

Analysis and Implementation of Polyphase Alternating Current Bi Ionic
Propulsion System for Desalination of Water

by

Suhas Krishna Kashyap

A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved November 2014 by the
Graduate Supervisory Committee:

Joseph Hui, Chair
Raja Ayyanar
Armando Rodriguez

ARIZONA STATE UNIVERSITY

December 2014

ABSTRACT

Scarcity of potable water is one of the major problems faced in the world today. Majority of this problem can be solved if technology is developed to obtain potable water from brackish or saline water. The present desalination methods face challenges such as high costs in terms of energy consumption and infrastructure, physical size of the system, requirement of membrane and high pressure systems and hence have been facing various issues in implementation of the same.

This research provides a new low pressure, low energy, portable method to desalinate water without the need for separation membranes, heat or chemical reactions. This method is energy efficient, cost effective, compact, environment friendly and suitable for portable desalination units. This technology, named as Polyphase Alternating current Bi-Ionic Propulsion System (PACBIPS) makes use of polyphase alternating current source to create a gradient in salt concentration. The gradient in salt concentration is achieved due to the creation of a traveling wave which attracts anions on its positive peak (crests) and cations on its negative peak (troughs) and travels along a central pipe thereby flushing the ions down.

Another method of PACBIPS is based on Helmholtz capacitor which involves the formation of an electric double layer between the electrode and electrolyte consisting of equal and opposite ions which can be approximated as a capacitor. Charging and discharging this capacitor helps adsorb the ions onto a carbon electrode which has high surface area and electrical conductivity. This desalinates seawater and provides pure water. Mathematical modeling, analysis and implementation of the two methods have

been presented in this work. The effects of zeta potential, electric field screening, electric mobility on desalination have been discussed.

DEDICATION

To my Parents, Teachers, Family and Friends.

ACKNOWLEDGMENTS

I would like to thank my advisor Prof. Joseph Hui for his support and guidance during the research work. His level of energy and enthusiasm to innovate has definitely been the major source inspiration for me during my graduate studies at Arizona State University.

I would like to thank Prof. Antonio Armando Rodriguez and Prof. Raja Ayyanar, the members of the Masters Thesis committee for their timely advices and guidance during this period.

My sincere thanks to all professors at Arizona State University whose courses helped me strengthen my technical foundation which was immensely helpful to carry out this research work.

I would like to thank Mr. Ronan Reynolds and Mr. Ankur Ghosh, engineers at Monarch Power for their technical inputs on various issues.

I would like to thank my parents Dr. S. K. Prasad and Mrs. H.A Vani and my sister Miss. Deepali K Kashyap for their constant support and encouragement to complete my Masters studies at Arizona State University.

I would like to thank all my grandparents and elders for their blessings. I would like to thank my friends for their moral support and help.

TABLE OF CONTENTS

	Page
LIST OF TABLES	vii
LIST OF FIGURES	viii
CHAPTER	
1 INTRODUCTION	1
1.1 Background	1
1.2 Motivation for the Research	7
1.3 Objectives of the Research	7
1.4 Scope of the Research.....	8
1.5 Organization of Thesis.....	8
2 LITERATURE SURVEY	9
2.1 Reverse Osmosis	9
2.2 Multi Stage Flash Distillation.....	12
2.3 Forward Osmosis	16
2.4 Electrodialysis	18
2.5 Capacitive Deionization.....	19
2.6 Polyphase Alternating Current Bi-Ionic Propulsion System.....	21
3 POLYPHASE ALTERNATING CURRENT BI-IONIC PROPULSION SYSTEM	23
3.1 Introduction	23
3.2 Forward Motion of the Traveling Wave	25
3.3 Desalination and Propulsion using PACBIPS	28
3.4 Design of the Desalination Unit	29

CHAPTER	Page
3.5 Design of Pontoon for Marine Transportation Application.....	38
3.6 Helmholtz Capacitor based Desaliantion Unit	42
3.7 Operation of Helmholtz Capacitor based Desalination Unit	47
4 MATHEMATICAL ANALYSIS AND RESULTS	48
4.1 Analysis of Electrodialysis	48
4.2 Analysis of PACBIPS	52
4.3 Analysis of Helmholtz Capacitor based PACBIPS	56
4.4 Implementation and Results	78
5 CONCLUSION	82
5.1 Concluding Remarks.....	82
5.2 Scope for Future Work	83
REFERENCES.....	84

LIST OF TABLES

Table		Page
4.1	Stability of the Colloid Depending on the Magnitude of Zeta Potential.....	61

LIST OF FIGURES

Figure		Page
1.1	Composition of the Total Water present in Earth	1
1.2	Relative Growth of Population by Countries in Percentage	3
1.3	Global Water Scarcity by Countries	3
1.4	Major Desalination Types with Respective Percentages of Installed Capacity.	6
1.5	Percentages of Total Worldwide Installed Capacity by Feed Water Category ...	6
2.1	Block Diagram Representation of Reverse Osmosis Process	10
2.2	Multi-Stage Flash Desalination Process and Temperature Profiles	13
2.3	Solvent Flows in Forward, Pressure Retarded and Reverse Osmosis	16
2.4	Four Stages of Capacitive Deionization Technology	20
3.1	Front Slanted View of the Entire Device for Desalination	30
3.2	Front Slanted View Exposing Components at Various Levels.....	31
3.3	Front Cross Section View of the Desalination Tube	33
3.4	Electrical Circuit for 6 Phase AC Generation and Frequency Controller	34
3.5	A View of the Pontoon Used for Marine Transportation Application	39
3.6	A Cross Section View of the Pontoon PACBIPS for Marine Transportation	40
3.7	Electric Field Graph of the Traveling Wave.....	41
3.8	Electrical Double Layer Capacitor Being Charged and Discharged	42
3.9	Three PACBIPS Cells in Series Being Controlled by an AC Source.....	45
4.1	Electrodialysis for the Desalination of Water	49
4.2	Electric Work Needed to Desalt a NaCl Electrolyte	51
4.3	Intertwined Electrode Arrangement Showing the Connected Phase	55

Figure	Page
4.4	Diffuse Layer Capacitance of EDL as a Function of Diffuse-Layer Potential 65
4.5	Charge Distribution in an Electrolyte Adjacent to a Negative Electrode..... 66
4.6	Charge Distribution in an Electrolyte Solution with Two Electrode System . 67
4.7	Equivalent Circuit Representing Charged Electrodes and Electrolyte68
4.8	Typical Slopes of $\frac{\partial q^-}{\partial q}$ versus Electrode Charge..... 70
4.9	Differential Charge Efficiency as a Function of Q_e for Different Q_d Values... 71
4.10	Differential Charge Efficiency as a Function of Q_d for Different Q_e Values 72
4.11	Differential Charge Efficiency as a Function of C_s for Different q_e Values .. 72
4.12	Schematic Representation of the Four Steps of Desalination 74
4.13	Setup of the PACBIPS System for Experimentation..... 78
4.14	Setup of the Helmholtz Capacitor Based PACBIPS System 79
4.15	Handheld Salinity Meter Used to Measure Salt Concentration 79
4.16	Salt Concentration versus Time for the PACBIPS System 80

CHAPTER 1

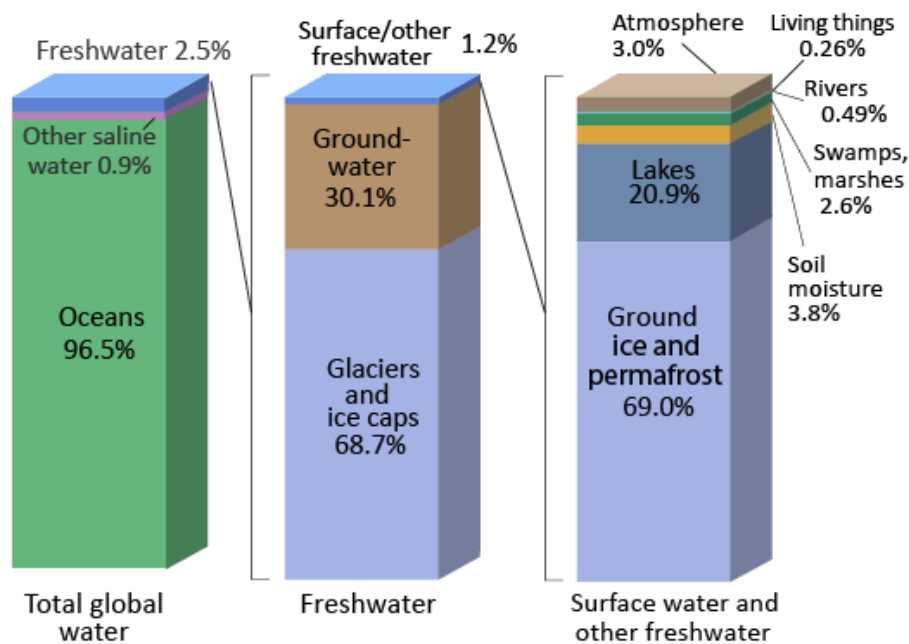
INTRODUCTION

1.1 Background

Fresh water scarcity is a problem faced by many regions of the world. Even though about 71% [1] of the world is covered by water, not all of it is potable. Unchecked growth of population and impairment of fresh water resources are one of the main reasons for the scarcity of potable water. This being more significant in dry regions, people in such areas have no option but to turn towards sea water for consumption, agriculture and drinking.

The distribution of earth's water can be seen in the bar chart in Figure 1[2].

Where is Earth's Water?



Source: Igor Shiklomanov's chapter "World fresh water resources" in Peter H. Gleick (editor), 1993, *Water in Crisis: A Guide to the World's Fresh Water Resources*.
NOTE: Numbers are rounded, so percent summations may not add to 100.

Figure 1.1 : Composition of the total water present in earth [2]

The first bar of figure 1 represents the total global water. From this, it can be seen that only 2.5% of all water present in earth is freshwater. The rest comes from saline sources such as oceans and some lakes.

The breakdown of fresh water on earth is shown in the second bar of figure 1.1, with 68.7% of all fresh water is lost in glaciers and ice caps which cannot be used, 30.1% of the fresh water is ground water. We are left with 1.2 % of surface water that is fresh and easy to obtain.

The third bar in figure 1.2 represents the total surface water and other freshwater present on earth. 69% of the freshwater present on the surface is lost as ground ice and permafrost.

Water scarcity can be defined as the imbalances between availability and demand of water. The major reasons for the decrease in availability and increase in demand are discussed below.

There is an increasing demand for fresh water because of [3]

- a. Exponential growth of population, particularly in dry regions
- b. Increase of individual demands
- c. Industrialization
- d. Excessive use for agriculture

It can be seen that the dry regions have more growth rate in population and hence will have more problems of water scarcity in the near future. These regions are mainly in Africa and middle east. It should also be noted that sea water and brackish water are abundantly available there.

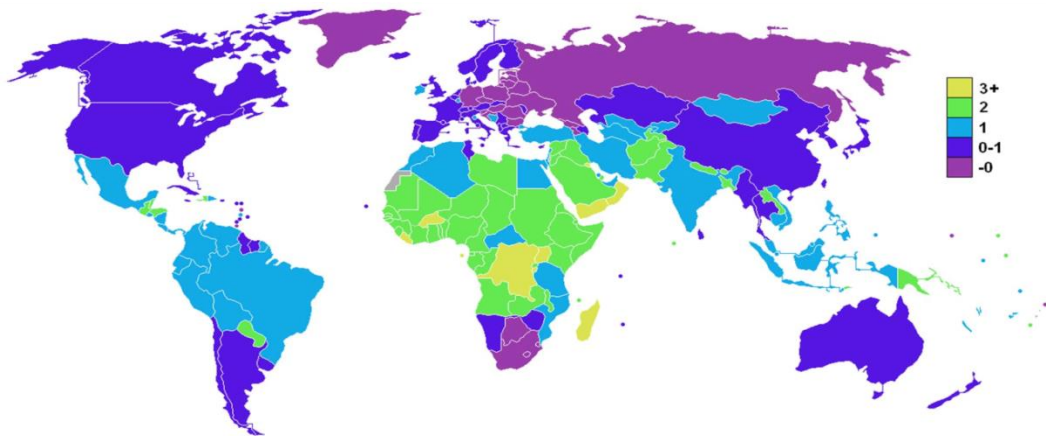


Figure 1.2 : Relative growth of population by countries in percentage [3]

There is a decreased availability of water due to [3]

- a. Dropping ground water level
- b. Intrusion of salt water
- c. Pollution of surface water
- d. Emptying of non-regenerative ground water reservoirs

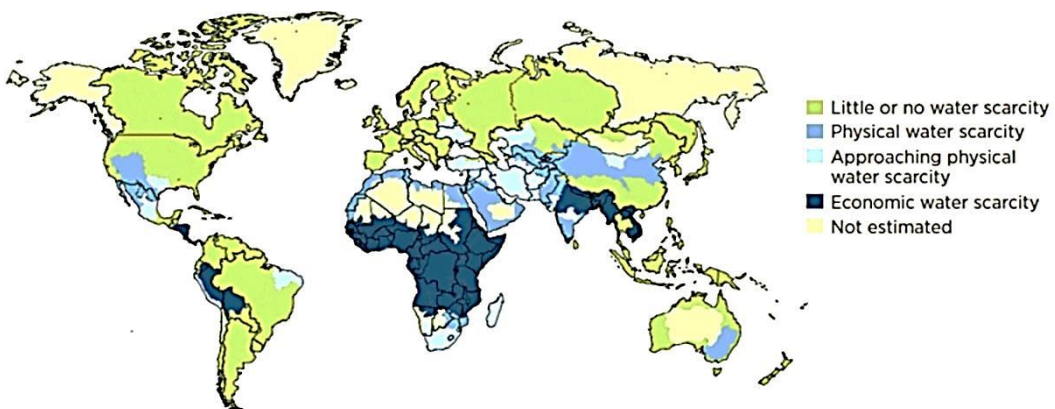


Figure 1.3: Global water scarcity by countries [4]

According to World Health Organization [3], almost 1 billion people in 2008 (nearly 15% of world population), and especially in the developing countries had no access to clean water. In today's advanced technology, it should be possible to feed clean water to the entire population if technology is used in these areas.

About 12 million deaths [3] per year occur due to shortage or consumption of improper water. Most of the migration of people from rural to urban areas in dry countries can be attributed to the search of clean water. Fulfilling the needs of clean water in rural areas can be another answer to solve the problem of extremely high population density in the urban areas.

Even though there is no clear definition of standards for water, it can be classified into three types based on the amount of dissolved solids (mainly salts) 3. The classification of water based on this consideration is as follows

- a. Sea water : 3.5% by weight in TDS (Total dissolved solids)
- b. Brackish water : 0.1 to 1% by weight in TDS
- c. Fresh water : < 0.05% by weight in TDS

World health organization recommends 0.1 % TDS maximum as the standard for potable water [3].

It can be seen that even though freshwater is limited and depleted, a majority of the source of water comes from oceans. Brackish water present in many places is not fit for potable purposes as well. Many dry regions of Asia and Africa which face the problem of water scarcity have access to brackish water and saline water.

The way to solve this problem will be to use desalination techniques and convert the available saline water into potable water. Even though there are many techniques to

desalinate water, these techniques are not cost effective and are very intensive on energy consumption. The high energy consumption and high cost make it impossible for people to have their own portable desalination units.

The major desalination technologies include

- a. Forward osmosis
- b. Reverse osmosis
- c. Multi stage distillation
- d. Electro deionization
- e. Electro dialysis

Among these [3], reverse osmosis is the most popular method which is being implemented. Reverse osmosis accounts for 60% by capacity of the major desalination units installed worldwide. Multi stage flash distillation comes second with 26.8% by capacity out of the total units installed. Figure 4 shows a pie chart showing the key desalination methods and the percentages of installed capacities.

Not all of the installed desalination plants use saline sea water as feed for the process. About 60% [3] of the units use sea water, brackish water feed is not behind with 21.5 % in the category.

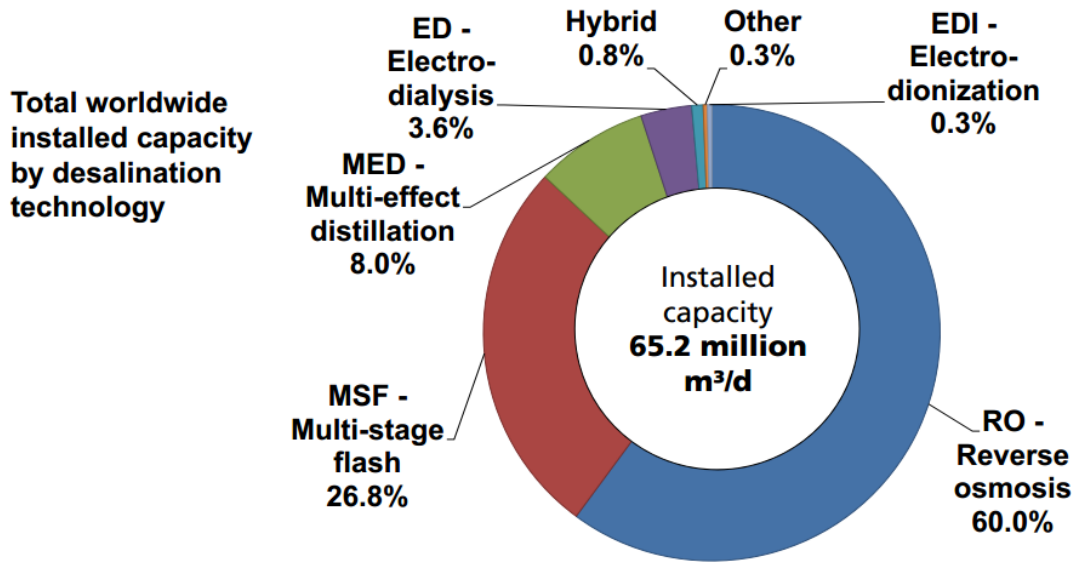


Figure 1.4 : major desalination types with the respective percentages of installed capacity [3]

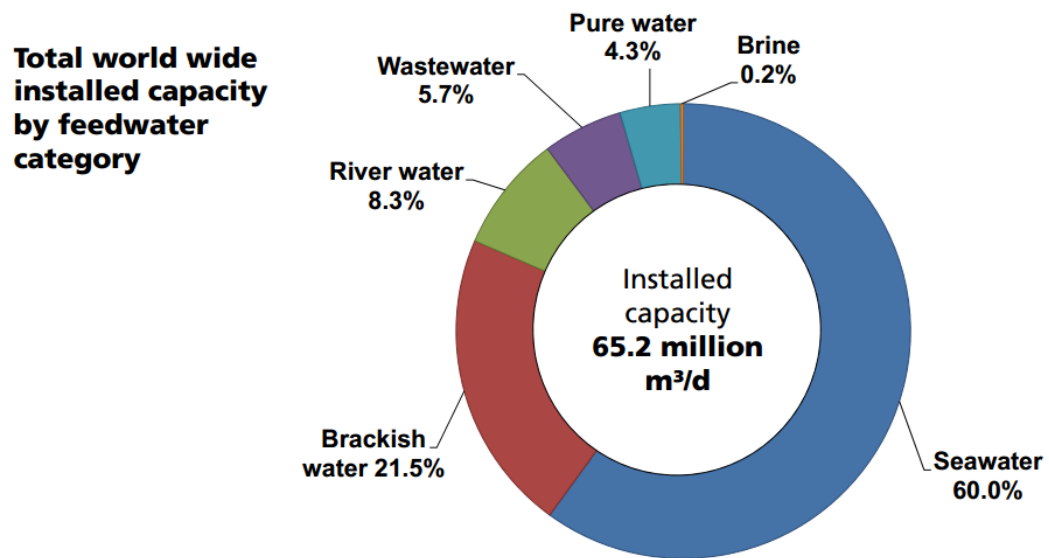


Figure 1.5 : percentages of total worldwide installed capacity by feed water category [3]

The above section shows that there is a need for potable water because of the increase in population and decrease in total available fresh water. We listed key technologies adopted to desalinate water are presented with graphs supporting them with respective percentages for each type of technology. Brackish water is also being used in desalination which can play a key role in solving the water problems of the world.

1.2 Motivation for the research

The abundance of brackish water as well as sea water serve as motivation to come up with innovative technologies for desalination. Even though there are many ways to desalinate water, these methods face challenges such as

- a. high energy consumption
- b. costly infrastructure required
- c. brine discharge

The motivation in this research is to propose a technique which would overcome the above problems and solve the water scarcity problem faced by 15% of the world population, mainly in developing and under-developed regions which are primarily dry.

1.3 Objectives of the research

The objective of this research is to implement and analyze a method to desalinate water so that we have the following features

- a. Less energy consumption and infrastructural costs
- b. Does not use a membrane to separate the ions
- c. Adsorbs the ions onto the surface with large capacitance
- d. Uses polyphase alternating current for powering the unit

1.4 Scope of the research

The scope of the research is limited to desalination of sodium chloride (NaCl) salt from water. Deionized water added with 3.5% Sodium Chloride by weight is considered to be equivalent to sea water. Further research need to be done to claim this technology as industrially scalable.

1.5 Organization of thesis

The thesis organization has been described in this subsection.

Chapter 1 introduces the problems of water scarcity, different methods of desalination, motivation, objectives and scope of the research.

Chapter 2 provides a detailed literature survey of different prominent desalination units, the advantages and disadvantages of the same, recent research advances of the methods.

Chapter 3 introduces the idea of PACBIPS and provides a mathematical formulation of the traveling wave. This chapter also provides details of the PACBIPS unit fabricated using 3D printed techniques and different parts of the same.

Chapter 4 provides mathematical modeling and analysis of the PACBIPS system. The electrical double layer capacitor and electro adsorption based desalination theory will be discussed. We also present the implementation and results of the desalination system.

Chapter 5 provides concluding remarks and outlines the scope for future work

CHAPTER 2

LITERATURE SURVEY

The literature associated with desalination of water is presented in this chapter. The major desalination technologies are described and the latest trends in research related to these technologies are presented. The key desalination technologies are reverse osmosis, multi-stage flash, multi-effect distillation, electro dialysis. Capacitive deionization technique is one of the most recent technologies which have made good impact on the recent research trends.

2.1 Reverse osmosis

Reverse osmosis is one of the oldest, yet most successful methods of desalination. About 60 % of the desalination units in the world today use this method. Reverse osmosis is a desalination method which uses a membrane which separates the feed water from the solids dissolved in it. Feed water is delivered with a certain pressure and this water enters the membrane and permeates through the tiny pores and permeate water which is pure is obtained from the other side. This method requires water to be delivered at a pressure which is capable of overcoming osmotic pressure driven by chemical potential. The membrane is designed to be selective. It has to allow molecules smaller than a certain size while blocking other molecules. This enables the solute is remained on one side of the membrane which is more pressurized while the pure solvent is passed through the membrane and can be collected from the other side.

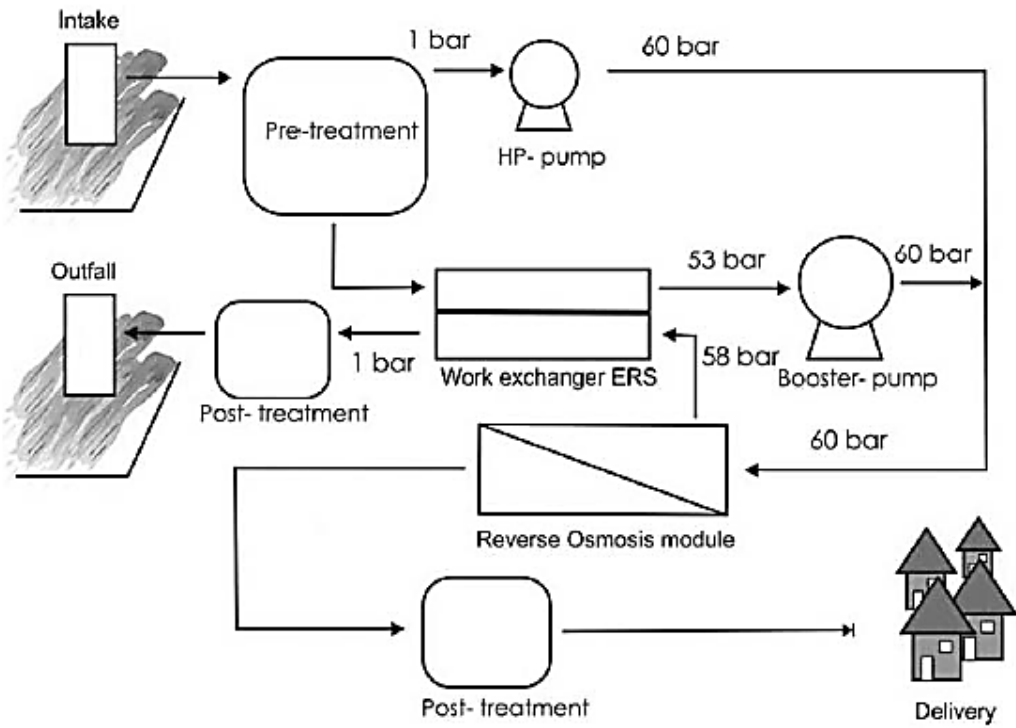


Figure 2.1 : Block diagram representation of Reverse osmosis process [5]

Reverse osmosis consists of these main components

- a. Water abstraction
- b. Pretreatment stage
- c. High pressure pump
- d. Separation membrane
- e. Energy recovery system
- f. Post treatment
- g. Control system

Separation membrane is used to separate the dissolved solids from the water and thereby obtain pure water.

A popular recent work on “State-of-the-art of reverse osmosis desalination” by Fritzmann et al, 2007 [5] describes the latest advances in reverse osmosis technology. Abstraction of feed water can be realized either through open wells or sea water intake systems. Open wells provide better quality water in terms of less algae, less total dissolved salts and less turbidity than sea water intake [6,7], but may require more space. Wells are used to feed water in brackish water desalination. Pretreatment stage is a stage in which suspended solids in water are removed. This stage ensures that there is no microbial growth in the membrane. In this stage, intake water constituents are adjusted and maintained at a particular pH value. Pumping system ensures that the height difference in the chain is overcome. High pressure pumps are used to increase the pressure of water flowing into the membrane as the pressure has to be more than the osmotic pressure. The membrane is capable of separating salt from saline water with a rejection ratio of 98% - 99 % depending on the membrane in use [6]. In post treatment, water is re-mineralized and its various constituents are adjusted to match drinking water standards. Figure 2.1 shows a reverse osmosis desalination unit with open sea water intake and energy recovery system.

Most of the recent research in reverse osmosis is related to development of membranes with better performance. The paper ‘Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes’, by Childress et al., shows that humic substances and surfactants are readily adsorb to the membrane surface and markedly influence the membrane surface charge.

The paper ‘Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes’ by Elimelech

(1997) et al., establishes a new thin film composite membrane in place of the conventional cellulose membrane.

The advantages of Reverse osmosis (RO) as explained in [10] are as follows

- a. RO systems are capable of removing both organic as well as inorganic pollutants
- b. RO systems require less energy as compared to other thermal methods of water desalination
- c. RO systems allow easy recovery of waste water streams
- d. RO processes have the capability to reduce considerably the volume of waste water streams
- e. Since the RO system is electrically driven, it can be easily powered by renewable energy systems

Reverse osmosis uses a membrane and does not involve the change in state of the feed water unlike other forms of desalination such as thermal methods. This makes reverse osmosis systems more energy efficient.

2.2 Multi stage flash distillation

Multi stage flash distillation is a method of desalination in which the feed water is desalted by flashing selected streams of water using heat exchangers. The multi stage flash plant involves multiple stages with each stage corresponding to a heat exchanger and a condenser. The plant has a low temperature end and a high temperature end and the intermediate stages have intermediate temperatures. The intermediate stages have different pressures with each corresponding to the boiling point of water at these temperatures.

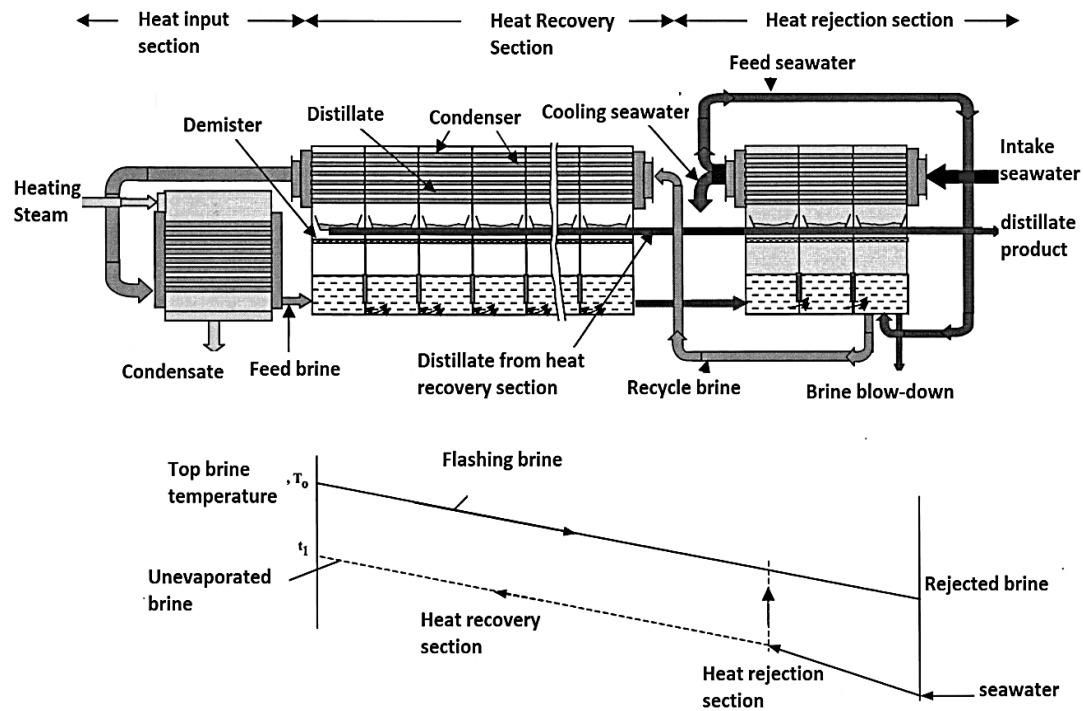


Figure 2.2 : Multi-stage flash desalination process and temperature profiles [11]

Figure 2.2 shows a schematic diagram of the multi stage flash desalination process. The system involves six main streams which are [11]

- a. Intake seawater
- b. Rejected cooling seawater
- c. Distillate product
- d. Rejected brine
- e. Brine recycle
- f. Heating steam

The system contains flashing stages, a brine heater, pumping units, venting system and a cooling water control loop. Flashing stage is a stage where water is flashed into heat by application of heat. The multiple flashing stages in the system are divided into heat

recovery and heat rejection systems. The heat rejection section is limited to 3 sections whereas the heat recovery section varies between 21 and 40 [11].

When the plant is operating in steady state, feed water enters the cold temperature inlet. It goes through a series of heaters and it finally reaches the maximum temperature at the end of the plant. Here it reaches the brine heater where it is supplied with additional heat.

The saturated heating steam with a temperature range of 97-117° C [11] drives the flashing process. The hot brine enters the first flashing stage, where a small amount of product vapor is formed. The temperature drop across the stages causes a drop in the stage pressure. The highest pressure is in the first stage which is the high temperature stage and the lowest pressure is in the last stage which has the lowest temperature. Pressure drop creates a way for the brine flow without use of the inter stage pumping units. This saves infrastructural costs for the pumping system.

Each stage independently acts like a desalination unit. In each stage, the flashed off vapor flows through the demister which condenses and removes droplets of unevaporated brine. The vapor then condenses on the outside surface of the preheater/condenser tubes. The condensed water collects on a tray in each of the stages and is finally drawn in to form the final product water, which is withdrawn from the last flashing stage.

The condensation process releases the vapor latent heat, which is used to preheat the brine recycle. The same process takes place in the heat rejection stage as well. This process makes the sea water hotter and results in it being equal to the temperature of flashing brine in the last stage of heat rejection stage. At this stage, the intake seawater stream leaves the heat rejection section, where it splits into two streams. The first stream

is the cooling seawater stream. This is rejected back to the sea. The second is the feed seawater stream which is mixed with brine pool in the last flashing stage in the heat rejection stage. Before this mixing takes place, the rejected brine stream is withdrawn from the brine pool. But, the brine recycle is withdrawn from a location after the mixing point. The brine blowdown is rejected to the sea and the brine recycle is introduced to the last stage of the heat recovery section.

Marcovecchio et al., in their work [12], ‘Optimization of hybrid desalination processes including multi stage flash and reverse osmosis systems’ have developed a mathematical model for the optimal synthesis and design of hybrid desalination plants, including multi stage flash. They propose a mathematical model in which optimization can be performed not only on operating conditions but also process configurations simultaneously. Thus, this model ensures correct definitions of flow rates, salt concentrations and temperature for each stream. It proposes relationship between membrane and thermal desalination processes.

Zel-Dessouky et al., in their work [13], ‘Multi-stage flash desalination: present and future outlook’ provide a summary of the different multi-stage flash desalination methods and a comparison between them. The study compares conventional multi stage flash distillation with improved multi stage flash distillation proposed by the authors and once-through arrangement of multi-stage flash distillation. The final comparison parameter is the salt concentration of rejected brine (in ppm) of the different methods. Other parameters such as flow rates, temperature, etc. have also been compared.

Hamed et al. (1999), in their work [14], ‘The performances of different antiscalants in multi-stage flash distillers’ have compared the performance of three types of antiscalants

in desalination units in Saudi Arabia. The antiscalants compared are Polycarboxylates, Polymaleic acid, Polyphosphonate. The study claims that one of the main ways to control alkaline scale formation in commercial MSF distillers was successful operation at low antiscalant dose rates. The dose rates proposed are as low as 0.8 and 2.2 ppm for low and high temperature respectively.

2.3 Forward osmosis

Forward osmosis is a membrane based desalination method in which osmotic pressure gradient is created across a membrane to create a flow in the feed water. The semi-permeable membrane is used to effect separation of water from dissolved solutes. The driving force for this process is the osmotic pressure gradient because of the difference of concentration.

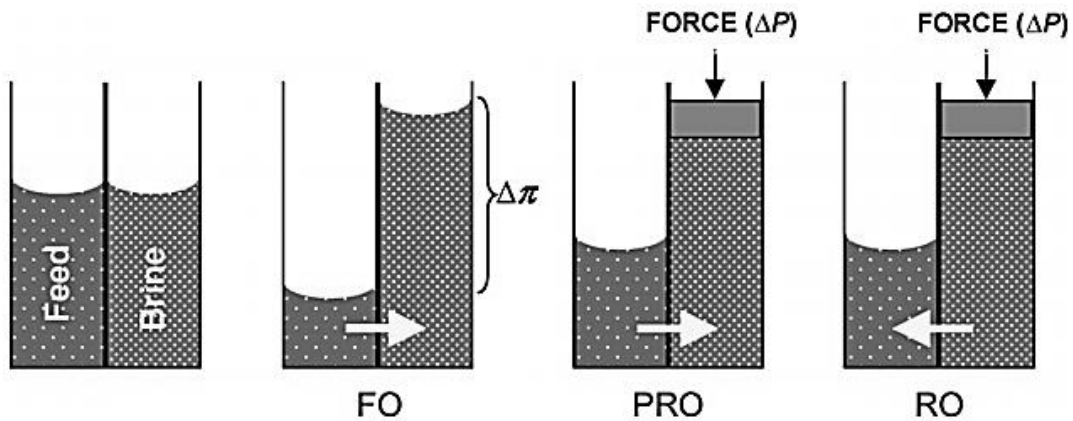


Figure 2.3: Solvent flows in Forward, pressure retarded and reverse osmosis

Figure 2.3 explains the difference between forward osmosis, reverse osmosis and pressure retarded osmosis in terms of solvent flow. Pressure retarded osmosis (PRO) can

be viewed as an intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to RO). However, the net water flux still is in the direction of the concentrated draw solution [16].

Any dense, non-porous, and selectively permeable material can be used as a membrane for FO. Such membranes [16] have been tested (in flat sheet and capillary configurations) in the past for various applications of FO. Early membrane researchers experimented with every type of membrane material available, including bladders of pigs, cattle, and fish; collodion (nitrocellulose); rubber; porcelain; and goldbeaters' skin.

During the 1990s, a special membrane [16] for FO was developed by Osmotek Inc. (Albany, Oregon) (currently Hydration Technologies Inc. (HTI)). This membrane has been tested in a wide variety of applications by different research groups [17-19]. It is also successfully used in commercial applications of water purification for military, emergency relief, and recreational purposes [20]. This proprietary membrane is thought to be made up of cellulose triacetate (CTA). It can be seen that the thickness of this membrane is less than 50 μm and can be seen as something different than the standard RO membranes.

RO membranes typically consist of a very thin active layer (of about 1 μm) and a thick porous support layer. The CTA FO membrane lacks a thick support layer. Instead, the embedded polyester mesh provides the support for this.

In summary, the desired characteristics of membranes for FO would be high density of the active layer for high solute rejection; a thin membrane with minimum porosity of the support layer for low internal concentrative polarization, and therefore, higher water flux; and high mechanical strength to sustain hydraulic pressure when used. The

development of improved semi-permeable membranes for FO is critical for advancing the field of FO.

Different types of membrane modules are available for forward osmosis. The most popular among these are plate-frame, spiral wound, tubular and hydration bags [16].

Plate-frame is the simplest device for packing flat sheet membranes in a module. Two of the main limitations in this type of module [16] are lack of adequate membrane support and low packing density. These limitations limit the operations to lower pressure operations and increases infrastructural and capital costs.

Spiral wound is another type of membrane module for osmosis. It is difficult [16] for this to be used for FO because the draw solution cannot be forced to flow inside the envelope formed by the membranes.

Hydration bag is another type of flat membrane module which contains two bags, one inside the other. The inside bag is the FO membrane and the outside membrane is the plastic bag consisting of the feed water to be treated.

Forward osmosis has been studied for a range of applications. Commercial applications, though still limited are emerging in the water purification industry (e.g., extraction bags) and in the pharmaceutical industry (e.g., osmotic pumps).

2.4 Electrodialysis

Another method of desalination uses the process of electrodialysis. The process is derived from electrolysis with the addition of membranes porous to ions next to the electrodes. Salt water flows into a chamber. Cations, for example the sodium ions of positive charge can pass through a porous membrane as the cations are attracted towards the negatively charged cathode. Anions, for example the chloride ions of negative are

attracted towards the positively charged anode. While they move towards the anode, they move across a membrane. In the process, the salt water that flows into the chamber is rid of both anions and cations and flows out of the other end of the chamber relatively pure.

Electro-dialysis uses Direct Current (DC) to remove ions. At the cathode side, sodium hydroxide (in the ionic form of Na^+ and OH^-) is generated. At the anode side, chlorine gas in a dissolved form is generated. These noxious chemicals are delivered to a recombination tank to regenerate the innocuous NaCl salt. Thus the electrolysis and resulting recombination not only generate undesirable chemicals but also waste energy as the recombination is exothermic.

2.5 Capacitive Deionization (CDI)

Capacitive deionization is a membrane less electrochemical desalination method which desalts water based on the application of a voltage across two electrodes. This method works by taking advantage of the excess ions adsorbed in the electrical double layer near the electrode-solution interface when the electrode is powered by an external power supply.

When the electrode has a high specific area, this adsorption becomes more significant. This factor becomes a key factor for electroadsorption quality and attractiveness for water treatment.

The electrical double layer can be expressed in terms of two capacitors in series. The two capacitors in series are capacitance between electrode and the adsorbed ion layer and capacitance between adsorbed ion layer and electrolyte solution.

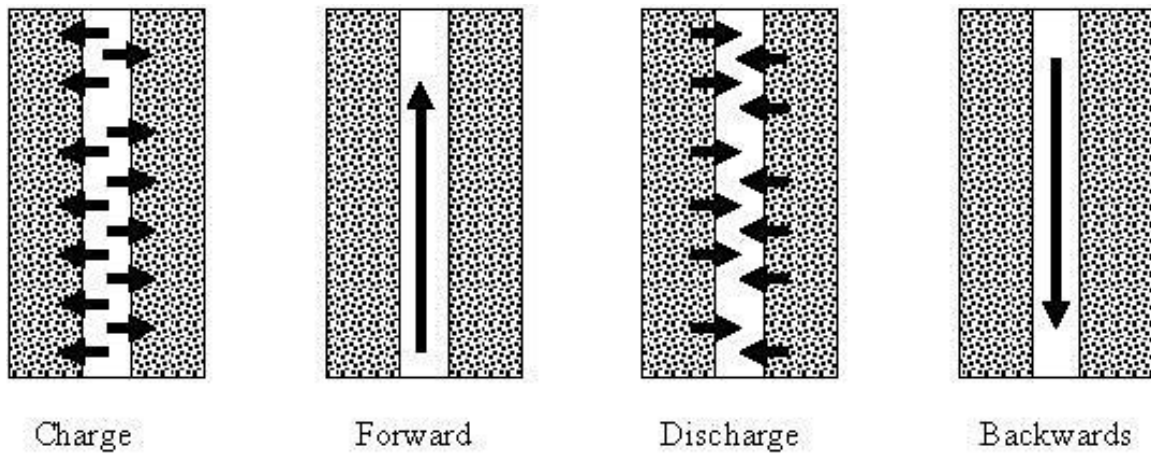


Figure 2.4 : Four stages of capacitive deionization technology

As seen in figure 2.4, capacitive deionization is done in four stages.

The four stages are

- a. Charging stage
- b. Forward movement
- c. Discharge stage
- d. Backward movement

Charging stage is the stage in which positive voltage is applied across the electrodes. This causes the ions in the electrolytic solution to get adsorbed into the adsorption layer which is normally a fiber glass composite.

In the next stage, water is pumped in the forward direction. This water which can be collected from the other end is deionized and hence is free from salts.

In the next stage, when the adsorption layer is full of ions, reverse voltage is applied to remove ions from this layer and then the ions enter the electrolytic solution. This solution flows backward. This is the final stage. Hence, there is a gradient in the salt concentration in the tube. This is the general principle of capacitive deionization technology.

Early studies on CDI date to the mid-1960s and the early 1970s. The concept was first introduced by Caudle et al. [21], who used porous carbon electrodes made of activated carbon powder in a flow-through mode for water desalination. Later, Johnson et al., [22] studied CDI as a process which is reversible. Their work comprised parametric studies with investigations of different types of electrode materials.

The investigation taken up by Johnson et al. was later discontinued as they were faced with the challenge of unstable electrode, especially the anode electrode. However, his study established that a low cost desalination technology can be derived out of this concept, provided that sufficiently stable high-surface area electrodes could be produced.

Following this work, Johnson and Newman [23] published a comprehensively theoretical analysis of ion adsorption on electrodes that are largely porous. The work of Johnson and Newman mainly gives us an idea of the basic factors that govern CDI. This research was accompanied by other efforts that tried to develop novel electrode materials for efficient and small and semi-pilot devices for CDI for desalination and treatment of saline water.

However, CDI has still not emerged as an alternative source for desalination. It still is not industrially scalable. It remains a project on pilot scale and demonstration units and not a valid commercial technology.

2.6 Polyphase alternating current bi-ionic propulsion system (PACBIPS)

Dr. Hui in the patent filed in 2014 [24], has claimed a new method which can purify water by creating a travelling wave by means of polyphase alternating current. This travelling wave has the ability to attract both the cations and anions in the electrolytic

solution. The positive crest of the wave attracts anions and negative trough of the wave attracts cations.

As the travelling wave moves forward, these ions get propelled away and thus the water is de-ionized. The propelled ion may also drive the motion of seawater by means of viscosity, providing a motive reaction to move a marine vehicle

The apparatus proposed in the patent removes dissolved salt from water with relatively low energy, and being of small size could have a big impact for farming and small communities without the need for large and energy intensive desalination plants.

The apparatus houses two tanks, one to store the deionized water and the other to store the saline water. The apparatus provides a salt concentration gradient between tanks by making ions travel from one tank to the other. The travelling ions are a result of the travelling wave created because of the applied polyphase alternating current.

This method is efficient as it does not involve chemical energy conversion, heat exchange. Thus, this method is claimed to have better energy efficiency than conventional methods such as multi stage flash, reverse osmosis, forward osmosis, etc.

CHAPTER 3

POLYPHASE ALTERNATING CURRENT BI-IONIC PROPULSION SYSTEM

This chapter introduces the idea of desalination by creating a traveling wave with the application of polyphase alternating current. The model of the desalination device is shown and the individual parts in the device are described.

3.1 Introduction

Polyphase alternating current bi-ionic propulsion system (PACBIPS) for desalination of water was proposed by dr. Joseph Hui in 2014 in the patent [24]. This method creates a traveling wave of Electric field by the application of polyphase alternating current. The traveling wave is created in the electrolytic solution. The cations of the solution are attracted by the negative troughs and the anions of the solution are attracted by the positive crests. The traveling wave propels the ions forward and hence the electrolytic solution is devoid of charges and is said to be deionized. Thus, the purpose of desalination is achieved. The propelled ion may also drive the motion of seawater by means of viscosity, providing a motive reaction to move a marine vehicle

The method is mainly used to purify water with low or medium salinity. This grade of water is also called brackish water. The desalination of this grade of water can solve the water scarcity problems of many regions for the purpose of agriculture and human consumption.

This apparatus consumes relatively less energy when compared to other forms of desalination, and being small size this has the capability to revolutionize desalination for farming and small communities and reduce the need for energy intensive large scale desalination plants.

Energy used for the desalination of water is said to be proportional to the amount of salt present in the solution. This method is therefore suitable for lower salt content removal such as blackish or polluted water.

The goal of the research was to make desalination free from significant infrastructural costs. So, this method is designed to use only electricity, for example that generated by solar panels, without the need for pressure, heat, dialysis, or semi-permeable membranes which require significant capital investments.

The traditional means of desalination includes multistage flash distillation, reverse osmosis, or electric dialysis. In these methods, large amount of energy is required to boil water, to force pure water devoid of salts through osmotic membranes, or push ions through dialysis membranes permeable to either positive or negative ions.

PACBIPS does not use heat, pressure, or chemical reactions as other methods do. It uses less energy by using electrostatic forces to directly de-ionize water. It also avoids chemical processes that occur at the electrodes and in the recombination reservoir.

PACBIPS does not use Direct current (DC) to create an ionic movement. Instead, it uses alternating current to create a conveyor belt of ions. This principle is very similar to the concept of linear induction motor, but it makes no use of an induced magnetic field to generate a magnetic motive force. The polyphase AC applied to the electrodes creates a traveling wave.

A simple analogy to this concept is ocean waves. Ocean waves are traveling waves. The up and down movement of water brings about a horizontal movement in the seawater towards the shore. A surfer takes advantage of the front slope of the traveling wave, using

its gravitational potential in the wave crest to realize his motion and travel towards the shore.

This invention uses electric field forces instead of gravitational field forces. Instead of inertial mass, it uses both positive and negative electrical charges. Thus we have cations which travel in the crest of the electric field wave, and anions which travel in the trough of the electric field wave. Both types of ions travel in the same direction of the traveling wave.

There are many methods to generate the traveling wave. One method is the use of polyphase AC power source that drives intertwining electrodes of successive phases of the AC voltage. These electrodes are insulated from the electrolyte and therefore no chemical process occurs at these electrodes. The electrodes therefore function more like capacitors holding charges to attract the oppositely charged ions.

Similar to oceanic surfing, the electrodes create time changing electric potential. Successive electrodes are of differing electric potential and therefore create an electric field from a lower potential electrode to the higher potential electrode. This differential electric field therefore drives the motion of the ions, with motion of cations towards the direction of lower electric potential and the motion of the anions towards the direction of higher electric potential.

3.2 Forward motion of the traveling wave

A polyphase AC source is defined as an AC source with two or more phases. Let the number of phases be denoted by ' N '. An AC source with $N = 2$ phases is sufficient to create a travelling wave. However, a traveling wave is said to be more continuous for a large N .

Considering a practical scenario, we assume $N = 3$ suffices to maintain the continuity of the traveling wave. We take advantage of the ubiquitous industrial three phase power source of frequency $f = 60 \text{ Hz}$.

The electrodes carrying these phase voltages need to be discrete. In our study, we assume them to be like rings around an insulating tube. The salty water flows through the insulating tube. More conveniently, the electrodes can be N long wires intertwined with each other. The electrodes for the same phase are spaced at a distance of ' d ' from each other. This can be achieved by placing electrodes labeled $1, 2, 3, \dots, N, 1, 2, 3, \dots$ and so on with the electrode ' i ' being tied to the i^{th} phase of N -phase AC power source.

$$V_i(t) = A \cos\left(2\pi\left(ft - \frac{i}{N}\right)\right)$$

The i^{th} electrode is placed at the location $x_i = \frac{id}{N}$

Considering the arrangement of intertwined wires mentioned earlier, we can say that the i^{th} electrode which starts at position x_i , makes intertwining full turns around the tube at the positions x_{N+i} , x_{2N+i} and so on, as described in the following equations

$$x_{N+i} = \frac{(N+i)d}{N}$$

$$x_{2N+i} = \frac{(2N+i)d}{N}$$

The traveling wave we wish to create has a wavelength $\lambda = d$, the electrode spacing. The velocity of the traveling wave is $v = fd$.

The traveling wave has a voltage dependent on both space and time

$$v(x, t) = A \cos\left(2\pi\left(ft - \frac{x}{d}\right)\right)$$

If we consider a crest with a phase 0 in the traveling wave,

$$ft - \frac{x}{d} = 0$$

$$x = fdt$$

$$x = vt$$

$$\text{because } v = fd$$

The discrete nature of the electrodes samples the continuous traveling wave such that $V_i(t) = V\left(x = \frac{id}{N}, t\right) = A \cos\left(2\pi\left(ft - \frac{i}{N}\right)\right)$

The voltage between these discrete electrodes can be defined as the linear interpolation of the respective voltages.

Taking the simplest case of Polyphase AC, we have $N=2$ and this gives

$$V_1(t) = -V_2(t) = V_3(t) = -V_4(t) = \dots \text{etc.}$$

This alternating signage gives an alternating electric field from one electrode to another electrode. The cations, which are positively charged, are accelerated in between two electrodes with electric field going from left to right; whereas the anions are accelerated in the same direction in the next pair of electrodes as the electric field is reversed in between the next pair because of the alternating signage.

If the velocity of the ions matches that of the velocity of the traveling wave, that is $v = fd$, the electric field reversal of the next pair of electrode will occur just in time for the ions to travel further down. This phenomenon is similar to the surfer being carried forward by the front of an oceanic wave.

This works similarly for other larger N , and in the limit of very large N , the piecewise linear traveling wave now resembles the continuous wave.

$$V_i(t) \approx A \cos(2\pi ft)$$

As described earlier, the cations are carried by the trough (negative voltage) of the traveling wave and the anions are carried by the crests (positive voltages) of the traveling wave.

3.3 Desalination and propulsion using PACBIPS

The flow of cations and anions in alternating band becomes a motive force for the electrolyte by means of viscosity of fluid flow. The flow is expected to be self-primed similar to the self-priming motion of the Tesla-three phase induction motor. Another priming method is seen from the equation for the velocity of the traveling wave $v = fd$, for which we may initiate motion of the electrolyte by starting with a small ' f ' at the beginning or a small ' d ' at the front end of the tube to give the initial thrust.

It is preferred to have vertical displacement of ions instead of horizontal displacement. In the application of desalting NaCl salt from seawater, the sodium (atomic weight 23) and chloride ion (atomic weight 35.5) are heavier than that of water (molecular weight 18). The viscosity of water ensures that the velocity of water increases from zero along the fluid-tube boundary to velocity of $v = fd$ at the center of the tube. It is proposed to have a counter flow in the center so that the ions are given a downward concentrating motive force, creating a concentration gradient of salt with the concentration being highest at the bottom of the tube. This fulfills the function of desalination.

The same electromotive force can be used to achieve marine propulsion for a high velocity of $v = fd$. In this case, both f and d will be much bigger. The boat designed based on this principle will have a motor which works on the same principle an electric car uses for the control of its velocity. The variable frequency is used to control the forward velocity

of the boat. Tubes which are also used as pontoons are lined on the inside with intertwined Polyphase electrodes. The spacing of the electrodes is variable. The spacing is small and then goes wide towards the fluid ejection end.

The frequency of the Polyphase AC power source can be controlled by a pulse width modulation (PWM) inverter to convert DC to AC. The DC source being either solar powered or a DC battery. The current of the Polyphase circuit can be controlled by the variable inductor placed in series with each of the electrode, with the current controlled according to ohm's law

$$I = \frac{V}{Z} ; \text{ where } Z = j2\pi fL + R$$

The complex impedance Z depends on the frequency f of the circuit, inductance L and the resistance R of the circuit.

3.4 Design of the desalination unit

This subsection describes the design and fabrication of the desalination unit built using solidworks modelling and 3D printing. Since there are a large number of parts in the following drawings, each part has been associated with a part number.

The external view of the desalination apparatus is shown in figure 3.1. An upper tank 101, which holds diluted electrolytic solution, has a desalinated water outlet 102. A lower tank 103, which holds concentrated electrolytic solution, has a strong brine outlet 104. As shown, there are four desalination tubes 105, 106, 107 and 108 that provide an electromotive force to move ions from the upper tank to the lower tank.

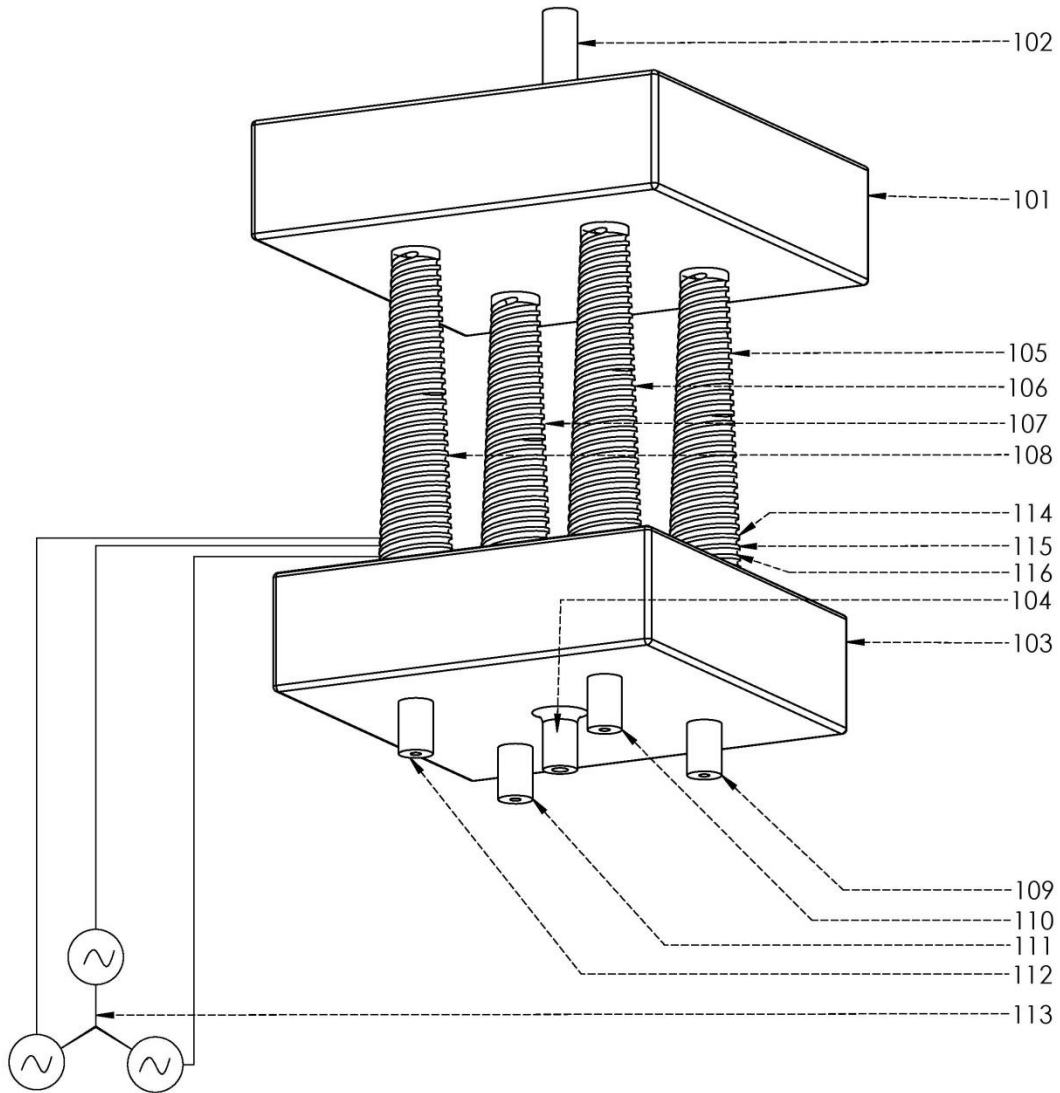


Figure 3.1 : Front slanted view of the entire device for desalination

Removed liquid from 102, 104 are replenished from fresh electrolytic solution into the tubes 105, 106, 107, 108 at the center of the tubes through the inlets 109, 110, 111, 112 respectively. The three phase power source 113 provides the electro motive forces for ions, as shown in the intertwined electrodes 114, 115, 116.

An exploded transparent view of the same desalination apparatus is shown in Figure 3.2. The lower tank 101 comprises a vessel for holding strong brine 201 with brine exit hole 202. The fresh brine inlets 109, 110, 111, 112 are further extended by tapering tubes 203, 204, 205, 206 respectively, so that fresh electrolytic solution is introduced in the middle and inside portion of the desalination tubes 105, 106, 107, 108 respectively

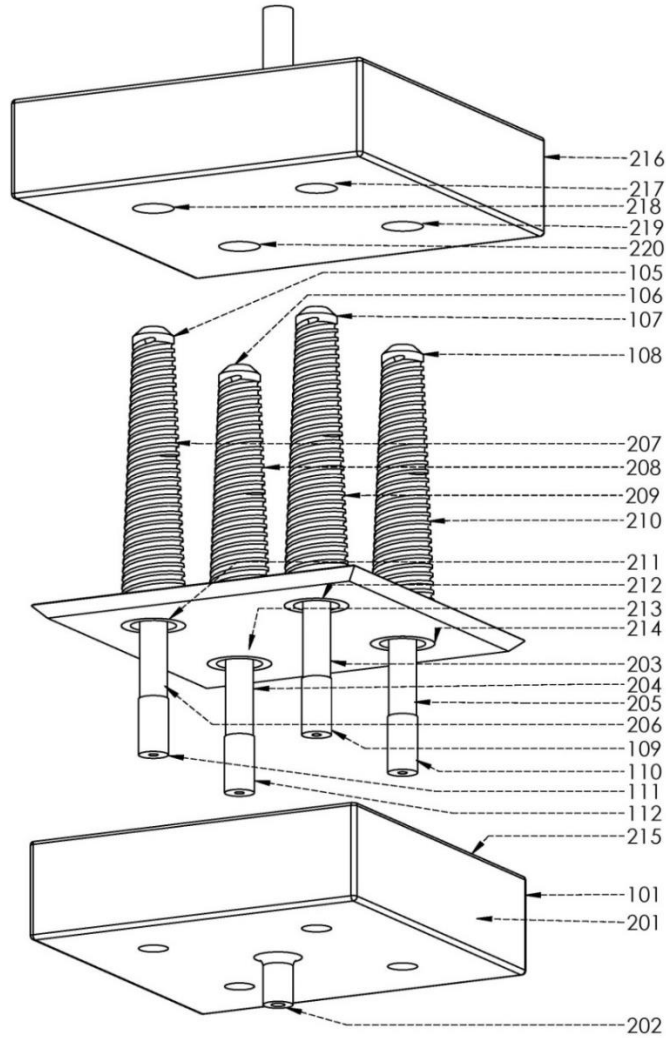


Figure 3.2 : Front slanted view of the desalination device exposing components at various levels

The desalination tube component of the apparatus is shown in the middle of Fig. 2. The tapering tubes 203, 204, 205, 206 are inserted into exit end of the desalination tubes 207, 208, 209, 210 through the holes 211, 212, 213, 214. The plate 215 is the cover for the lower tank 101.

The intertwined electrodes provide a downward electromotive force for ions from the fresh electrolyte coming upward into the middle of the desalination tubes. The diluted electrolyte flows into the upper tank 216 from the desalination tubes 207, 208, 209, 210 through the holes 217, 218, 219, 220.

The desalination tubes also tend to draw ions from the upper tank 216, thus creating an increasing concentration gradient of salinity towards the bottom of the tank. Relatively purified water can be extracted from the top for consumption when the salinity reading by a fluidic resistance sensor 221 becomes low. Depending on the purity needed, the extracted fluid may be further purified by a similar apparatus in multiple stages. Similarly, the concentrated brine may also be extracted from the lower tank when the salinity reading by a fluidic resistance sensor 222 becomes high. The extraction of fluid in either the upper or lower tank draws in fresh fluid to be desalinated.

Figure 3.3 shows a solid cross-sectional view of the same apparatus for a single desalination tube, illustrating the electrical wiring and motion of fluid and ions. Fresh electrolyte 301 enters the desalination tube, flowing upward. The three-phase intertwined electrodes 302, 303, 304 are shown. For the sake of illustration, the middle electrode 303 is shown to have a neutral voltage of 0V, while the electrode 302 has a negative voltage and electrode 304 has a positive voltage. Thus cations are attracted to the electrode 302, and anions are attracted to the electrode 304 at that moment.

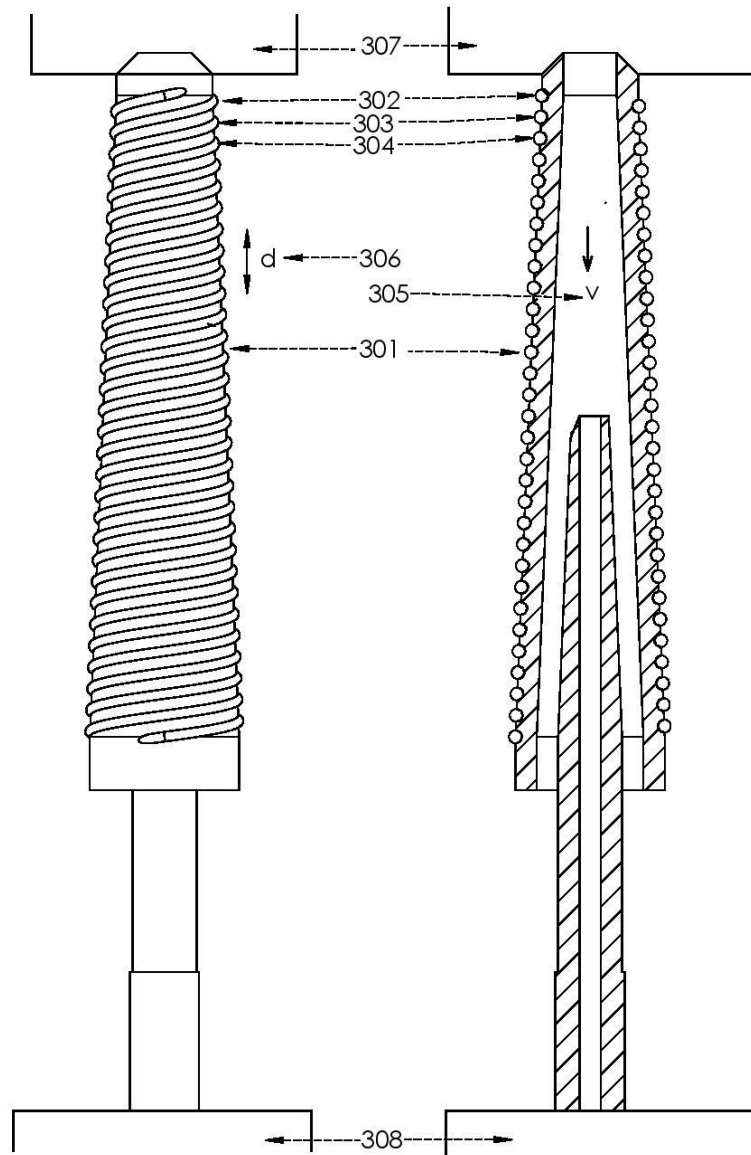


Figure 3.3 : Front cross section view of the desalination tube

As the electrodes are driven by Polyphase Alternating Current (PAC), the ions are driven by the traveling electric wave down the tube with a velocity v such that $v = f d$, where f is the frequency of the PAC, and d is the wavelength of the traveling wave, which is the distance d for the electrode to make one complete turn.

Thus ions are driven from the upper tank to the lower tank, as shown in the relatively dilute ions and concentrated ions in the upper tank and lower tank respectively.

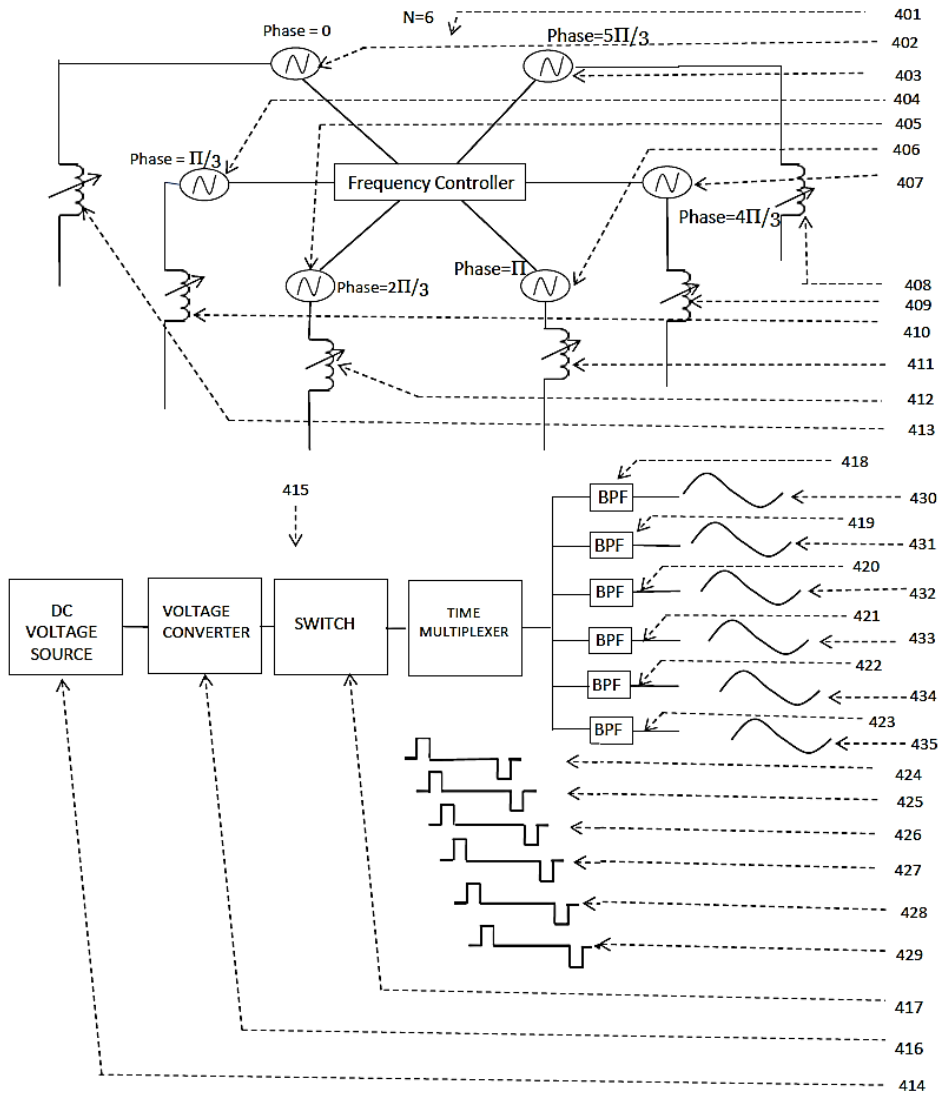


Figure 3.4 : Electrical circuit for 6 phase AC generation and frequency controller

The electric circuit is shown in figure 3.4. The PAC power source could be the standard 240V split phase (+120V, -120V) power, or the six-phase power source 401. Each electrode is connected to one of the phase of the PAC 402, 403, 404, 405, 406, 407. In figure 3.4, the other end of the electrode is connected to a common neutral terminal, and then the voltage is 120V PAC across each electrode. If the two ends of each electrode are connected to two successive phases of the 208V six-phase PAC, there would be a 208V PAC across each electrode, thus providing a higher electrode voltage.

A higher voltage AC source may accelerate ions faster, thus enabling priming of the fluid from a zero flow velocity when the AC source is switched on. In steady state, the fluid flow tends to be approximately equal to the velocity $v = f d$ of the traveling wave.

Thus, the use of higher voltage is advantageous to transfer of electric forces onto ions, which then drive the surrounding water molecules by means of viscosity. A figure of merit is that a static electric field of 1V/cm tends to move ions in a stationary fluid at a terminal velocity of the order of 1 mm per second. An AC electric field of 60 Hertz frequency would travel about 20 micron within a cycle of less than 20 milliseconds (1/60 seconds = 16.7 milliseconds). If we use a 120V AC power for each of the three-phase AC, we may have a distance d in the order of millimeters for effective self-priming.

For marine locomotion, the frequency may range from lower than 10Hertz to KH for accelerating the fluid flow from zero velocity to say 36km/hour (24 mph or 10 meters per second). Thus, a 1 kHz frequency and a distance $d = 1$ cm would give a fluid velocity of $v = f d = 10$ meters per second. To provide sufficient electromotive force for ion acceleration, a large electric field is necessary.

For desalination, a large current is advantageous for ion removal. Seawater typically has 35 grams of salt dissolved in 1 liter of water, or 3.5% by weight. One mole (6.02×10^{23} molecules) of salt weighs 35.5 grams for the chloride ion and 23 grams for the sodium ion. Thus one liter of seawater therefore has slightly more than half a mole of salt. Therefore to desalinate one liter of seawater, it would involve an electric charge of more than 50,000 Coulombs. Faraday constant, which is the amount of charge in one mole of electrons, is about 100,000 Coulombs. This explains why electro-dialysis is energy inefficient for desalination. Even at a low DC voltage of 1V in an electrolytic cell of a cube of 1cm per dimension, we would require 50,000 Coulomb x 1 Volt, equal to 50,000 Joules to desalination 1 liter of water. Much of that energy is wasted in the production of toxic sodium hydroxide and chlorine gas, which much be recombined to form NaCl salt again in the recombination tank, wasting energy in that exothermic recombination process.

Electromotive desalination by PACBIPS does not involve a chemical process, and energy is used to attract ions to the electrodes as well as providing kinetic energy to move electrolyte close to the surface of the desalination tube. The kinetic energy needed is relatively small at a low fluid flow rate of 1 mm/s. The larger energy consumption of attracting ions to the electrodes can be made small by means of a small cross section of the desalination tubes such that ions need not travel more than 1 mm to the electrode across that cross section. The vertical motion of ions is facilitated by fluid motion.

For power from industrial three-phase AC power source, we can typically draw up to 100A of current. To control current flow in each of the electrode, we may use an inductor 408, 409, 410, 411, 412, 413 for each of the six-phase terminal 402, 403, 404, 405, 406, 407 respectively. According to Ohm's law $I = V/Z$ where $Z = j2\pi fL + R$, where Z is the

complex impedance dependent on the inductance L and resistance R present in the inductor and the electrodes. Instead of using an inductor, we may use a resistor to regulate the current I , which could be undesirable as ohmic resistance is wasteful to turn electricity into waste heat.

The PAC power could also be generated instead by a solar photovoltaic or battery power source 414. This alternative power source could facilitate water desalination and marine propulsion locally by means of energy generated by solar PV cells or stored in a chemical battery. Using PV cells with battery storage to drive a marine vehicle by our PAC method would enable very efficient propulsion of marine vehicle, while the same propulsion system can also be used to desalinate seawater for human consumption.

The use of solar PV panels and/or chemical batteries to supply a constant DC power requires a DC-to-polyphase-AC inverter 415. The DC power source, properly voltage adjusted by a voltage converter 416 is gated by switch 417 to time multiplexed current into N (equals to 6 in Fig. 4) circuits 418, 419, 420, 421, 422, 423. This method is known as Pulse Width Modulation (PWM).

The multiplexing acts in 12 time slots within a frame of duration $1/f$ seconds. In the first time slot, a positive pulse of current A is sent into circuit 418, and in the seventh time slot a negative pulse of current $-A$ is sent into the same circuit as illustrated in the current chart 424. Likewise we have the current chart 425 for circuit 419 with positive current flow in the second time slot and negative current flow in the eighth time slot. Similarly, we have the current chart 426 for circuit 420 with positive current flow in the third time slot and negative current flow in the ninth time slot. We have the current chart 427 for circuit 421 with positive current flow in the fourth time slot and negative current flow in the tenth time

slot. We have the current chart 428 for circuit 422 with positive current flow in the fifth time slot and negative current flow in the eleventh time slot. We have the current chart 429 for circuit 423 with positive current flow in the sixth time slot and negative current flow in the twelfth time slot.

Each of these periodic positive and negative current pulses are filtered by a narrow band pass filter 418, 419, 420, 421, 422, 423 with center frequency f . The output of the filter is an alternating current 430, 431, 432, 433, 434, 435 of a staggered phase determined by the timing of the pulses.

For the purpose of priming, the frequency f increases gradually from zero to the desirable frequency as dictated by the velocity requirement $v = f d$. The frequency is controlled simply by the duty cycle of repetition for the pair of pulses for each circuit. Controlling the frequency f and the current I allow us to control the speed and power output of PACBIPS for marine propulsion.

This method of generation is simple for any polyphase number $N > 2$, which could be advantageously large (for example $N = 6$) for marine propulsion purposes.

3.5 Design of the pontoon for marine transportation application

A design of a pontoon PACBIPS for marine transportation is shown in figure 3.5. The pontoon comprises a metallic or fiber composite tube 501 for mechanical support and floatation.

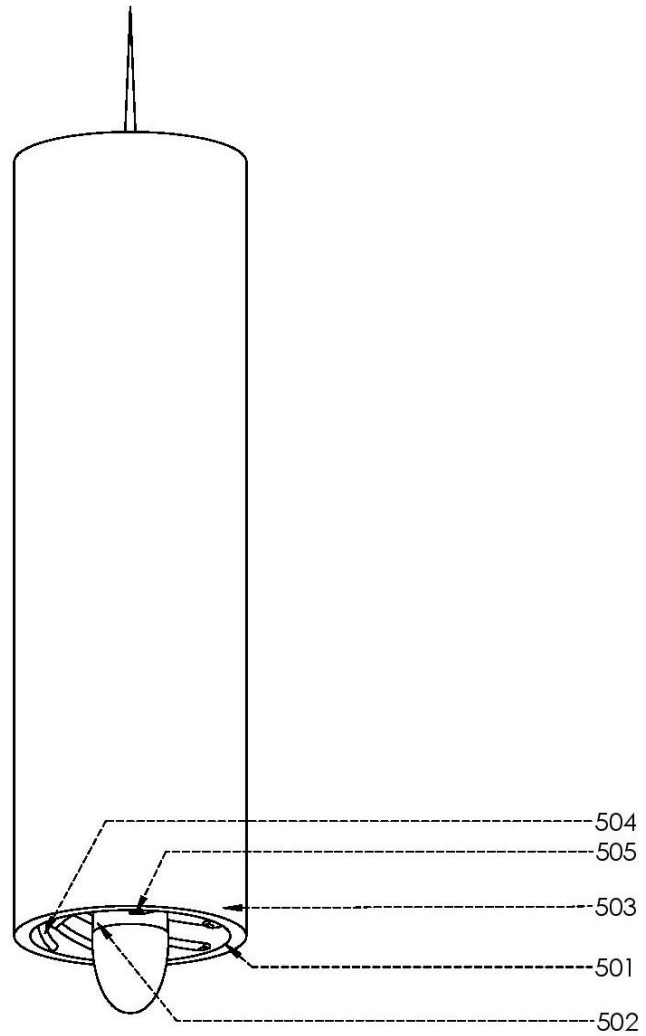


Figure 3.5 : A view of the pontoon used for marine transportation application

The tube supports in the center a flow regulator **502** designed to funnel a smooth fluid flow at a higher velocity towards the end of the tube **503**. The flow regulator, if hollow with air within, also provides buoyancy to a marine platform supported by two PACBIPS pontoons.

Two sets of intertwining electrodes 504, 505, respectively adjacent to the inside of the tube 501 and to the outside of the regulator 502. These PACBIPS together accelerate seawater towards the end of the tube 503.

Figure 3.6 shows a cross section view of the pontoon PACBIPS to illustrate the electrical system. The two sets of intertwining electrodes 601, 602 are adjacent to the tube 603 and regulator 604. These electrodes may have an uneven spacing, for example with distance d between successive turn of an electrode increasing down the length of the tube. For the purpose of illustration, we maintain a linear increase of d .

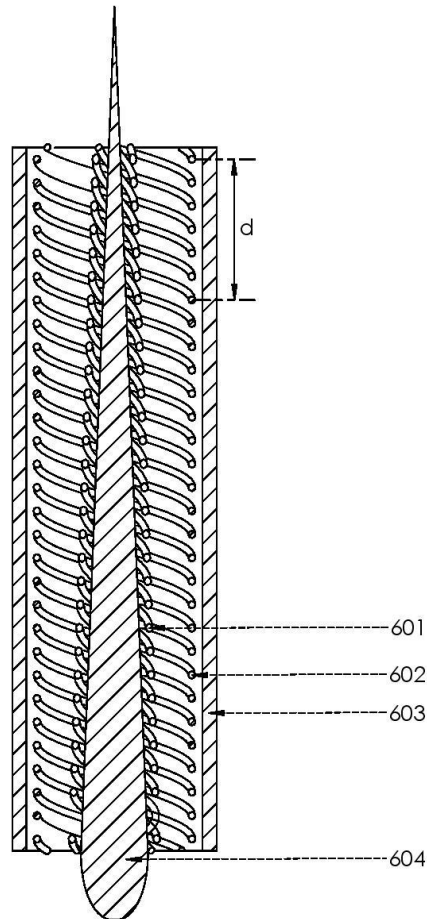


Figure 3.6: A cross section view of the pontoon PACBIPS for marine transportation

The flow of seawater is on both sides of the electrodes. In the figure, we use $N = 6$ polyphase with the phase number illustrated by 1, 2, 3, 4, 5, 6. For a larger motive force on the ions, we recommend using a higher voltage so the voltage difference between successive electrodes remains significantly large.

Figure 3.7 shows the electric field chart 701 of the traveling wave as well as resulting travel velocity v 702 down the pontoon PACBIPS. To produce thrust against water and wind resistance, the ejected water velocity should be multiples of the boat velocity. Additional sets of electrodes may be needed to provide extra thrust at the aft section of the pontoon PACBIPS.

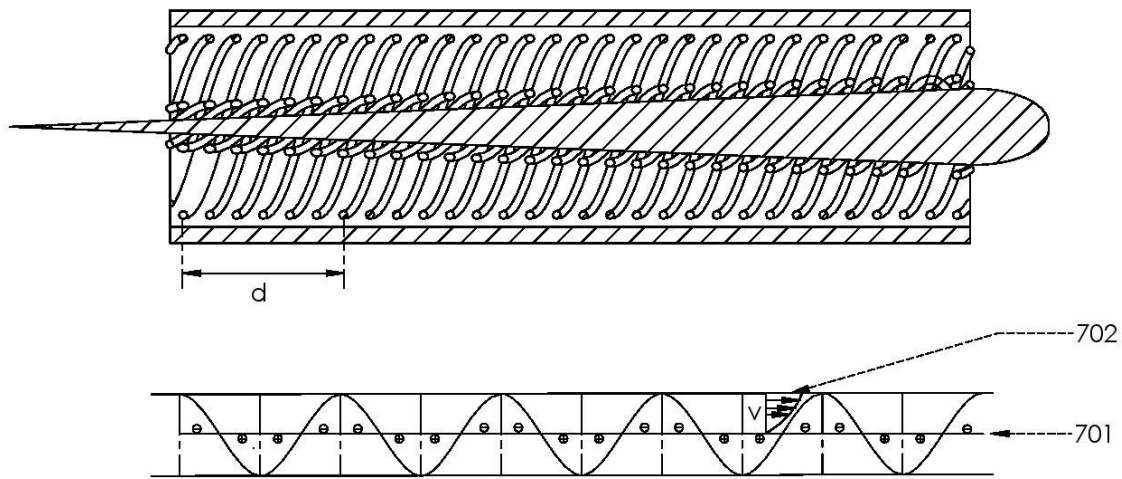


Figure 3.7 : Electric field graph of the traveling wave

3.6 Helmholtz capacitor based desalination unit

Helmholtz capacitor is a double layer capacitor model which forms at the interface between the electrode to which voltage is applied and the adjacent electrolyte. At this interface boundary, two layers of ions with opposite charges is formed when a voltage is applied to the electrode. This phenomenon is explained by the illustration in figure 3.8

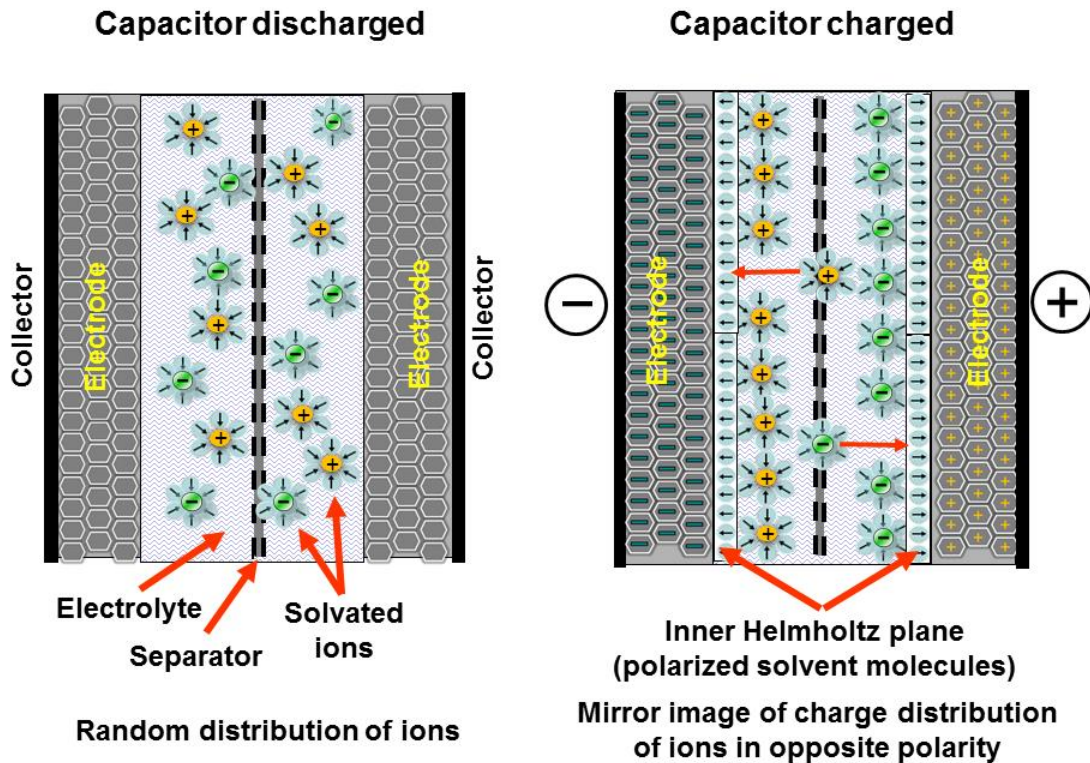


Figure 3.8 : Electrical double layer capacitor being charged and discharged

As seen in figure 3.8, the ions are in random locations when there is no voltage across the electrode. When a DC voltage is applied to the electrode, the Helmholtz capacitor gets charged and the ions form a layer in the solution-electrode interface. The other layer is in the surface lattice structure of the electrode. These two layers consist of

ions that are opposite in charge. The two layers are separated by solvent molecules. The separation layer consists of water molecules in our case. The molecule monolayer forms the Inner Helmholtz plane (IHP). It adheres by physical adsorption on the surface of the electrode and separates the oppositely polarized ions from each other, thus becoming a molecular dielectric.

The dimension of the molecule layer is often in the order of 0.1 nm. This changes for different solvents, electrode, applied electric field and other parameters. This length is described as Debye length.

Since Debye length is very small, the field created by this Helmholtz capacitor is very large. Considering a voltage 'v' of 2V applied to a carbon electrode with salty water being the electrolyte, and assuming the Debye length 'd' to be 0.2 nm.

We get the Electric field E,

$$E = \frac{V}{d}$$

$E = 5000 \text{ kV / mm}$, at the junction.

To compare this figure with values from other capacitor types requires estimation for electrolytic capacitors, the capacitors with the thinnest dielectric under the conventional capacitors. The voltage proof of aluminum oxide, the dielectric layer of aluminum electrolytic capacitors, is approximately 1.4 nm/V. For a 6.3 V capacitor therefore the layer is 8.8 nm. The electric field is $6.3 \text{ V} / 8.8 \text{ nm} = 716 \text{ kV/mm}$, around 7 times lower than in the double-layer. The field strength of some 5000 kV/mm is unrealizable in conventional capacitors.

No conventional dielectric material could prevent charge carrier breakthrough. In a double-layer capacitor the chemical stability of the solvent's molecular bonds prevents breakthrough.

Another implementation of PACBIPS for desalination makes use of this Helmholtz capacitor to good effect. The idea is to have a central tube for water flow. This tube will be surrounded by a layer of fiber glass, copper electrode and carbon fiber. The fiber glass ensures the ions adsorb to its surface. A fiber glass layer with a large surface area is chosen. The electrode to which voltage is applied to is made of copper and has a high value of conductivity. The carbon fiber layers are to improve conductivity and also provide a large surface area. Carbon fiber material with high conductivity and large surface area is chosen.

These three layers then repeat over again to form the second set of the above described materials. This forms a PACBIPS cell. There are multiple cells similar to that and this forms a PACBIPS desalination unit. Each unit in the cell is identical and has exact same properties such that the voltage applied across the unit divides across each cell in equal quantity.

If a voltage of V is applied across the desalination unit and we have n cells in the unit, then the voltage across each unit should be equal to V/n .

For example, we have 10 PACBIPS units and if 12 V is applied to the desalination unit, we will have 1.2 V developed across each unit.

The long passage, item 1 in the center takes in salty water at the top and returns relatively deionized water at the bottom. The deionization process is progressive throughout the passage and is achieved by the effect of the multiple PACBIPS cells surrounding the passage.

The first concentric layer, item 2 is a porous non-conducting tube such as one formed by a tubular weaved fiber glass composite, forms a continuous flow boundary for the electrolyte to be deionized.

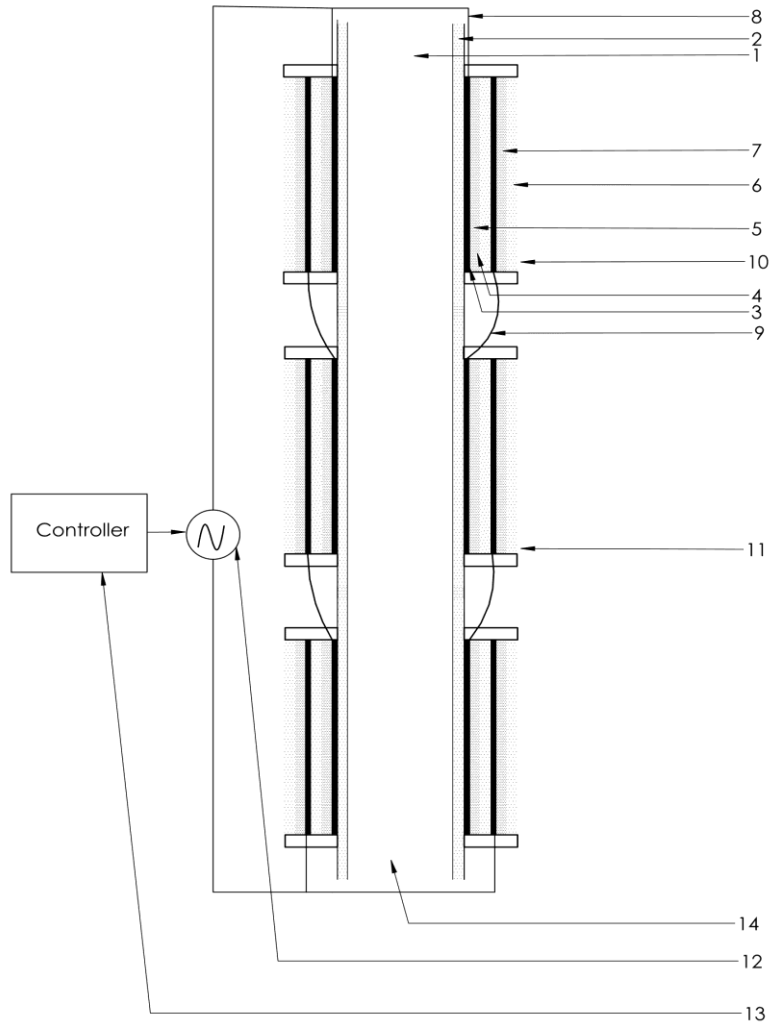


Figure 3.9 : Three PACBIPS cells in series being controlled by an AC source

The next layer, item 3 is a metallic mesh that is porous for ion passage, is the electrode that includes the large surface capacitive material that is the carbon fiber electrode described below.

The next layer, item 4 is a high surface area material such as carbon aerosol or a weaved carbon fiber tube, serves as an absorbent for the anions if the electrode is positively charged, or an absorbent for the cations if the electrode is negatively charged.

The metallic mesh and weaved carbon fiber tube form the electrode, item 5 for the Helmholtz capacitor.

Item 6, another layer of porous insulating tube such as one formed by a tubular weaved fiber glass composite, insulates the electrode to the next electrode item 7.

Item 7, comprising items 3 to 6, forms another electrode for ion absorption.

Item 8, an electrical lead wire to item 3, is connected to a terminal the AC power source.

Item 9, an electrical lead wire to item 5, connects the second electrode of the PACBIPS cell item 10 to the first electrode of the next PACBIPS cells item 11.

Item 12 is an AC power source that powers the stack of PACBIPS cells connected in series. The antipodal terminal of the AC power source is connected to the second electrode of the last PACBIPS cell in the series of PACBIPS cells.

Item 13 controls the frequency, voltage, and current of the AC power source. The voltage of the AC power source is series divided among the PACBIP cells. The individual cell voltage should be not much larger the Gibbs free energy voltage of the anion, i.e. 1.4V for the chloride ion in sea water.

The current needed is determined by the capacitance of the super capacitors in series. The frequency is determined by ion mobility and the distance separation between the two electrodes of a PACBIPS cell.

Item 14 is an exit of the relatively deionized electrolyte, which may be fit for use or may be further deionized.

3.7 Operation of the Helmholtz capacitor based PACBIPS

The goal of this PACBIPS desalination unit is to achieve desalination of water without using a membrane and by operating at low pressure. This is achieved by creating a concentration gradient of salt in the electrolyte flowing through the passage in the center of the desalination unit.

The salty electrolyte is made to enter the passage in the center of the unit. The desalination unit consists of about 10 cells connected in series with each other. Alternating voltage with a peak of about 12 V is applied to the unit. This ensures that about 1.2V is developed across each cell. When the positive voltage is applied, the ions get adsorbed onto the electrode. The Sodium ion (Na^+) gets adsorbed to the negatively charged electrode and the Chlorine ion (Cl^-) gets adsorbed to the positively charged electrode and relatively deionized water is obtained at the bottom of the passage. This water is fed to the next cell and thereby it is further deionized. Water is pumped out at regular intervals when the salinity meter reads a certain value that is fit for drinking. Similarly, salty water can be extracted from the top of the passage as well.

This process keeps repeating at each and every cell and the water obtained at the end of the passage will be deionized. The number of cells, applied voltage and time duration of desalination depends on the purity of water needed.

CHAPTER 4

MATHEMATICAL ANALYSIS AND RESULTS

This chapter provides a mathematical model for the polyphase alternating current bi-ionic propulsion system. A mathematical model for the electric double layer formation is also presented and analyzed. The model for the Helmholtz capacitor based PACBIPS unit is also presented. The mathematical model of electro dialysis is presented and analyzed. The chapter also presents analysis on electron field shielding principle, zeta potential of the double layer and the mobility of ions.

4.1 Analysis of Electrodialysis

The analysis of electrodialysis is considered as the DC version of the AC style PACBIPS system of desalination. Electrodialysis is similar to PACBIPS in the way that it uses an applied voltage to desalinate water. Another commonality is that the process depends on ion transport in solution. However, electrodialysis requires a membrane to filter the salt particles from water and hence PACBIPS is a much better approach to desalinate water. Electrodialysis has been successfully used for desalination of brackish water in commercial applications.

Electrodialysis involves transporting ions due to an electric field across a membrane. Cation- and anion- exchange membranes are placed between the cathode and anode. When a potential difference is applied between the two electrodes, the cations are drawn towards the cathode (negative electrode) and the anions are drawn towards the anode (positive electrode).

Cations migrate through cation exchange membrane while they are retained by the anion exchange membrane. The opposite occurs with the anions which migrate through the

anion-exchange membranes but not through the cation exchange membrane. This movement causes rise in the concentration (brine streams) and the decrease in the adjacent dilute streams from which purified water exits.

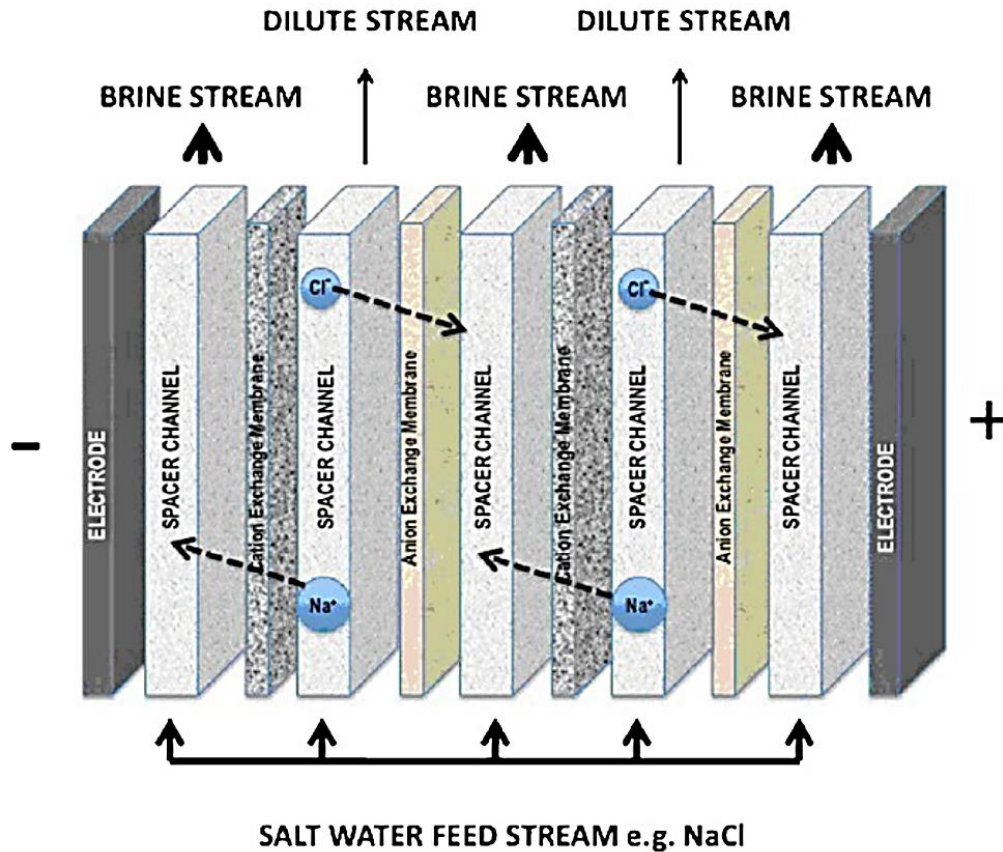
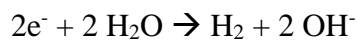


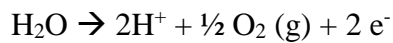
Figure 4.1 : Electrodialysis for the desalination of water [26]

In electrodialysis, anode and cathode reactions may occur at each electrode depending on the pH of water and the potential applied.

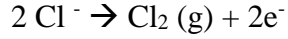
Cathode reaction :



Anode reaction :



Or



In this process, hydrogen gas may be generated at the cathode and either oxygen or chlorine gas (depending on the concentration of the electrolyte) is generated at the anode. The amount of gas evolved depends on the potential applied. These gases are subsequently let off from the electrodes or recombined to maintain the pH. Sometimes the gases are used for other applications as well.

The net energy consumption is the work applied to remove the dissolved ions from the solution [26] :

$$W_{ED} = W_{deionization} = \frac{E_{deionization}}{\eta_d} = V \frac{I_m t}{\eta_d}$$

where W is work, E is energy in Joules, V is the cell voltage in V, I_m is the minimum theoretical current necessary to remove a given amount of ions in Amperes, t is time in s and η_d is the deionization or current efficiency, a measure of ion transport across the ion exchange membranes for the given current.

Additionally, the minimum theoretical current, I_m , is the product of the flow rate times the change in concentration from the inlet to the outlet [26] :

$$I_m = zFQ_f\Delta C$$

where, z = charge of the ion ; F = Faraday constant (96485 Amp s /mol) ; Q_f = diluent flow-rate, L/s; ΔC = change of ion concentration from inlet to outlet, mol/L.

Combining the above two equations, the net energy consumption is

$$W_{ED} = V \frac{zFQ_f\Delta Ct}{\eta_d}$$

Using the equation and assuming $\eta_d = 1$, we have calculated the minimum theoretical work to produce 1 m³ (0.27 k gal) of a solution containing 300 mg/L of NaCl

from solutions of different concentrations. The operating cell voltage of 1.2V is assumed. Results plotted in figure 4.2 show the work done in kWh/m³ versus the concentration of NaCl in mg/L.

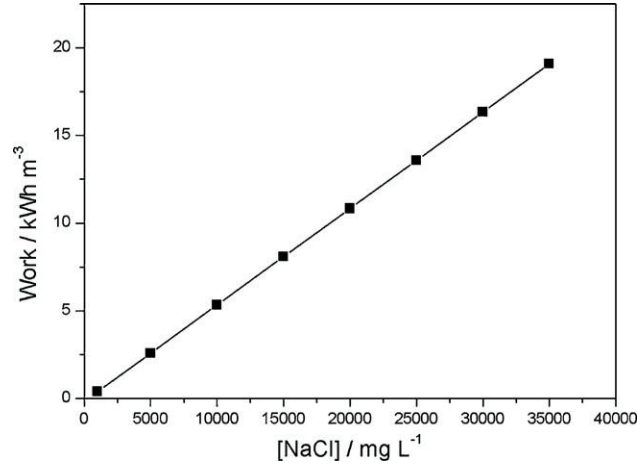


Figure 4.2 : Electric work needed to desalt a NaCl electrolyte by electro dialysis

[26]

Even though current efficiency is assumed to be 100%, it is not so in practice. It is important that this current efficiency remains more than 80% in commercial grade applications. Low current efficiency indicates splitting of water molecules or back diffusion of ions from concentrate stream to dilute stream.

Combining the above mentioned equations, the following expression can be derived for current efficiency [26]

$$\eta_d = \frac{I_m}{I} = \frac{zFQ_f\Delta C}{I}$$

where, I is the practically applied current, in Amperes

It can be seen that the current efficiency is directly dependent on the concentration of the inlet feed. This can be explained based on the fact that there are more charge carriers when the feed has a higher concentration of ions.

4.2 Analysis of PACBIPS

PACBIPS is can be thought of as a method which deionizes water based on the application of electromotive force which is the basic principle of electro dialysis. Although the method sounds similar, PACBIPS is much better in performance and cost when compared with electro dialysis. The improved efficiency results because of the fact that this method does not use a membrane, high pressure system or chemical conversions for the desalination.

PACBIPS creates a traveling wave to drive down the ions and hence desalinate water. The traveling wave is created by a Polyphase AC source. The traveling wave thus created attracts anions on its negative peak or trough and cations on its positive peak or crests. The creation of traveling wave and its role in desalination is explained in this section.

A polyphase AC source is defined as an AC source with two or more phases. Let the number of phases be denoted by N . An AC source with $N=2$ phases is sufficient to create a travelling wave. However, a traveling wave is said to be more continuous for a large N .

Considering a practical scenario, we assume $N=3$ suffices to maintain the continuity of the traveling wave. We take advantage of the ubiquitous industrial three phase power source of frequency $f=60$ Hz.

The electrodes carrying these phase voltages need to be discrete. In our study, we assume them to be like rings around an insulating tube. The salty water flows through the insulating tube. More conveniently, the electrodes can be N long wires intertwined with each other. The electrodes for the same phase are spaced at a distance of d from each other. This can be achieved by placing electrodes labeled $1, 2, 3, \dots, N, 1, 2, 3, \dots$ and so on with the electrode i being tied to the i^{th} phase of N -phase AC power source.

$$V_i(t) = A \cos\left(2\pi\left(ft - \frac{i}{N}\right)\right)$$

The i^{th} electrode is placed at the location $x_i = \frac{id}{N}$

Considering the arrangement of intertwined wires as shown in figure 4.3, we can say that the i^{th} electrode which starts at position x_i , makes intertwining full turns around the tube at the positions x_{N+i} , x_{2N+i} and so on, as described in the following equations

$$x_{N+i} = \frac{(N+i)d}{N}$$

$$x_{2N+i} = \frac{(2N+i)d}{N}$$

The traveling wave we wish to create has a wavelength $\lambda = d$, the electrode spacing. The velocity of the traveling wave is $v = fd$.

The traveling wave has a voltage dependent on both space and time

$$v(x, t) = A \cos\left(2\pi\left(ft - \frac{x}{d}\right)\right)$$

If we consider a crest with a phase 0 in the traveling wave,

$$ft - \frac{x}{d} = 0$$

$$x = fdt$$

$$x = vt$$

because $v = fd$

The discrete nature of the electrodes samples the continuous traveling wave such that

$$V_i(t) = V\left(x = \frac{id}{N}, t\right) = A \cos\left(2\pi\left(ft - \frac{i}{N}\right)\right)$$

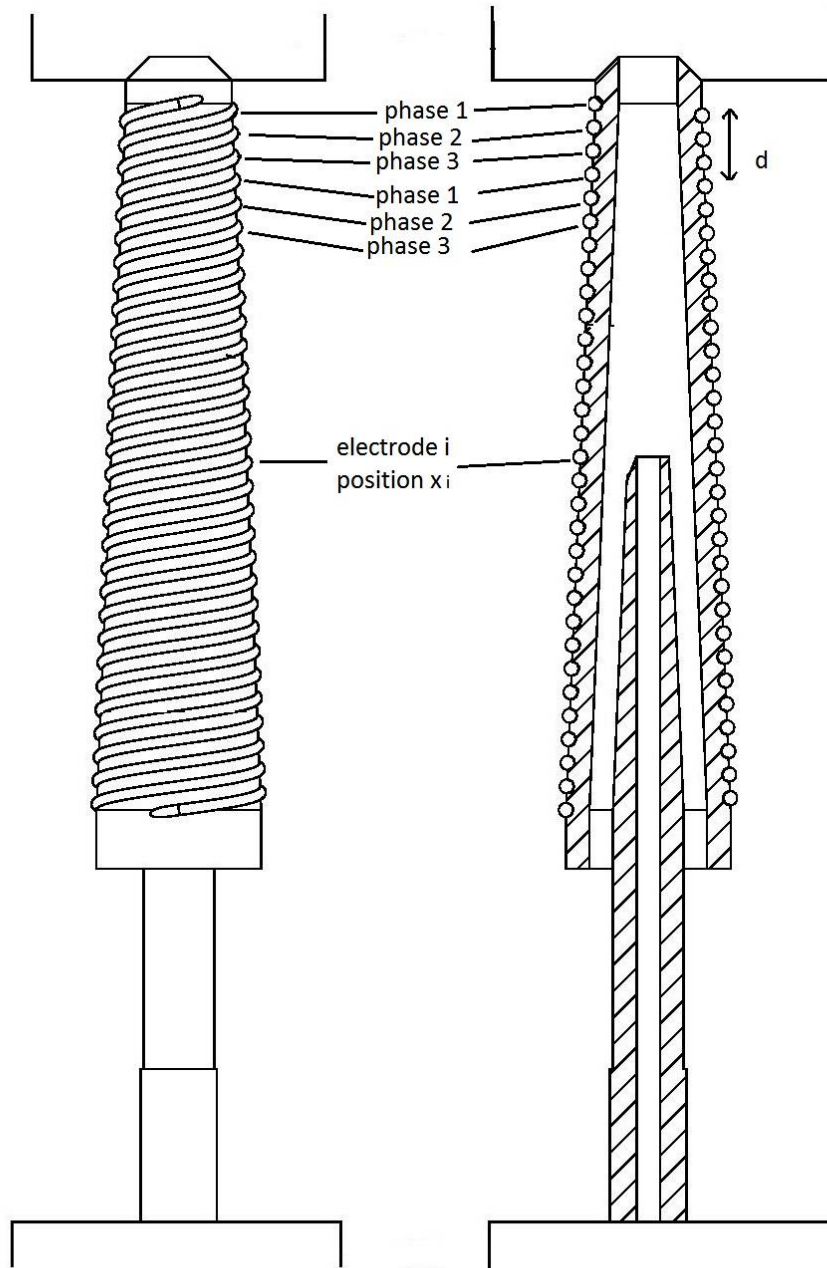


Figure 4.3 : Intertwined electrode arrangement showing the connected phase

The voltage between these discrete electrodes can be defined as the linear interpolation of the respective voltages.

Taking the simplest case of polyphase AC, we have $N=2$ and this gives

$$V_1(t) = -V_2(t) = V_3(t) = -V_4(t) = \dots \text{etc.}$$

This alternating signage gives an alternating electric field from one electrode to another electrode. The cations, which are positively charged are accelerated in between two electrodes with electric field going from left to right; whereas the anions are accelerated in the same direction in the next pair of electrodes as the electric field is reversed in between the next pair because of the alternating signage.

If the velocity of the ions matches that of the velocity of the traveling wave, that is $v=fd$, the electric field reversal of the next pair of electrode will occur just in time for the ions to travel further down. This phenomenon is similar to the surfer being carried forward by the front of an oceanic wave.

This works similarly for other larger N , and in the limit of very large N , the piecewise linear traveling wave now resembles the continuous wave.

$$V_i(t) \approx A \cos(2\pi ft)$$

As described earlier, the cations are carried by the trough (negative voltage) of the traveling wave and the anions are carried by the crests (positive voltages) of the traveling wave.

4.3 Analysis of Helmholtz capacitor based PACBIPS

The Helmholtz capacitor based PACBIPS works on the model of the earlier PACBIPS. This method however is much better than the previous method of PACBIPS as it relies on the creation of an electrical double layer in the electrolyte solution and uses this

electrical double layer to good effect in order to create a concentration gradient of ions and thus desalinate water. The crux of the method is the creation of an electrical double layer.

When a surface is immersed in an aqueous solution, a discontinuity is formed at the interface where variables such as electric potential and electrolyte concentration change significantly from the aqueous phase to another phase. Because of the different chemical potentials between the two phases, charge separation often occurs at the interfacial region. This interfacial region together with the charged surface, is called as an electrical double layer.

Phenomena such as electric field shielding and effects of zeta potential can affect the performance of the desalination unit. Electric field shielding is the damping of electric field caused by the presence of mobile charge carriers. It is an important part of the behavior of charge carrying fluids such as ionized gases, electrolytes and electronic conductors such as semiconductors and metals. In a fluid with a given relative dielectric constant ϵ_r , composed of electrically charged constituent particles, each particle interacts with the other particles in terms of the coulomb force which can be defined by F in the following equation

$$F = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r^2}$$

This interaction complicates the theoretical treatment of the fluid flow. Consider a fluid composed of electrons with abundance of positive charges in the background. Each electron possesses a negative charge by itself. According to Coulomb's law, negative charges repel each other. Consequently, this electron will repel other electrons around it and create a small region around itself in which there are fewer electrons. This region can be treated as a positively-charged "screening hole". Viewed from a large distance, this

screening hole has the effect of a positive charge which cancels the electric field produced by the electron. Only at short distances, inside the hole region, can the electron's field be detected.

Electric field screening depends a lot on the electrolyte and the material which is in contact with the electrolyte. However, the layer adjacent to the electrolyte also has an impact in terms of electric field screening. This material is to be chosen such that the effect of electric field screening is reduced.

The shielding of electric field can impede the electric field penetrating into the electrolyte. This can impede the rate of desalination and the effect to which desalination is performed. Hence, electric field shielding is one of the concerns of desalination by the methods of PACBIPS.

The mobility of ions in the electrolyte is yet another factor in the design of desalination systems. The electric field to be applied gives rise to the mobility of the ions that are being driven. The mobility of the ions further defines the drift velocity of the particles. This gives a specification constraint in terms of the time taken by the particle to reach a certain point at a given distance. This gives the time period and hence frequency of the applied wave if an alternating square wave is applied to the desalination device.

Electrical mobility is the ability of charged particles to move through a medium in response to an electric field that is pulling them. The separation of ions according to mobility of the gas phase is called ion mobility spectrometry. In liquid phase, it is called electrophoresis.

When a charged particle in a gas or liquid is acted upon by a uniform electric field, it will be accelerated until it reaches a constant drift velocity according to the formula

$$v_d = \mu E$$

Where v_d is the drift velocity (m/s)

E is the magnitude of the applied electric field (V/m)

μ is the mobility (m^2/Vs)

In other words, the electrical mobility is defined as the ration of the drift velocity to the magnitude of the applied electric field.

Electric mobility is directly proportional to the net charge on the particle as the particles which have more charge are better conductors of the electric field and can be driven down faster.

Electrical mobility of spherical particles much larger than the mean free path of the molecules of the medium is inversely proportional to the diameter of the particles; for spherical particles much smaller than the mean free path, the electrical mobility is inversely proportional to the square of the particle diameter.

In general, higher the diameter of a particle, lower is its electrical mobility. The amount of electric field required to drive down a particle is directly proportional to the size of the particle and this can be clearly seen from their mobility.

Without any applied electric field, electrons move around randomly. Therefore, on average there will be no net motion of charge carriers in any particular direction over time.

However, when an electric field is applied, each electron is accelerated by the electric field. If the electron were in a vacuum, it would be accelerated to faster velocities (called ballistic transport). However, in a solid or a liquid, the electron repeatedly scatters off crystal defects, phonons, impurities, etc. Therefore, it does not accelerate faster and

faster; but instead it moves with a finite average velocity called the drift velocity. This net electron motion is usually much slower than the normally occurring random motion.

Zeta potential is another important quantity to consider in the design of the PACBIPS based desalination device design. Zeta potential is also known as electrokinetic potential. From a theoretical point of view, zeta potential is the electric potential in the interfacial double layer (DL) at the location of the slipping plane relative to a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. In the formation of the electric double layer between the electrode and the electrolyte solution, the effect of zeta potential is a key component. This defines the stability of the electric double layer interface without which, desalination cannot be performed.

The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the potential is small, attractive forces may exceed this repulsion and the dispersion may break and flocculate. Colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the table 4.1.

The pH at which zeta potential is zero corresponds to the isoelectric pH and corresponds to the least stable pH value for that suspension. Zeta potential is not measurable directly but it can be calculated using theoretical models and an

experimentally-determined electrophoretic mobility or dynamic electrophoretic mobility. Zeta potential is dependent on several factors such as pH, conductivity, concentration of electrolyte as well as the electrode material. The pH of the solution, its conductivity and concentration of the electrolyte keep changing when the desalination takes place. Hence, these factors cannot be controlled. However, an electrode material which has high value of zeta potential needs to be chosen.

Table 4.1 : Stability of the colloid depending on the magnitude of zeta potential

Magnitude of Zeta Potential (mV)	Stability behavior of the colloid
0 to 10	Rapid coagulation or flocculation
10 to 30	Incipient instability
30 to 40	Moderate stability
40 to 60	Good stability
More than 60	Excellent stability

As mentioned before, PACBIPS uses electric potential to drive charged species to the electrodes. It is therefore a low pressure process of deionization that has a very good possibility to directly compete with reverse osmosis or distillation. The principle of the work can be traced to the work of Helmholtz and to the modeling of the electric double layer by Guoy-Chapman as explained further below.

Factors such as surface polarization, adsorption of ions and orientation of polar molecules make the region between two different phases have a complex distribution of charges. This interface is known as the double layer. Historically, there have been various models describing the double layer. The earliest model was proposed by Helmholtz in 1883, who describes the distribution of charges at the double layer as in the case of a capacitor: surface accumulates charge of one sign while the solution accumulates opposite

charges. A second model developed by Guoy-Chapman in 1913 took into account the gradient of electron density at a charged interface, the so-called Thomas-Fermi screening distance and its variation with distance from the surface. The consequence of this screening is that there exists a distribution of electric charge in the double layer region depending on the potential at the surface. In this model, other factors such as Boltzmann distribution due to thermal effects were also included. However, this model described ions as point charges. As a result, it predicted unrealistic high capacitance values due to extremely short distances.

Lastly in 1924, Stern completed the model by assuming that the double layer can be divided into an “inner” region where ion distribution followed Langmuir’s adsorption isotherm, while the region further from the surface could be described with the Gouy-Chapman model. Thus, the total capacitance can be calculated like a series union of both, inner double layer and diffuse layer.

The Guoy-Chapman theory[28] for the modeling of an electric double layer is discussed below. In order to maintain the overall electroneutrality of the system, an excess of charge on the surface side of the interface must attract an equal amount of opposite charged ions in the diffuse layer, in which the electrical potential distribution is given by the Poisson equation:

$$\nabla^2\psi = -\frac{\rho}{\varepsilon}$$

Where ∇^2 is the Laplacian operator, ψ is the relative electrical potential between the diffuse layer and the bulk phase, ε is the dielectric constant of the medium, and ρ is the volume charge density given by

$$\rho = \sum_i N_i z_i e \tag{2}$$

In this expression, z_i is the valency of ions of type i , e is the elementary charge, and N_i is the number of ions of type i . According to the Boltzmann distribution, N_i can be expressed as

$$N_i = N_{i0} \exp \left[-\frac{z_i e (\phi - \phi_b)}{kT} \right] \quad (3)$$

where k is the Boltzmann constant, T is the absolute temperature, N_{i0} is the bulk concentration of ions, and ϕ and ϕ_b are the absolute electrical potentials in the double layer region and in the bulk phase, respectively. It is convenient to define the reference electrical potential located in the bulk phase; therefore, $\phi_b = 0$ and can be represented by ψ . When Eqs. 1, 2, and 3 are combined, the Poisson–Boltzmann equation is then obtained:

$$\nabla^2 \psi = -\frac{e}{\epsilon} \sum_i N_{i0} z_i e \exp \left(\frac{-z_i e \psi}{kT} \right) \quad (4)$$

If the solution contains only single z: z-type electrolyte, Eq. 4 can be further simplified for a one-dimensional EDL system:

$$\frac{d^2 \psi}{dx^2} = \frac{2N_0 z e}{\epsilon} \sinh \left(\frac{z e \psi}{kT} \right) \quad (5)$$

The second-order differential equation given by Eq. 5 can be integrated by multiplying both sides by $2(d\psi/dx)$, followed by integration with respect to x :

$$\int \frac{d}{dx} \left(\frac{d\psi}{dx} \right)^2 dx = \int \frac{2N_0 z e}{\epsilon} \sinh \left(\frac{z e \psi}{kT} \right) d\psi \quad (6)$$

Integrating from the bulk solution where $\psi = 0$ and $d\psi/dx = 0$ up to some point in the double layer yields the first-order differential equation of ψ

$$\frac{d\psi}{dx} = -\frac{2KkT}{ze} \sinh \left(\frac{ze\psi}{2kT} \right) \quad (7)$$

where $k = (2N_A I e^2 / \epsilon kT)^{1/2}$ is the Debye–Huckel parameter for a symmetrical 1:1 electrolyte, I is the ionic strength, and N is Avogadro's number.

The charge density in the diffuse layer σ_d is related the volume charge density ρ by

$$\sigma_d = \int_d^\infty \rho dx \quad (8)$$

From Eq. 1, ρ can also be expressed as a second-order derivative of the electrical potential for a one-dimensional system; therefore,

$$\sigma_d = \int_\infty^d \varepsilon \frac{d^2\psi}{dx^2} dx = \varepsilon \left[\frac{d\psi}{dx} \right]_\infty^d \quad (9)$$

Since $\psi=0$ as $x \rightarrow \infty$, the derivative $(d\psi/dx) = 0$ as $x \rightarrow \infty$ and $\sigma_d = \varepsilon \left(\frac{d\psi}{dx} \right)_{x=d}$.

From Eq. 7, a useful relationship between ψ_d and σ_d can be obtained

$$\sigma_d = \frac{-2\varepsilon K k T}{ze} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (10)$$

By definition, the differential capacitance of the diffuse double layer, C_d , can be expressed as

$$C_d = -\frac{d\sigma_d}{d\psi_d} \quad (11)$$

Taking the derivative of Eq. 10 with respect to ψ_d , the expression of C_d can therefore be obtained as

$$C_d = \varepsilon K \cosh\left(\frac{ze\psi_d}{2kT}\right) \quad (12)$$

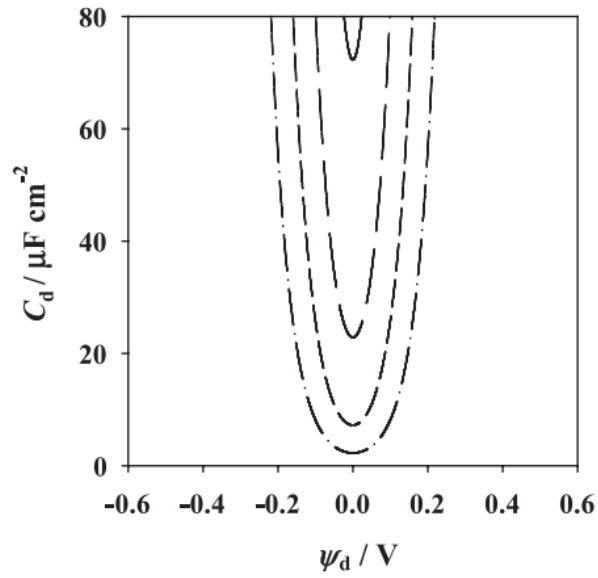


Figure 4.4 : Diffuse layer capacitance [28] of the EDL as a function of diffuse-layer potential for several concentration based on eqn. 12 : solid line, 0.1M ; long-dashed line, 0.01M; short-dashed line, 0.001M; dot-dashed line, 0.0001M

Figure 4.4 shows the values of C_d as a function of ψ_d , the potential at the electrode double layer. As shown in the figure, C_d is very small at very low electrolyte concentration and becomes higher for higher concentrations.

As described by the Guoy-Chapman model, at any interface between the electrolyte and another medium (liquid in this case), there exists regions with excess charges while the whole interface system is electrically neutral. The two sides of this layer carry equal and opposite charge similar to a capacitor and this is called as an “electrical double layer”.

According to Guoy-Chapman-Stern theory [29], the electrical capacity of the interface can be expressed as the sum of two capacitors in series

$$\frac{1}{C_T} = \frac{1}{C_{M-H}} + \frac{1}{C_{H-S}} \quad (13)$$

Where C_T is the electrical capacity of the interface, C_{M-H} is the capacity of the compact double layer between the electrode surface, M and the plane of closest approach for the ions, H and C_{H-S} is the capacity of the “diffuse” double layer spanning from plane H into the electrolyte solution.

According to Guoy-Chapman model the excess charge q on the surface can be described by,

$$q = \left(\frac{2RT\varepsilon C_s}{\pi} \right)^{\frac{1}{2}} \sinh \left(\frac{|z|\tau\phi_H}{2RT} \right) \quad (14)$$

The electrical capacity of the diffuse double layer can be obtained by differentiating eqn. 14 with respect to ϕ_H

$$C_{H-S} = |z|\tau \left(\frac{\varepsilon C_s}{2RT\pi} \right)^{\frac{1}{2}} \cosh \left(\frac{|z|\tau\phi_H}{2RT} \right) \quad (15)$$

The excess charge distribution is schematically represented schematically in figures 4.5 and 4.6. The modeling is based on Guoy-Chapman-Stern model

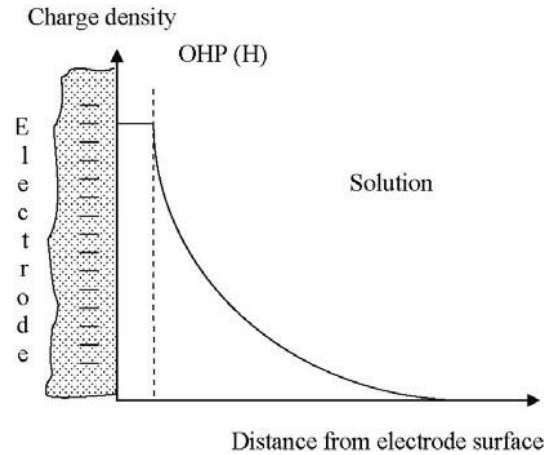


Figure 4.5 Charge distribution in an electrolyte adjacent to a negative electrode [30]

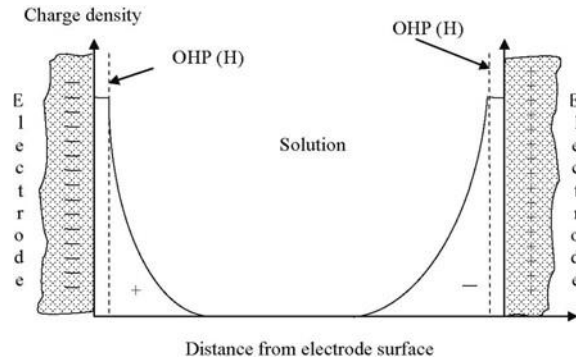


Figure 4.6 : Charge distribution in an electrolyte solution with two electrode system

[30]

It can be seen from eqn. 15 that the electrical capacity of the double layer varies directly proportional to $C_S^{1/2}$. It can also be seen that the capacitances reach a very high value for short distances. This high capacity is very critical for the functioning of PACBIPS system. Considering a electrode-solution system with a specific capacity of $C_T = 10\mu\text{F} / \text{cm}^2$ and assuming a voltage change of 1V, we would obtain an excess charge of 10 u coulomb / cm^2 . This may not be considered a considerable quantity for desalination. However, if an electrode with high specific surface area is used, this can achieve desalination.

Equivalent circuit representing a pair of charged electrodes is shown in fig. 4.7. The two capacitances are represented by C_T . The electrical resistance of the electrode material and the solution is represented by R_M and R_S respectively.

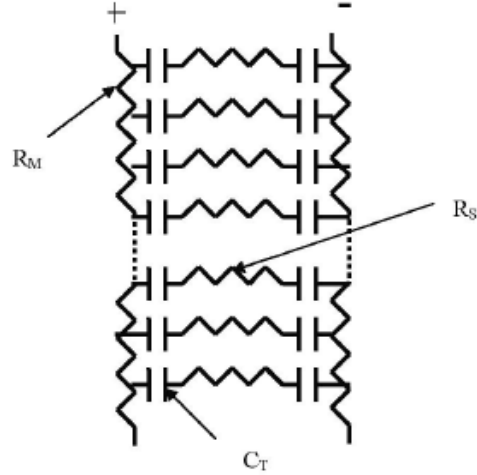


Figure 4.7 : Equivalent circuit representing charged electrodes and electrolyte

Y Oren [30] has proposed a model for the Analysis of desalting by charging a two electrode system. This model has been incorporated into the PACBIPS system. Charging C_T by providing positive voltage to the electrodes will increase anion adsorption and cation desorption. An electronic desalination method works by transferring charge from one electrode to the other. Let the transferred charge be represented by Δq_e . Anions are adsorbed from the positively charged electrode while they are desorbed from the negatively charged electrode.

The two cell charge co-ordinates for the electrode system q_e and q_d are defined as follows.

$$q_d = \mu_1 q_1 + \mu_2 q_2$$

$$2q_e = \mu_1 q_1 - \mu_2 q_2$$

$$\text{and } \mu_1 = \frac{g_1}{g_1 + g_2}, \mu_2 = \frac{g_2}{g_1 + g_2} \quad (16)$$

In the above expression, q_1 and q_2 are the charges per unit weight and g_1 and g_2 are the weights of electrode 1 and electrode 2 respectively. It can be seen that q_d is the total

charge and q_e is the charge exchanged between the two electrodes. These values are calculated per unit weight of the total electrode material.

The average charge efficiency for charging a step of the system comprising two identical electrodes from q_{e1} to q_{e2} is defined as

$$F \frac{\Delta n_s}{\Delta q_e} = \frac{F}{q_{e2} - q_{e1}} \int_{q_{e1}}^{q_{e2}} \left(\frac{\partial n_s}{\partial q_e} \right)_{q_d} dq_e \quad (17)$$

where, $\frac{\partial n_s}{\partial q_e}$ is the differential charge efficiency at constant q_d .

$F \left(\frac{\partial n_s}{\partial w} \right)_{q_d}$ represents the net salt adsorbed per unit of electrical charging work in the complete cell. This can also be termed as the differential energy efficiency. W is the electrical work of charging the double layer.

$$dw = \Delta E dq_e = \frac{q_e}{C_T} dq_e \quad (18)$$

$$\text{Accordingly, } F \left(\frac{\partial n_s}{\partial w} \right)_{q_d} = F \frac{C_T}{q_e} \left(\frac{\partial n_s}{\partial q_e} \right)_{q_d} \quad (19)$$

The differential charge efficiency can be expressed by the individual charges as follows:

$$F \left(\frac{\partial n_s}{\partial q_e} \right)_{q_d} = \frac{\partial q_1^-}{\partial q_1} - \frac{\partial q_2^-}{\partial q_2} = \frac{\partial q_1^+}{\partial q_1} - \frac{\partial q_2^+}{\partial q_2} \quad (20)$$

At the extreme conditions, i.e., where electrodes 1 and 2 are highly positively and negatively charged, respectively, the following approximations hold

$$\frac{\partial q_1^-}{\partial q_1} = 1, \frac{\partial q_2^-}{\partial q_2} = 0, \frac{\partial q_1^+}{\partial q_1} = 1, \frac{\partial q_2^+}{\partial q_2} = 0 \quad (21)$$

When these limiting values are inserted into Eqn. 20, the efficiency approaches unity, which is maximum. Thus, for the two-electrode cell to approach its highest

desalination capacity and differential energy efficiency, the electrodes should be maintained at the extreme opposite charge values.

The effect of the electrolyte concentration on the charge efficiency must also be taken into account. As the bulk concentration increases, the concentration of ions bearing the same charge as that of the electrode at the double layer interface region also increases. Therefore, ion depletion from that region is less likely. Due to this, charge efficiency may become lower at higher concentrations and may never reach unity [30].

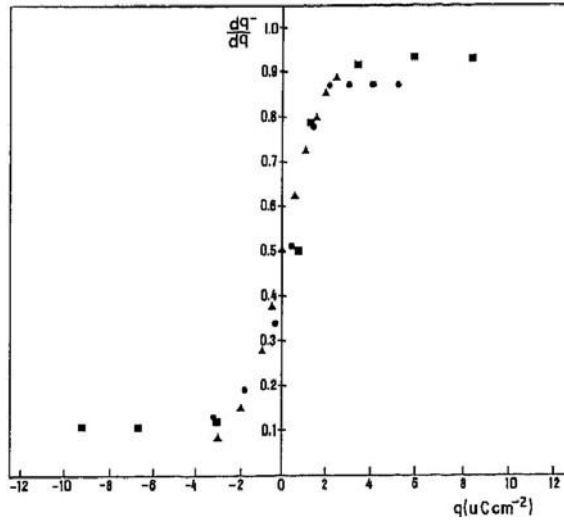


Figure 4.8 : Typical slopes of $\frac{\partial q^-}{\partial q}$ versus electrode charge. Reprinted from [31].

In figure 4.8, the slopes of $\frac{\partial q^-}{\partial q}$ versus electrode charge have been plotted. Triangle denotes FC-12 carbon electrodes. Circle indicates Guoy-Chapman-Stern model with $\epsilon=30$. Square indicates KF solution on mercury electrodes.

By introducing the individual parts in Eqn. 20 in terms of the Gouy–Chapman model and using the above charge coordinates, expression 22 follows [30]:

$$F \left(\frac{\partial n_s}{\partial q_e} \right) = \frac{1}{2} \left\{ \frac{Q_e + (Q_d/2)}{\left((Q_e + (Q_d/2))^2 + \mu_1^2 \right)^{1/2}} + \frac{Q_e - (Q_d/2)}{\left((Q_e - (Q_d/2))^2 + \mu_2^2 \right)^{1/2}} \right\} \quad (22)$$

where $A = (2RT\epsilon_0 C_s)^{1/2}$, $Q_d = q_d/2A$ and $Q_e = q_e/2A$ and C_s is the concentration of the solution.

The differential charge efficiency and the differential energy efficiency as derived from Eqs. (16), (19) and (22) are shown as a function of Q_e for different Q_d values in Figures. 4.9 and 4.10, respectively. It is apparent that unlike the adsorption charge efficiency, the adsorption energy efficiency drops for high Q_e values and acquires maxima for intermediate values. This is due to the square power dependence of the capacitor energy on charge, while ion adsorption is, at most, proportional to the charge. For both efficiencies, the optimal values are obtained for $Q_d = 0$ [30]. In fig. 4.11, it can also be seen that the differential charge efficiency is inversely proportional to C_s , the bulk concentration of the solution.

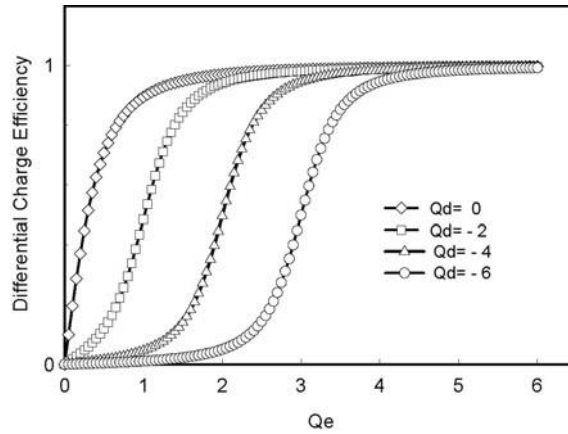


Figure 4.9 : Differential charge efficiency as a function of Q_e for different Q_d values

[30]

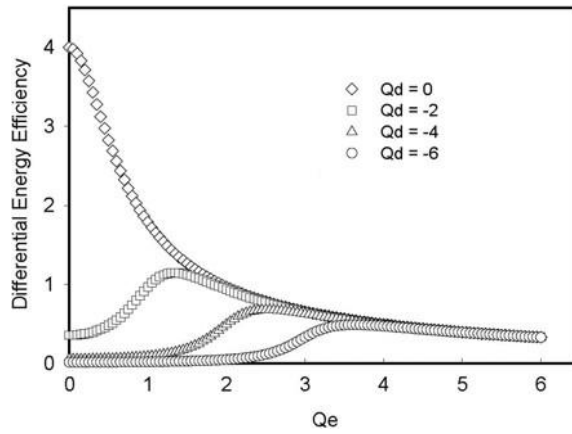


Figure 4.10 : Differential charge efficiency as a function of Q_d for different Q_e values [30]

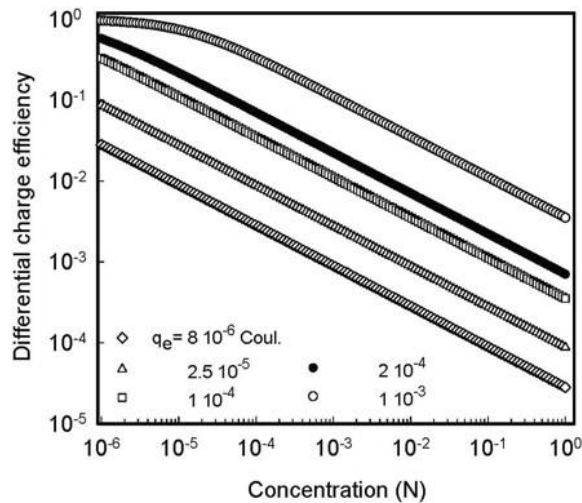


Figure 4.11 : Differential charge efficiency as a function of C_s for different q_e values and $q_d=0$ [30]

The correct choice of the electrode material is a very critical issue for the success of the PACBIPS method for desalination. The electrode material needs to be suitable for desalination of water and needs to possess the following capabilities.

1. Specific surface area (surface area per unit weight) available must be as large as possible for the good adsorption of ions into the electrode surface
2. Electrical conductivity must be as high as possible
3. Fast response of the entire electrode material
4. Chemical and electrochemical stability for wide range of concentrations
5. Shape according to design requirements
6. Must not support scaling, biofouling and organic fouling

In the light of these requirements, carbon fiber is chosen as the material for the electrode.

Desalination process is done in four steps which are described as follows and shown in figure 4.12.

1. Absorption:

In this stage, the ions get adsorbed to the electrode material. This is achieved by the application of potential difference across the electrodes. The excess ions form the electrical double layer

2. Forward pumping:

When the ions get adsorbed, the water in the pipe is devoid of the ions and hence has relatively less salt concentration. This pure water is recovered by pumping.

3. Desorption :

This is also an electrically induced step in which reverse voltage is applied to remove the salts that are adsorbed in step 1.

4. Backward pumping:

This step involves backward pumping of the solution in the pipe. This water contains high concentration of salts.

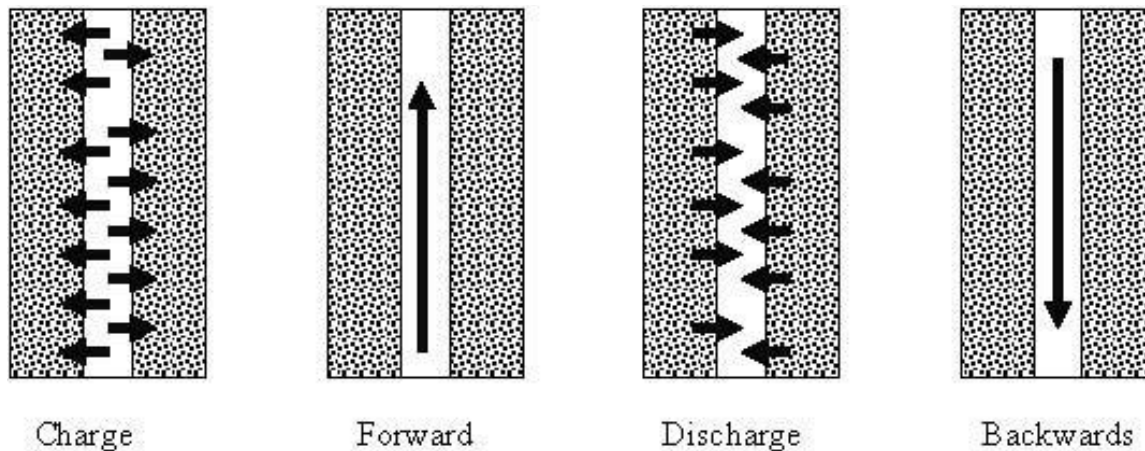


Figure 4.12: Schematic Representation of the four steps of desalination

Step 1 and step 3 are achieved by the application of an alternating voltage of about 12 V for a 10 cell system such that 1.2 V per system is obtained.

The analysis of the capacitor based PACBIPS is explained in this section. The analysis provides key features of the system that have been theoretically calculated. The time taken to desalinate 1 liter of 3.5% NaCl based sea water has been derived based on the RC modelling of the system. An alternating voltage of 12 V which reverses polarity based on a specific frequency has been assumed as the input energy source for this system.

Let us assume that we have 10 PACBIPS cells in series which forms the PACBIPS system. Higher the number of cells, more desalination takes place in a given duration of time. Let us apply 12 V D.C. across these 10 identical cells. Hence, we have 1.2V per cell as the resistance of the cells will be equal owing to the identical geometry and material.

Let us assume the cells are cylindrical and have a diameter of 1cm and a height of 10 cm. A longer geometry is advocated to have a larger surface area. Hence, the volume of the cell will be 7.85 cm^3 and the surface area will be 31.4 cm^2 .

Since we have 10 such cells in series, the total volume of the unit is 79 cm³ and the total surface area is 314 cm². The PACBIPS cells have electrolyte in the central tube and the electrode for voltage application. This forms an electric double layer and can be approximated as a Helmholtz capacitor. The electrolyte combined with the electrode offer a certain amount of resistance. Hence, we have a RC model for the system. Desalination involves charging and discharging this RC network and extracting the relatively deionized water.

The expressions for R and C can be obtained from the model developed by Yunam Oren for the capacitive deionization theory [30].

$$C_T = |z|F \left(\frac{\varepsilon C_s}{2RT\pi} \right)^{\frac{1}{2}} \cosh \left(\frac{|z|F\phi_H}{2RT} \right)$$

Where, C_T is the capacitance of the system, F is the Faraday number, ε is the permittivity of the solution, C_s is the concentration of solution in mols, R is the universal gas constant, T is the temperature, ϕ_H is the potential of the solution at the double layer.

We are mostly interested in the zero potential capacitance. By using the corresponding values for carbon electrode in this equation, we can calculate the specific capacitance of the layer which is obtained as 10 uF / cm². This quantity is measured with respect to specific surface area of the electrode. Hence, ideal way of increasing the capacitance is by increasing the area of the electrode. This means that the ion removal capacity increases as well.

$$R = \frac{2L}{\sigma + K} + \frac{L_s}{K}$$

Where, L is the length of the electrode and L_s is the length of the solution. K is the electrical conductivity of the solution and σ is the electrical conductivity of the solution.

The electrode here is the carbon fiber electrode whose conductivity is plugged in. The electrolyte is the salt water solution and the conductivity of which is around 85 mS/cm. This yields a resistance of about 2Ω for the system. Resistance decreases with increase in solution concentration. But, the change is not considerably high.

The carbon fiber selected was of the type CF-17 and had a very high surface area. The diameter of the braid is 1.25 inch. To compute surface area, a 240 cm long section was chosen and the weight was measured. The surface area for this was about 23.92 m Weight of the section was weighed as 50 g. The number of strands was about 4000 per fiber. Hence we have a surface area of $5000 \text{ cm}^2/\text{g}$. The surface area is computed as follows.

$$\text{Surface area} = \frac{\text{Total surface area}}{\text{weight of the carbon electrode}}$$

Surface area of the carbon fiber used = $5000 \text{ cm}^2/\text{g}$, where the total surface area takes into account the strand size of the fiber and the number of strands per fiber.

The salts can be removed by charging the capacitor in the RC network. The values for R and C have been obtained. The total capacitance is obtained by multiplying the surface area with the capacitance per area. The time taken to charge a capacitor from 10% to 90% is $2.2 RC$

$$\text{Time taken for one charging cycle} = 2.2 RC$$

Hence, the time taken for one charging cycle is 0.0377s.

The capacitor voltage follows the relation, $V(t) = 1.2 \left(1 - e^{-\frac{t}{RC}}\right)$ where t is time in seconds. It has been established that the voltage applied is 1.2 V

Let us calculate the amount of salt removed in this short duration of time. Let the amount of salt removed in one charging cycle be Q .

$$Q = C\Delta V$$

Where C is the capacitance of the layer and ΔV is the amount of voltage applied to remove the charge. The amount of charge removed directly relates to the amount of salt removed in the system. For the given system it is calculated as follows,

$$\text{Amount of charge removed in one charging cycle, } Q = C\Delta V = 0.0226C$$

One mole of charge is 96500 C which the Faraday number is. Hence, number of moles of salt removed is $(0.0226/96500)$ moles. The molecular weight of NaCl is $23\text{g} + 35\text{g} = 58\text{g}$.

$$\text{Salt removed (in weight)} = \frac{Q}{F} \times \text{Molecular weight} \times \text{No. of cells}$$

Hence, the total amount of salt removed per unit cycle is 1.3 mg. One cycle is 0.0377s. So, time taken to remove 1 g of salt is 27.7 s.

The amount of salt in 3.5% water in the given system can be calculated as follows

$$\text{Amount of salt} = \frac{35}{1000} \times \text{Volume of the container}$$

This is because 1 liter of water is 1000 cm which is also equal to 1000g or 1kg by weight and one liter of salt water has 35g of salt in it. This shows that the amount of salt in 79 cm³ of the solution is 76.7 s. Time taken to desalinate 1 liter as per linear extension is 16 minutes.

$$\text{Power consumed} = \frac{V^2}{R}$$

The power consumption is found to be 72 W. Energy consumption is 1.92 kWh/m³ excluding the cost of pumping and infrastructure.

4.4 Implementation and results

Figure 4.13 and Figure 4.14 show the PACBIPS desalination unit being tested. The unit in figure 4.13 was modelled using solidworks and 3D printer. The intertwined wires to which the AC is applied was made of copper. The unit involving 3 phase AC Power is protected by a GFCI and a circuit breaker of 5A. The current through each of the phases is limited by an inductor of 0.1H. The inductor is chosen as a resistor creates loss of energy in terms of heat dissipation. Water mixed with salt to form 3.5% salt concentration of NaCl in water is used as the electrolyte. The experiment is performed and the solution is tested with a handheld salinity meter after certain duration of time. The handheld salinity meter has a capability to measure salinity in the range of 0.1% to 10% with an accuracy of 0.15% and is shown in Figure 4.15.



Figure 4.13 : Setup of the PACBIPS system for experimentation



Figure 4.14 : Setup of the Helmholtz capacitor based PACBIPS system



Figure 4.15 : Handheld salinity meter used to measure salt concentration

Figure 4.16 shows the desalination curve for the PACBIPS system and figure 4.17 shows the desalination curve for the Helmholtz capacitor based PACBIPS system. The plot shows the salinity versus time duration (in hours).

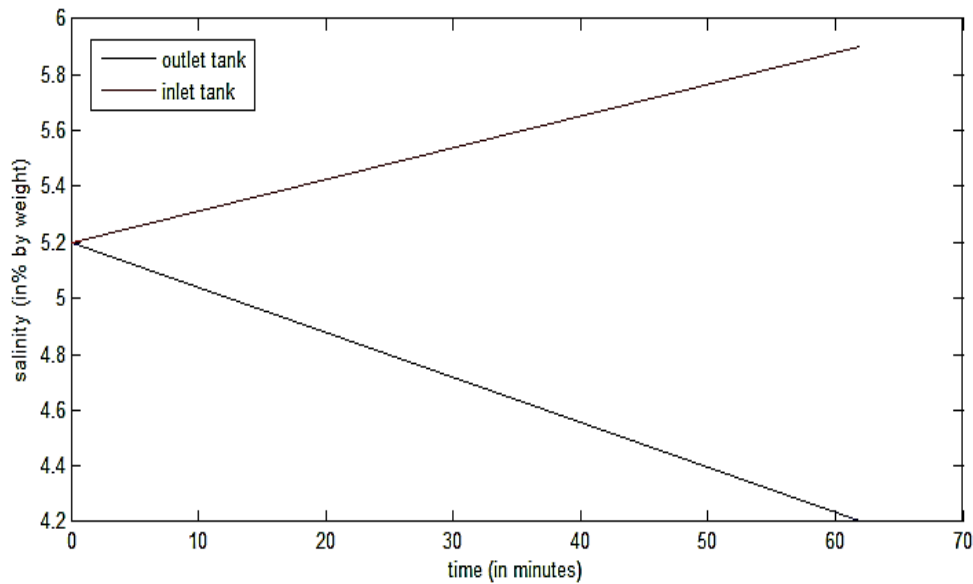


Figure 4.16 : Salt concentration versus time (in hours) for the PACBIPS system

The results of the implemented desalination have been presented. There are a lot of factors which can be tweaked to get better desalination rates. The key factors among them are

1. Specific area of the carbon electrode

Using suitable carbon electrode with higher specific area can result in better desalination efficiency.

2. Electric field shielding

Further studies needs to be carried out to check if electric field shielding has any effect on desalination and how this can be eliminated if present.

3. The thickness of the 3D printed desalination unit

The thinner the material, more the electric field penetrates into the system and better will be the desalination efficiency.

4. Zeta potential

Zeta potential defines the stability of the electric double layer and is a property of the electrode-electrolyte interface. This cannot be directly measured and needs to be theoretically calculated. Having an electrode with a higher zeta potential can improve stability of the electric double layer and hence desalination efficiency.

5. Frequency of operation

Electric mobility of the ions defines the velocity of the ions and this must be considered to change the frequency of operation accordingly. This will also lead to better desalination efficiency.

CHAPTER 5

CONCLUSION

In this chapter, concluding remarks of the research are presented. This chapter also defines scope for future work.

5.1 Concluding remarks

The mathematical analysis and implementation of polyphase alternating current bi ionic propulsion system for desalination of water has been described in this thesis. The mathematical modeling has been based on Guoy-Chapman-Stern theory for electric double layer and Y Oren theory for desalting by electro adsorption. Several conclusions can be drawn from this research work

Unlike membrane based processes such as reverse osmosis, PACBIPS does not require membranes or high pressure system. This eliminates the need to have high pressure equipment such as pipes and pumps and reduces the infrastructural costs making this system cost efficient.

Another advantage of having a membrane less system is that the system does not have to prevent scaling or organic fouling as these mostly take place at the membranes.

Unlike heating processes such as Distillation, PACBIPS does not require change in state of water from liquid to gas. This saves a lot of energy and makes the system energy efficient.

Helmholtz capacitor based PACBIPS requires low voltage for operation not exceeding several volts. This makes the system safe and drastically reduces the risks of electrical hazards.

PACBIPS can be operated from solar energy in remote areas making the unit portable. This makes the desalination unit environmentally clean.

Further studies on concepts such as electrode material, electron field screening, electric mobility is necessary to make this an industrially scalable unit.

5.2 Scope for future work

The PACBIPS technology for desalination of water has a lot of scope for further development in order to improve desalination efficiency, reduce desalination costs, and reduce energy consumption further. The scope for future work can be outlined as follows

The electrode material for PACBIPS can be developed to have larger available surface area for ion adsorption. This can be done by a careful design of the pore structure by using material such as Carbon nanotubes.

Frequency controller can be introduced to change the frequency of operation based on the salt concentration and the mobility of ions in order to optimize time and energy consumption.

The system can be modelled as a feedback system by introducing flow rate and controlling the same for better desalination results.

The effects of electric field screening and the implications of the same in PACBIPS can be studied and the system can be redesigned to minimize such effects.

REFERENCES

1. How much water is there on, in, and above the Earth?, The USGS water science school, (<http://water.usgs.gov/edu/earthhowmuch.html>)
2. Igor Shiklomanov's chapter, World fresh water resources in Peter H. Gleick (editor), 1993, *Water in Crisis: A Guide to the World's Fresh Water Resources* (Oxford University Press, New York).
3. Joachim Koschikowski, Water desalination: when and where will it make sense? , a presentation, Washington, Feb.21 2011
4. United Nations World Water Development Report 4. Volume 1: Managing Water under Uncertainty and Risk
5. C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, *Desalination*, Volume 216, Issues 1–3, 5 October 2007, Pages 1-76, ISSN 0011-9164, <http://dx.doi.org/10.1016/j.desal.2006.12.009>. (<http://www.sciencedirect.com/science/article/pii/S0011916407004250>)
6. M. Wilf, Fundamentals of RO–NF technology, International Conference on Desalination Costing, Limassol, 2004.
7. J.M. Veza, Desalination in the Canary Islands: an update, *Desalination*, 133 (2001) 259–270.
8. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes Amy E. Childress, Menachem Elimelech
9. Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes Menachem Elimelech, Xiaohua Zhu, Amy E. Childress, Seungkwan Hong
10. Garud, R. (2011). A Short Review on Process and Applications of Reverse Osmosis. *Universal Journal of Environmental Research and Technology*, 1(3), 233-238.
11. Hisham T El-Dessouky, Hisham M Ettouney, Yousef Al-Roumi, Multi-stage flash desalination: present and future outlook, *Chemical Engineering Journal*, Volume 73, Issue 2, May 1999, Pages 173-190, ISSN 1385-8947, [http://dx.doi.org/10.1016/S1385-8947\(99\)00035](http://dx.doi.org/10.1016/S1385-8947(99)00035) (<http://www.sciencedirect.com/science/article/pii/S1385894799000352>)

12. Marcovecchio, M. (2011). Optimization of Hybrid Desalination Processes Including Multi Stage Flash and Reverse Osmosis Systems. In *Desalination, Trends and Technologies*. Intech.
13. Hisham T El-Dessouky, Hisham M Ettouney, Yousef Al-Roumi, Multi-stage flash desalination: present and future outlook, *Chemical Engineering Journal*, Volume 73, Issue 2, May 1999, Pages 173-190, ISSN 1385-8947, [http://dx.doi.org/10.1016/S1385-8947\(99\)00035-2](http://dx.doi.org/10.1016/S1385-8947(99)00035-2) (<http://www.sciencedirect.com/science/article/pii/S1385894799000352>)
14. Hamed, Osman A. "the performance of different antiscalants in multi-stage flash distillers." *Second Acquired Experience Symposium* (1997). Print.
15. Tzahi Y. Cath, Amy E. Childress, Menachem Elimelech, Forward osmosis: Principles, applications, and recent developments, *Journal of Membrane Science*, Volume 281, Issues 1–2, 15 September 2006, Pages 70-87, ISSN 0376-7388,
16. E.G. Beaudry, J.R. Herron, Direct osmosis for concentrating wastewater, in: *Proceedings of the 27th International Conference on Environmental Systems*, Lake Tahoe, NV, July 14–17, 1997
17. R.J. York, R.S. Thiel, E.G. Beaudry, Full-scale experience of direct osmosis concentration applied to leachate management
18. J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by a novel ammonia–carbon dioxide forward osmosis process: influence of draw and feed solution concentrations on process performance, *J. Membr.Sci.* 278 (2006) 114–123
19. T.Y. Cath, V.D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space. II. Combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater, *J. Membr. Sci.* 257 (2005) 111–119
20. C. Biberdorf, Filter in a pouch, *The Warrior* (2004) 3
21. D.D. Caudle, J.H. Tucker, J.L. Cooper, B.B. Arnold and A. Papastamataki, Electrochemical demineralization of water with carbon electrodes, *Research Report*, Oklahoma University Research Institute, 1966
22. A.M. Johnson, A.W. Venolia, J. Newman, R.G. Wilbourne, C.M. Wong, W.S. Gillam, S. Johnson and R.H. Horowitz, Electrosorb process for desalting water,

- Office of Saline Water Research and Development, Progress Report No 516, US Department of the Interior, Publication 200 056, 1970
23. A.M. Johnson and J. Newman, Desalting by means of porous carbon electrodes. *J. Electrochem. Soc.*, 118(3) (1971) 510–517.
 24. Joseph Hui (2014), Polyphase alternating current bi-ionic propulsion system for desalination and marine transportation, filed U.S. Patent.
 25. Abdul Karim Mayere, “Solar Powered Desalination”. PhD thesis, University of Nottingham
 26. Marc A. Anderson, Ana L. Cudero, Jesus Palma, Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete?, *Electrochimica Acta*, Volume 55, Issue 12, 30 April 2010, Pages 3845-3856, ISSN 0013-4686, <http://dx.doi.org/10.1016/j.electacta.2010.02.012>.
 27. T.A. Davis, in: M.C. Porter (Ed.), *Handbook of Industrial Membrane Technology*, Noyes, Park Ridge, NJ, 1990.
 28. Yang, K., Yiacoumi, S., & Tsouris, C. (2007). Electrical Double-Layer Formation. *Dekker Encyclopedia of Nanoscience and Nanotechnology*, 10.1081/E-ENN-120009064.
 29. P. Delahay, *Double Layer and Electrode Kinetics*, Interscience, Wiley, New York, 1966.
 30. Yoram Oren, Capacitive deionization (CDI) for desalination and water treatment — past, present and future (a review), *Desalination*, Volume 228, Issues 1–3, 15 August 2008, Pages 10-29, ISSN 0011-9164, <http://dx.doi.org/10.1016/j.desal.2007.08.005>. (<http://www.sciencedirect.com/science/article/pii/S0011916408002294>)
 31. Y. Oren and A. Soffer, Water desalting by means of electrochemical parametric pumping. I The equilibrium properties of a batch unit cell. *J. Appl. Electrochem.*, 13 (1983) 473–487.