cell, ED, EDR and other electrochemical techniques into a single electrochemical unit. This is an achievable engineering task that could make electrochemistry the future produced water treatment technology. Although electrochemistry is not yet a very popular method for the treatment of produced water today, it is very promising and may be the future technology for the management of produced water.

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