Recovery of Nutrients from Drain Channel of CAN and NP Plants

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Certificate

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Dedication

To our parents, who were a source of constant support and helped us become the people we are today.

Acknowledgements

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Abstract

This project is aimed at recovering the nutrients, namely nitrates and phosphates, that are being lost in the drain channels of the calcium ammonium nitrate (CAN) and nitrophosphate (NP) plants at Pak-Arab Fertilizers, Multan. In the current operating conditions, the plant is losing water at a rate of 15 m^3/hr with a total dissolved solid (TDS) content of approximately 23,000. The water has to be treated in the effluent treatment plant (ETP) to bring the effluents to environmental standards. A scheme to recover the water along with the nutrients has been devised, bringing the plant to zero liquid discharge (ZLD) standards. The prominent processes that are put into practice are reverse osmosis (RO), electrodialysis (ED), crystallization and filtration. The effluent streams are combined and then sent through the suggested schemes. After the effluent streams have been processed, the recovered water is valued at over 12 tons per hour and the recoverable solids amount to 404.87 kg per hour, out of which 189.28 kg are retrieved in usable form and 215.59 kg are recycled.

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Chapter 1

Introduction

1.1 Background

The world today faces an unprecedented crisis as climate change, pollution and overpopulation have taken their toll on the environment and the resources left for humans to use are under great stress. One of the most critically stressed resource currently and ironically is water. The earth consists 70% of water but most of that is found within the oceans and is not fit for human consumption due to the high amounts of dissolved salts. This only leaves fresh water sources for the use of the ever-growing human population.

The fresh water resources are not only finite but pollution and mismanagement has rendered a growing proportion of them useless. One of the largest contributors to fresh water pollution is industrial establishments. Industry not only uses a large amount of water but it pollutes an even greater amount. Effluents from industrial plants are discharged into the environment and end up making their way into freshwater bodies such as lakes and rivers.

According to the World Economic Forum, water scarcity is the single largest ‘global risk’ that confronts the planet over the next decade. It is estimated that over 2 billion people live under severe water scarcity. This is a whopping one third of the whole population of the world. In addition to this, over half of all the major cities in the world face extreme water scarcity. It is estimated that a large number of countries will be facing water scarcity and drought like conditions with the decade.

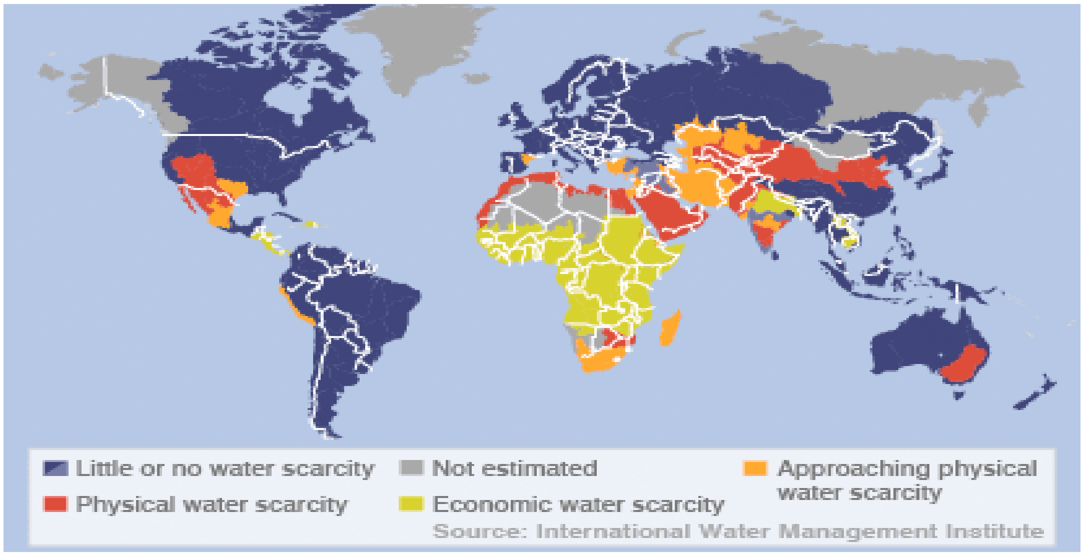


Figure 1: Global water scarcity distribution

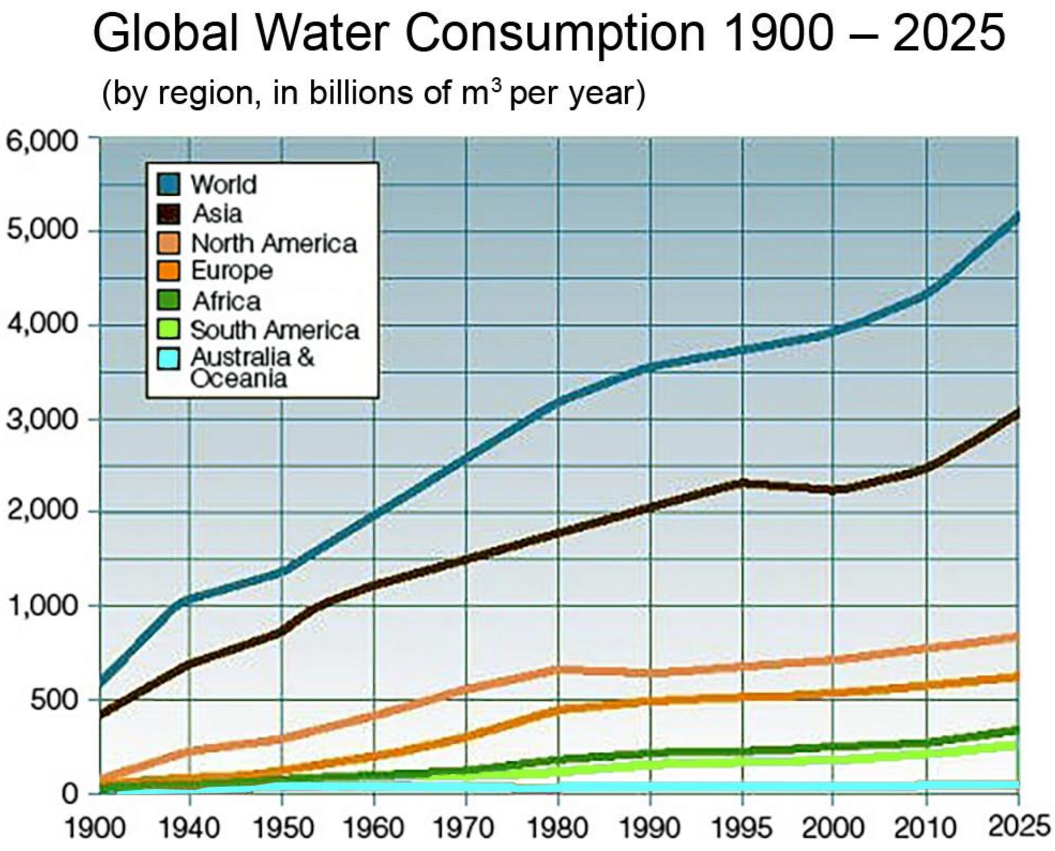


Figure 2: Global water consumption

At this point it is important to note that the fresh water resources only account for 3% of the earth's water supply (the rest is seawater) and only 0.014 % is both fresh and easily accessible. Ironically, even this meager percentage is enough for the human population to get by sustainably but poor management of resources has caused great escalation in this crisis. There is an inadequate water management system or no water management system in most of the countries in the world. Climate change has exacerbated this issue by creating extremely wet areas and extremely dry areas. Both of these extremes inhibit the ability of humans to conserve and manage the water while fulfilling their needs.

In the view of the current scenario, there is a global push to come up with more efficient water management systems. Governments and private organizations all around the world are spearheading the movement and pouring in thousands of dollars and work hours into this initiative. Governmental regulations on effluent discharge have also tightened and industry is under great pressure to reduce the amount of pollution it produces.

Third world countries are especially vulnerable to this crisis. India and China have identified the problem and have adopted an aggressive approach to deal with it. Pakistan sits on a ticking time bomb and it is considered one of the most water stressed countries in the world. According to estimates, it is the third country to be affected most by water climate change and water shortage by the year 2025. It needs to take radical measures if it intends to avert the damage that will be caused by the upcoming water crisis. The situation for Pakistan is grimmer because of the fact that Pakistan is largely an agrarian country. The economy is completely dependent on agriculture and the agriculture is in turn dependent on irrigation.

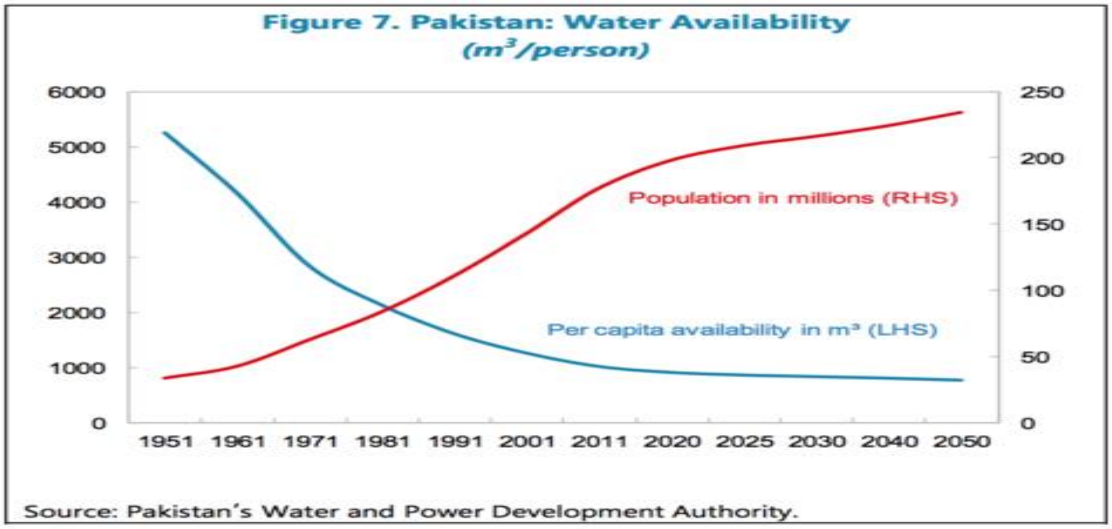


Figure 3: Water availability in Pakistan

A water shortage in Pakistan means that the country will not have enough water to sustain the agricultural economy. A major blow to the agriculture will not only deal a deathblow to the economy but will cause large scale famine too which can result in widespread death and destruction in theory.

1.2 Pak-Arab Fertilizers

Pak Arab Fertilizer (PFL) is one of the leading fertilizer companies in Pakistan. For the last 38 years, it has been the sole and foremost producer of compound fertilizers such as Nitrophosphate (NP) and Calcium Ammonium Nitrate (CAN). In addition to this, the company also produces urea.

The complete list of products offered by the company is as follows

- Nitrophosphate (NP)
- Calcium Ammonium Nitrate (CAN)
- Urea
- Diammonium Phosphate (DAP)

To manufacture the said products, the company has numerous production facilities. The production facilities owned by the company are listed down as follows

1.2.1 Ammonia Plant

It is based on Kellogg process. The plant started the production in November 1978. The capacity of the plant is 910 MTPD, which was further increase to 960 MTPD in April, 1986 due to the addition of a Purge Gas Recovery Unit. The plant is designed to operate 330 days annually.

1.2.2 Nitric Acid Plant

There are total 03 lines of Nitric Acid plant at PFL.

- **Two identical lines named as "The New Nitric Acid plant"** each with a capacity of 600 metric tons per day HNO_3.
- This is Ostwald's medium pressure process.

Third line is, Old Nitric Acid plant, the capacity is 180 MT/Day.

- The Old Nitric Acid Plant is designed by GIRDLER USA and is commissioned in 1959.
- It is a high-pressure process.

Liquid Ammonia is heated before it is gets mixed with filtered air. The ammonia-air mixture is then filtered and fed into the ammonia burner in which the oxidation of ammonia takes place in the presence of a Catalyst which 90% Platinum (Pt) & 10% Rhodium (Rh).

The product gas which contains nitrous oxides gets cooled through waste heat boiler and other heat exchangers. The cool gas is then fed into the absorption towers, in which NOx gases are then absorbed in process water to produce Nitric Acid, having concentration around 60%.

1.2.3 Urea Plant

In Pak-Arab Fertilizer Multan, there is one Urea plant having a capacity of 300 metric tons per day. This plant employs Snamprogetti (SAIPEM) Ammonia stripping technology. In addition to standard urea plant sections, the PFL urea plant also handles a pressurized ammonia storage facility and an ammonia cylinder/bowser filling facility.

The gaseous Carbon Dioxide is compressed in reciprocating compressor and is fed to reactor where it meets with liquid ammonia and recycle carbamate solution. The reaction is two step and gives almost 60% molar conversion based on carbon dioxide. This process also yields water. In later decomposition stages the solution containing urea, carbamate and water is heated at a reduced pressure to decompose and recycle carbamate. Finally, water is evaporated in a two stage vacuum evaporation system to get urea melt. This urea melt is sprayed through prilling bucket in prilling tower where contact with atmospheric air solidifies it in the shape of prills. The resultant product is 99.7% urea with remaining water

1.2.4 Nitrophosphate Plant

Nitro Phosphate (NP) plant is based on modern European technology. The Plant has been designed to use imported rock phosphate without compromising on product quality. The Plant is capable of producing 1,015 MTPD of NP. NP is a prilled fertilizer in which each prill has evenly distributed amounts of nitrogen (22 +/- 0.5%) and phosphorus (20 +/- 0.5%).

1.3 Zero Liquid Discharge (ZLD) Plant

A number of technologies were developed over the recent decades to tackle water related problems by the industry. One of these was the ‘Zero Liquid Discharge’ approach. A Zero Liquid Discharge or ZLD approach essentially means that a plant/ industrial settlement will not discharge any liquid effluent. All the liquid will be extracted and reused whereas the solid waste will be disposed of or used separately. ZLD is a radical approach and deals with the problem aggressively by eliminating wastage from the root.

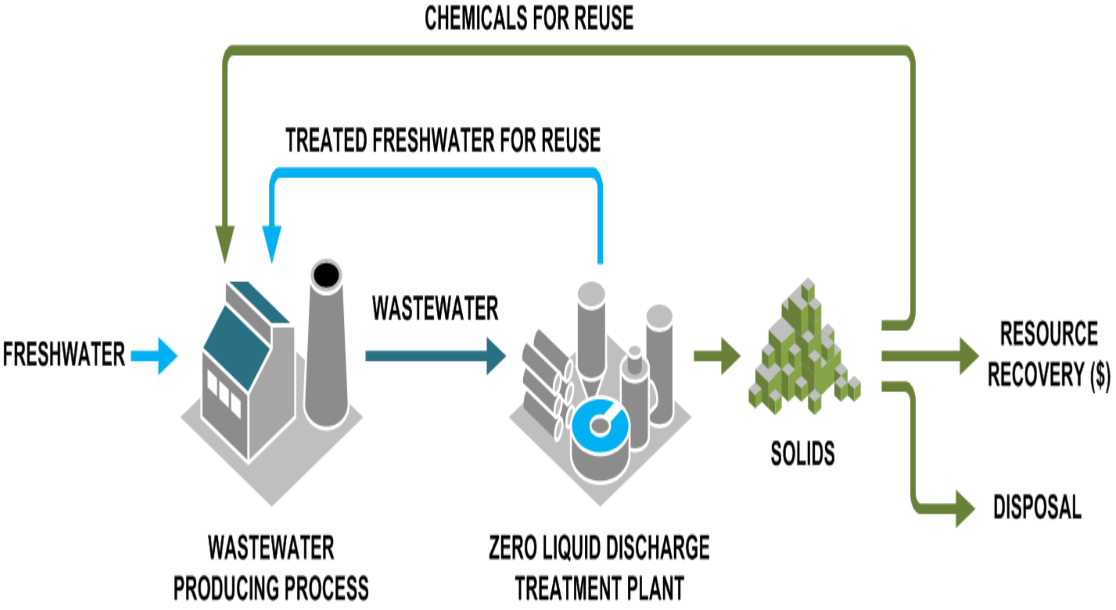


Figure 4: ZLD Process

This approach was developed in the USA when the authorities discovered that the Colorado River was being polluted by power plants excessively. To prevent further pollution, the government passed regulations that said that the plants were not to discharge any liquid effluent. This was the first time that legislative foundation was laid for the development of this approach. The power plants were now obliged to follow this new protocol that was set by the government and this galvanized them into developing the first working ZLD plants.

The initial approach used was largely thermal. Mechanical vapor compression (MVC) evaporators were used in conjunction with crystallizers to eliminate liquid discharge and extract solid waste. The legislation by the government was largely successful as the pollution in the river was curbed by the new provisions.

The technology used by these plants soon found its way into other places worldwide. Environmental regulations imposed by governments made way for the introduction of ZLD. Countries like Russia, China and India were quick to adopt this approach as it was considered beneficial for the industry and environment. The Indian state of Tamil Nadu has made it compulsory for all industrial settlements to make sure that they comply with ZLD standards.

1.3.1 Applications of ZLD

Treatment and recycling of industrial waste effluents

- Artificial fuels
- Primary processing
- Refining of Oil
- Microelectronics
- Cogeneration
- Textile
- Mining of Coal
- Fertilizer
- Production of Ethanol
- Solid waste
- Manufacturing of batteries
- PVC manufacturing
- Petroleum Industry
- Coal liquefaction
- Treatment of municipal waste water

The initial challenges faced by ZLD were that of a very high initial investment and high running cost hence the approach was only profitable in the longer run and in places where water disposal was otherwise very costly. All the initial ZLD plants used thermal technology. MVC evaporators and crystallizers were used. Both these unit operations are very costly to set up and have high running costs.

1.3.2 Limitations of ZLD

Presently, the major drivers for using ZLD are

- Even though ZLD is very expensive in most cases; it becomes more economical when long distant waste needs to be transported.
- Environmental regulation on discharge of specific solutes (salt, toxic elements, nitrate, etc.)
- Increased water consumption requirements due to population boom and scarcity of drinking water.
- It is a very tempting option from an economical point of view since water Etraction from conventional resources become more and more expensive
- Environmentally friendly solution

Still ZLD has drawbacks, probably, the most significant are

- Very high capital and operating cost
- It has to be designed specifically for each case
- Difficulties to deal with complex streams (e.g., petrochemical)

This problem was soon tackled by the introduction of technologies such as reverse osmosis (RO), electrodialysis (ED), forward osmosis (FO) and membrane distillation. Membrane technologies as the ones mentioned provided cheaper alternatives to the costly evaporators. This also allowed for flexibility too.

1.3.3 Conventional Thermal ZLD Technology

- The conventional ZLD is based on evaporation and crystallization operations
- Evaporation intends to achieve >90% water recovery
- Crystallization can help achieve 100% recovery
- Solids may be sent for further filtration

- Latent heat of vaporization is recovered
- Operational Costs are very high (20-40 kWh/m^3 vs. 2-3 kWh/m^3 in desalination).

1.3.4 Hybrid ZLD Technologies

- Due to high costs, there has been a lot of research going on to employ more energy saving technologies.
- Natural Evaporation, although slow, but has large foot prints.
- Another reason to pursue this research is the presences of suspended solids which complicates water treatment. Available solutions:
    - Conventional bioremediation
    - MBR/UF pretreatment

1.3.5 ZLD Combined with RO

RO is currently the most cost-effective solution available for desalting. The main purpose is to recover as much water as possible.

The ZLD cost drops as RO recovery increases. The recovery in RO is however limited by 3 main factors

- The greater the TDS, the greater the Osmotic Pressure
- Scaling caused by soluble salts
- Fouling

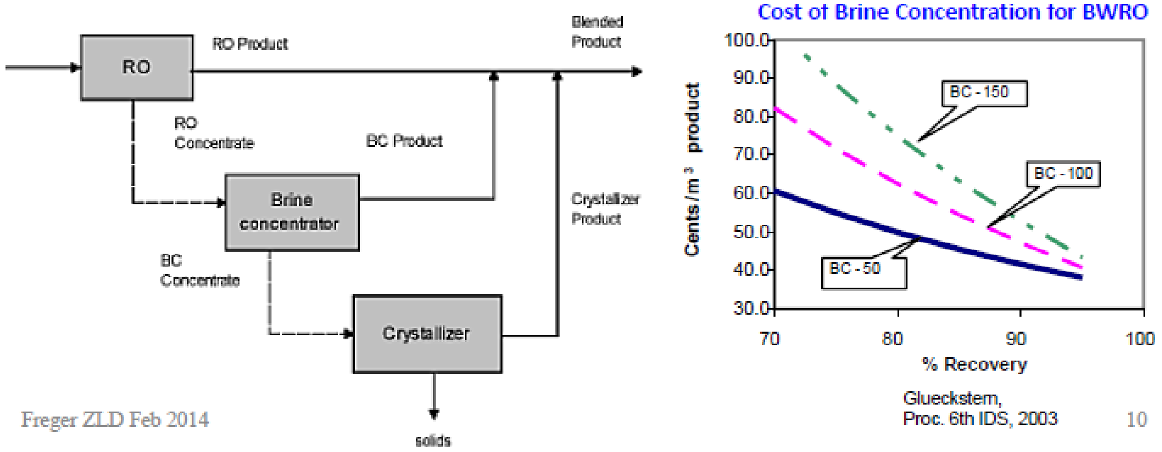


Figure 5: ZLD combined with RO

1.3.6 ZLD Combined with ED

- Since ED is not limited by the amount of TDS, so it is very efficient in this case.
- Generally, the operating cost of ED is greater than RO but less than crystallization.

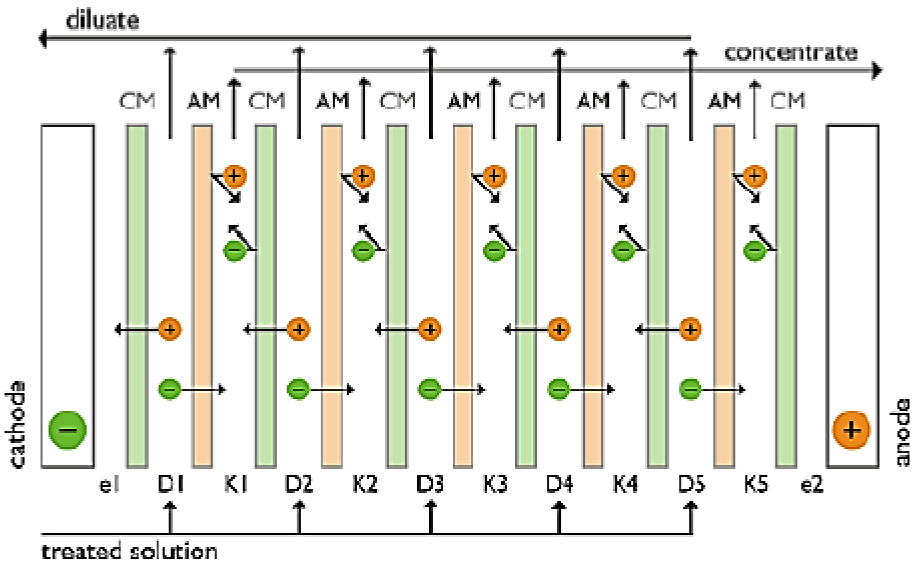


Figure 6: ZLD combined with ED

Chapter 2

Literature Review

2.1 Industrial Information

The project has been carried out on the effluent of the CAN and NP plants of Pak Arab Fertilizer Ltd. The composition and flow rates of these feeds were obtained from the industry. The effluent comes from 3 different plants namely the CAN, NP and CN plant. The data on each is as follows:

Volumetric flow rate	4250L/hr
TDS	13000 ppm (13000 mg/L)
pH	8.5
Mass flow rate (water)	4250 kg/hr
Mass flow rate (solute)	55.25 kg/hr

Table 1: CAN Plant Stream Specifications

Component	Mass Fraction	Mass Flow rate
NH_4NO_3	0.377	20.83 kg/hr
HNO_3	0.623	34.43 kg/hr

Table 2: CAN Plant Stream Composition

Volumetric flow rate	5000L/hr
TDS	61000 ppm (61000 mg/L)
pH	8
Mass flow rate (water)	5000 kg/hr
Mass flow rate (solute)	305 kg/hr

Table 3: CN Plant Stream Specifications

Component	Mass Fraction	Mass Flow rate

NH_4NO_3	0.062	18.91 kg/hr
HNO_3	0.938	286.09 kg/hr

Table 4: CN Plant Stream Compositions

Volumetric flow rate	6000L/hr
TDS	16000 ppm (16000 mg/L)
pH	4
Mass flow rate (water)	6000 kg/hr
Mass flow rate (solute)	96 kg/hr

Table 5: NP Plant Stream Specifications

Component	Mass Fraction	Mass Flow rate
NH_4	0.09	8.64 kg/hr
HNO_3	0.486	46.67 kg/hr
PO_4	0.424	40.70 kg/hr

Table 6: NP Plant Stream Compositions

Volumetric flow rate	15250 L/hr
Mass flow rate (water)	15250 kg/hr
Mass flow rate (solute)	456.25 kg/hr

Table 7: Combined Stream Specifications

For the combined stream, we will analyze the ions that are present instead of the compounds as ions are of consideration in the unit operation that follows (Reverse Osmosis). The breakdown of the combined stream according to ions present is as follows

Component	Mass flow rate(kg/hr)	Concentration (kg solute/L solvent)	Concentration (g solute/ L solvent)	Concentration (g solute/ 100ml solvent)
NH_4^+	17.64	0.00116	1.16	0.116
NO_3^{1-}	292.32	0.0192	19.2	1.92
PO_4^{3-}	40.70	0.00267	2.67	0.267

Table 8: Combined Stream Compositions

Chapter 3

Current Technology

3.1 Effluent Treatment Plant

The influent to the effluent treatment plan is the gravity fall water from the cooling towers. This water contains nitrate, fluoride and phosphate ions in solution. The effluent treatment plant works to reduce the concentration of these ions, ensuring environment standards of effluent discharge are met.

The basic chemical treatment takes into account the relatively insoluble nature of the calcium and fluoride ions. These chemicals are precipitated upon addition of lime slurry to the influent liquor. In order to ensure maximum efficiency of the process, approximately three times the stoichiometric amount of lime is added to the solution, increasing the pH value to 11. This pH value is unacceptable for discharge purpose, due to which the solution must be dosed with carbon dioxide to precipitate the sparingly soluble calcium carbonate.

The effluent treatment plant is designed to run 24 hours a day, with sufficient flexibility to accommodate the varying concentrations of the ions that are entering the plant. The stages within the effluent treatment plant are discussed in the subsequent sections.

3.1.1 Flash Mixing Chamber

Raw water from the plants is fed directly into the flash mixing chamber where it is mixed with the recycled supernatant liquor from the Radiflo thickener and sludge presses. Lime is dosed at this point and continuous in-line mixing takes place via motorized mixers mounted at the top of the chamber.

Tanks	1
Water depth	2 m
Capacity	204 m^3/hr
Agitator speed	76 RPM

Table 9: Flash Mixing Chamber Specifications

3.1.2 Reaction Tank

The discharge from the mixing chamber flows downwards by gravity to the primary mixing zone of the first Clereflo tank, in which it is agitated and thoroughly mixed with recirculated sludge. The liquor is then sent to the secondary reaction zone of the tank by hydraulic action of the rotor.

After the secondary mixing zone, the slurry is carried downwards on to the surface of the downwardly moving slurry inside the slurry pool. All of the slurry is in directionally controlled motion, radial and downward, and volumes of clarified water are displaced from it by the introduction of the volumes of incoming raw water. The remaining volumes of slurry are drawn back into the primary mixing zone by the rotor.

The design of the reaction tanks dictates that heavy slurry particles are retrieved from the bottom of the tank, while the lighter ones are swept into the slurry pockets off of the surface of the water in the tank by the action of the suspended scrapper. The slurry pockets are emptied manually, while the discharge of the slurry from the bottom is controlled by timed switches, opening to allow slurry to leave.

Tanks	2
Water depth	3.1 m
Capacity	210 m^3/hr
Agitator speed	8 RPM

Table 10: Reaction Tank Specifications

3.1.3 Neutralization tank

The clarified solution is fed to the second set of tanks, which work in a manner similar to the first tank. The primary difference exists in the dosing of carbon dioxide, which is done in order to reduce the pH of the water from 11 to an environmentally acceptable value of about 7-8. The pH is reduced by the reaction of lime with calcium carbonate to produce precipitates of calcium carbonate.

3.1.4 Sludge thickener

Automatically timed valves are set to coincide with the rotation of the scrappers in the reaction tanks to allow sludge to be discharged into the sludge thickener.

The thickener is spanned by a fixed bridge from which is suspended a rotating scrapper boom and picket fence. The slow rotation of the boom and picket fence allows partial separation of the sludge from the water; the heavier sludge falling to the bottom and water rising over the recover weir to discharge into the supernatant water recovery tank.

3.1.5 Sludge presses

Two sludge presses are installed above a covered area where sludge is pumped automatically. The sludge is pressed and the dewatered cake is discharged into a container area, while the recovered water falls into the supernatant recovery pit.

Type	Cloth filter press
Number	2
Capacity	0.8 m^3/hr
Scrapper speed	0.0255 RPM

Table 11: Press Filter Specifications

3.1.6 Water outlet

The treated water is discharged to a sump where it is mixed with effluents from other sources and then overflows a weir into a final sump. The final collected volume of the effluents is discharged to a nearby river

3.2 Limitations and Problems of the ETP

The effluent treatment plant serves to meet environmental standards of effluent; however, it does not recover any of the nutrients being lost. The nutrients that are lost promote the fertility of soil, and upon leeching to waterways, they initiate eutrophication. The eutrophication in rivers and other water bodies decreases the oxygen content, resulting in death of the organisms existing in the water, devastating the ecosystem. Moreover, the leeched nutrients, primarily the nitrates, are responsible for problems such as blue baby syndrome when they leech into water bodies designated for human consumption.

The solid waste generated in the processing taking place within the effluent treatment plant is extremely bulky, making transport expensive, and is also not as useful as the intermediates being produced before it. The result is the loss of useful product in the form of sludge.

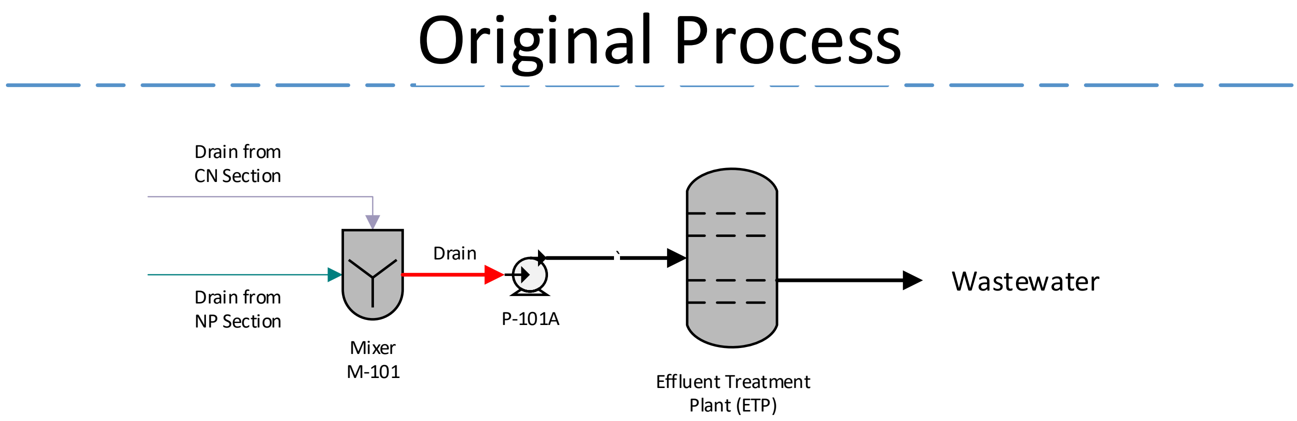
Other problems with the ETP include the release of considerable amounts of free and aqueous ammonia, creating further health hazards. The manual operation of the sludge pockets also creates a hazard for human health.

Chapter 4

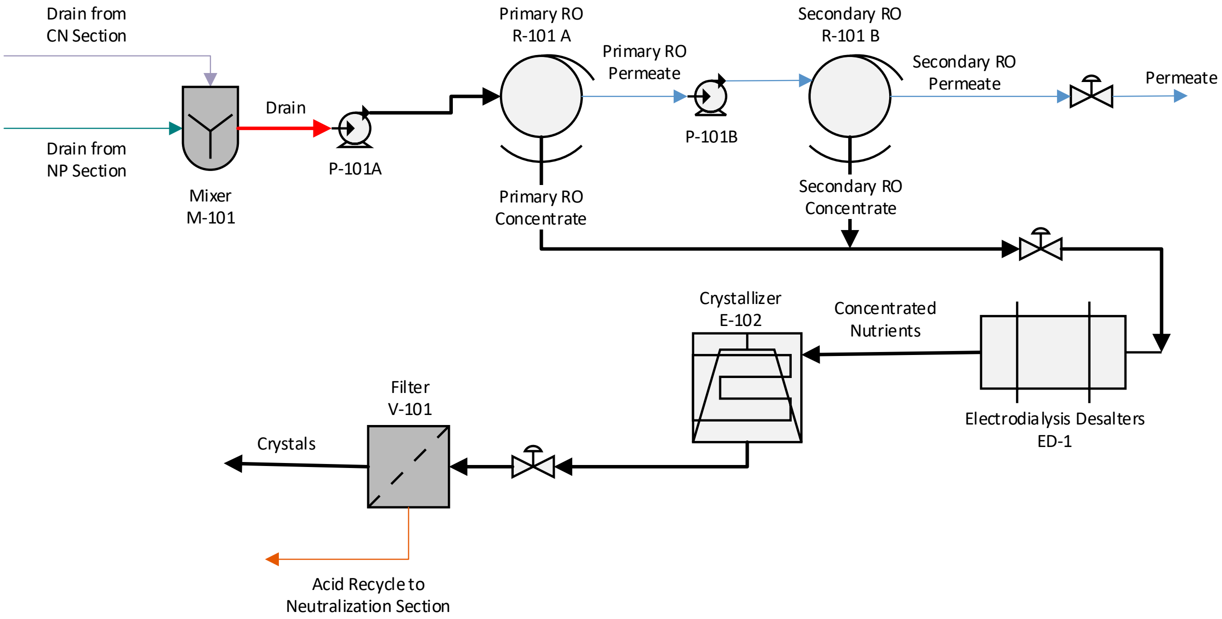
Proposed Process

4.1 Process Flow Diagram

The proposed process consists of a reverse osmosis filter to remove the nutrient ions from the water. The permeate stream is then further purified using a second reverse osmosis filter. The concentrates streams from both RO filters are combined and fed to an electrostatic desalting unit. The electrodialysis unit then concentrates the salts, producing a purified stream of water and sending the concentrated solution to the crystallizers, in order to prepare the nutrient salts for extraction. After the phase separation has been carried out, filters are used to recover the salts.



Proposed Process



4.1.1 Reverse Osmosis Membrane

Osmosis is a natural process in which a solution with lower concentration moves to a solution with higher concentration because of difference in concentration. This movement takes place by a natural tendency of the solution.

This process usually occurs in plants in which the solution has to move from low concentration to higher concentration through semi-permeable membrane. It is a type of membrane which allows some of the solute particles dissolved in solvent to pass through while other particles are retained.

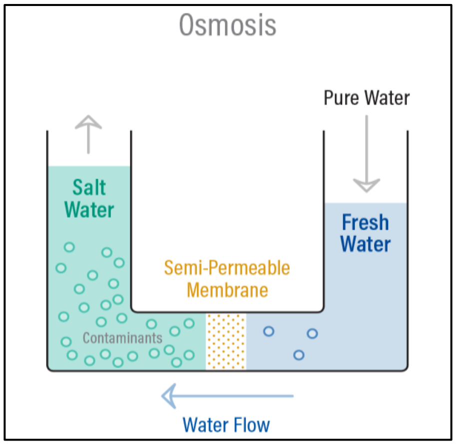


Figure 7: Osmosis Driving Force

It is a process opposite to osmosis in which force, in the form of pressure, is applied to reverse the natural tendency of the solution. Reverse Osmosis process causes the solvent to pass through the semi permeable membrane with some dissolved solids. It is the process used most widely in industries now-a-days to filter impurities from water.

Reverse Osmosis works by applying pressure, usually by a pump, to increase the pressure on the higher concentration side of the RO membrane and force the water to travel to other side with lower concentration through a semi-permeable membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure applied depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the *osmotic pressure*.

The desalinated water that is treated is called *permeate* (or product) water. The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the *reject* (or concentrate) stream.

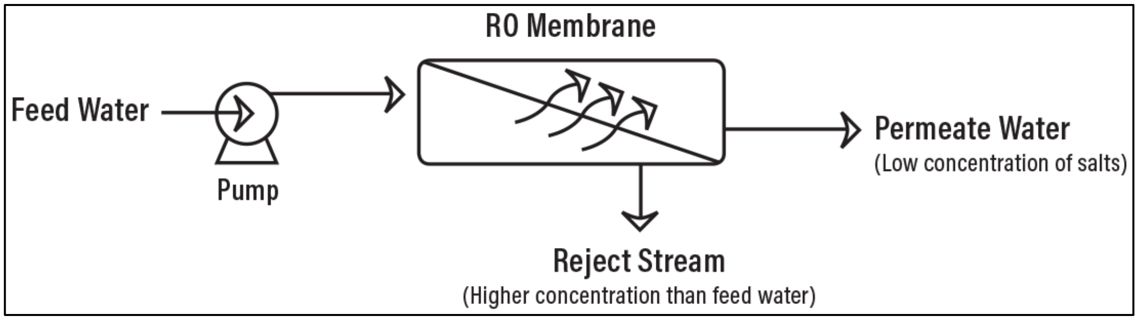


Figure 8: Reverse Osmosis Process

Feed water passes through the membrane while dissolved solids having size greater than the pore size of the membrane will not pass. In this way, water is treated to reduce the mineral content it holds. Reject Stream can be resent to the pump to increase the quantity of water purified.

It is important to understand that an RO system employs cross filtration rather than standard filtration where the contaminants are collected within the filter media. With **cross filtration**, the solution passes through the filter, or crosses the filter, with two outlets: the filtered water goes one way and the contaminated water goes another way. To avoid build-up of contaminants, cross flow filtration allows water to sweep away contaminant build up and also allow enough turbulence to keep the membrane surface clean.

Reverse Osmosis removes dissolved salts (ions), particles, colloids, organics, bacteria and pyrogens from the feed water. An RO membrane rejects contaminants based on their size and charge. Any contaminant that has a molecular weight greater than 200 is likely rejected by a properly running RO system. Likewise, the greater the ionic charge of the contaminant, the more likely it will be unable to pass through the RO membrane. For example, a sodium ion has only one charge (monovalent) and is not rejected by the RO membrane as well as calcium for example, which has two charges. Likewise, this is why an RO system does not remove gases such as CO_2 very well because they are not highly ionized (charged) while in solution and have a very low molecular weight. Because an RO system does not remove gases, the permeate water can have a slightly lower than normal pH level depending on CO_2 levels in the feed water as the CO_2 is converted to carbonic acid.

4.1.2 Electrodialysis

The outlet of the RO system is not concentrated enough for crystallization to take place hence the need arises for further concentration. To achieve this end, an electrodialysis plant has been incorporated into the solution. The design of any ED plant starts with the determination of the required membrane area for a certain capacity. The said is calculated using the following design equation

$$\mathrm{A}_T = \frac{\eta \mathrm{F}}{\mathrm{i}\xi}$$

where $\eta$is the separation rate in mol/s, F is the Faraday constant, i is the applied current density in A/m2 and $\xi$is the current efficiency. This area represents the total cell area that consists of a cation and an anion exchange membrane and is the most important parameter in the designing of an electrodialysis plant.

We know the following about the feed inlet to the ED plant

- Volumetric flow rate: 11.98 m^3/hr = 3.33L /s
- Concentration: 0.974 mol /L
- Molar flow rate: 3.24 mol /s

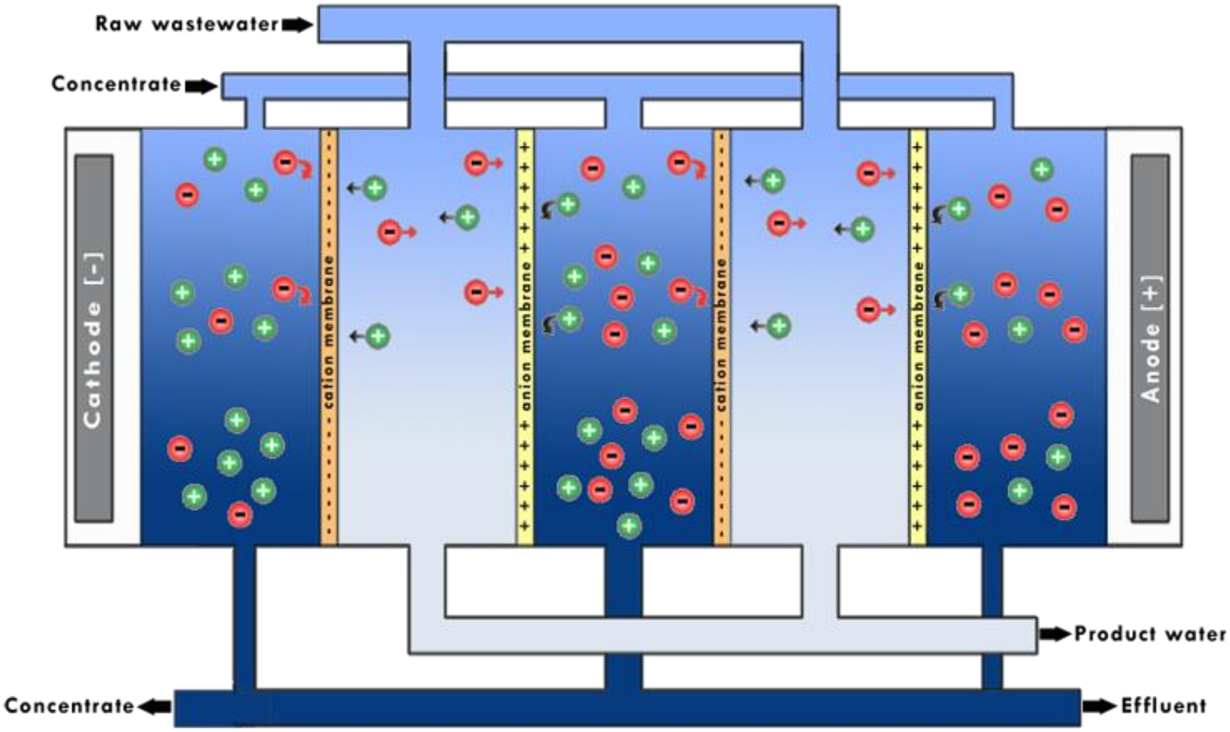


Figure 9: Movement of ions in electrodialysis

ED plants operate above an efficiency of 90% and literature on ED plants generally assumes 90% to be the base value at which the plants operate hence the ED plant in this project has been designed to give an efficiency of 90%. This efficiency physically means that 90% of all the salts in the inlet stream are extracted by the ED plant. Using this value of efficiency and knowing the molar flow rate of the inlet stream, the value of η is calculated

$$\eta = 0.9 * 3.24 \frac{mol}{s} = 2.92 \frac{mol}{s}$$

F is the Faraday's Constant and has the following value

$$F = 96485.33289 \frac{C}{mol}$$

i is the applied current density. The applied current density is a parameter that can be played with to achieve desirable results however it is limited by two things

- Limiting current density
- Cost of electricity

The applied current density needs to have a value of that below the limiting current density has a value higher can cause the breakdown of water into its ions. In addition to this, the higher the current density applied, the higher the cost of electricity.

A suitable compromise between all of these was achieved with a value of 100 $\frac{A}{m^2}$

Lastly, the industry standard value of 0.9 was selected for the current efficiency and these values were incorporated into the design equation to come up with required membrane area.

$$\mathrm{A}_T = 3130.41\ m^2$$

This is the area of the membrane required for the ED plant if the said values are used in its operation. This area gives a recovery of 75 % and an efficiency of 90%

The next important parameter that needs to be found is the resistance of the ED. The cation-exchange membranes used were CR67 HMR412 (Ionics, Inc., USA), and the anion-exchange membranes AR204 SXZR 3679 (Ionics, Inc., USA). The resistances of these membranes are $0.00065\Omega\mathrm{m}^2$ and $0.00059\ \Omega\mathrm{m}^2$. The average combined resistance becomes $0.00062\ \Omega\mathrm{m}^2$. The total power required by the ED plant becomes

$$0.00062\ \Omega\mathrm{m}^2 \times\ (100\frac{A}{m^2})^2 = 6.2\frac{W}{m^2}$$

$$\text{Energy Consumption} = \frac{6.2W \times 3600}{1000} = 22.32\ \text{kWh}$$

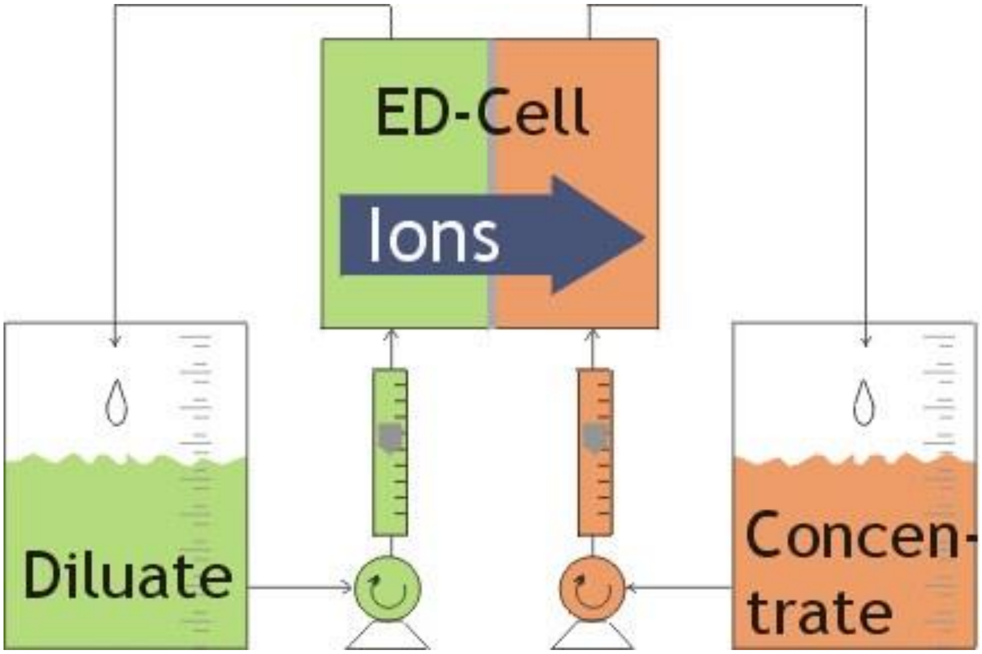


Figure 10: Products of electrodialysis

4.1.3 Crystallization

Crystallizers are utilized in industry to attain liquid-solid separation. they're a crucial piece of chemical process instrumentation as a result of they're capable of generating high purity product with a comparatively low energy input.

Forced-circulation crystallization is that the most generally used crystallization methodology in industry. Forced-circulation crystallizers, are phase change crystallizers. They produce a super-saturated solution by evaporating the solvent of a saturated solution. The substance of this saturated solution then cools, forming crystals. These varieties of crystallizers square measure classified as mixed-suspension, mixed-product-removal (MSMPR) crystallizers. The key assumption of an MSMPR crystallizer is that the suspension is absolutely mixed and uniform throughout the system.

Crystallizer Equipment:

There is a large form of equipment used to perform the crystallization process, known as crystallizers. Such equipment will be classified into four main types:

1. Bulk solution crystallizers.
2. Precipitation vessels.

3. Melt crystallizers forming multiple crystals.
4. Melt crystallizers forming large high-purity single crystals.

All these types of equipment have aspects in common:

- A region where supersaturation is produced which is the driving force for the crystallization.
- A region for crystal growth.

A full procedure is too complex for this article; however, some key aspects are outlined below. For further details, refer to any of the books given in the reference list.

Application:

These crystallizers are used for producing salts and different chemical in industries.

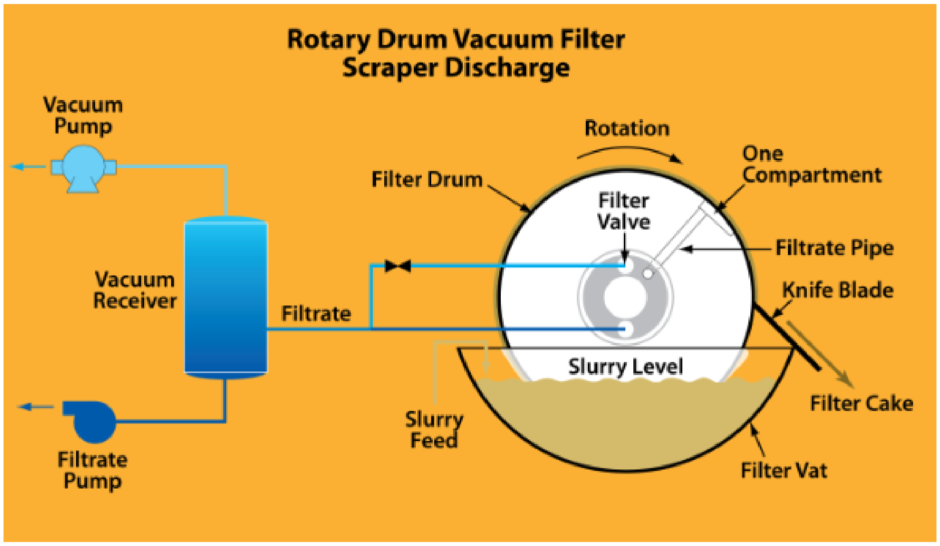
4.1.4 Filtration

Rotary Drum Vacuum Filters are used for the separation of liquids & solids and offer great versatility when it comes to meet the demands of the industry. The rotary drum vacuum filter offers:

- Continuous Operation
- Application Versatility
- Wide Range of Sizes

How does it work?

The RDVF is a continuous process. It involves the following steps:



1) The drum rotates and is partially submerged in the feed.

2) Vacuum is applied using a liquid ring vacuum pump or other means.

3) The vacuum pulls the air and continues to remove moisture as the drum rotates.

4) The cake is discharged from the drum through a knife blade to a conveyor or chute to the next process step.

If the cake can be washed to extract more product. Additional drying of the cake follows washing.

Selection Criteria for Rotary Vacuum Drum Filter

If your process involves any of the following, then the Rotary Drum Vacuum Filter may fit your needs.

- Solid & liquid Separation
- Product recovery
- Clarification of liquid product
- Washing for cake purity
- Clarification of a wastewater stream

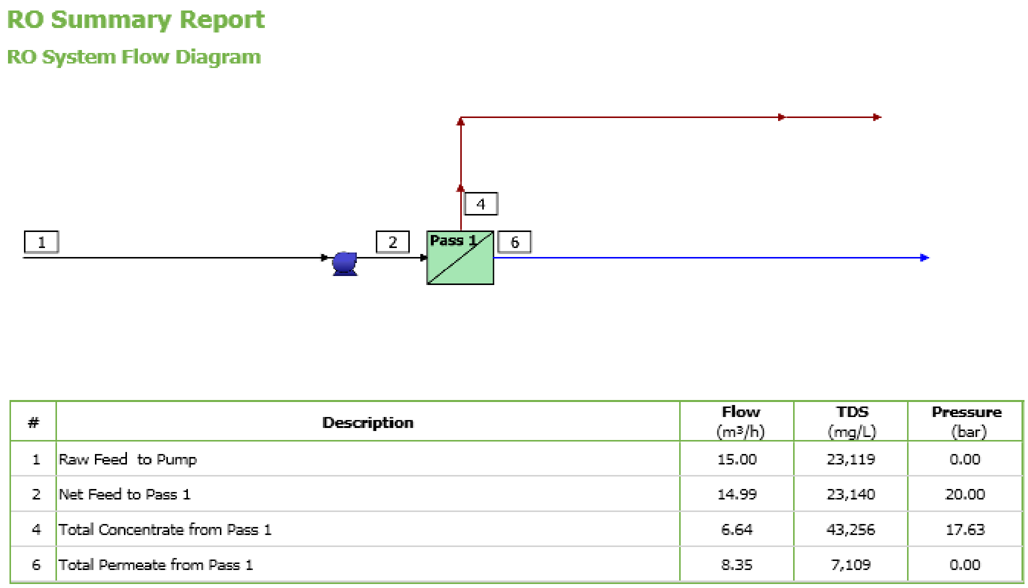
4.2 Simulation of Reverse Osmosis Membrane

Since the simulation of RO is not possible on Aspen Hysis, we carried out the Simulation of our RO Plant on a software called Water Application Value Engine (WAVE). It is the official design software of DOW Chemicals for the simulation of DOW FILMTEC™ RO Membranes.

SW30HRLE-400

4.2.1 Simulation of 1st RO Plant:

Following is the process flow diagram of our 1st RO SW30HRLE-400 Membrane:



RO Summary Report

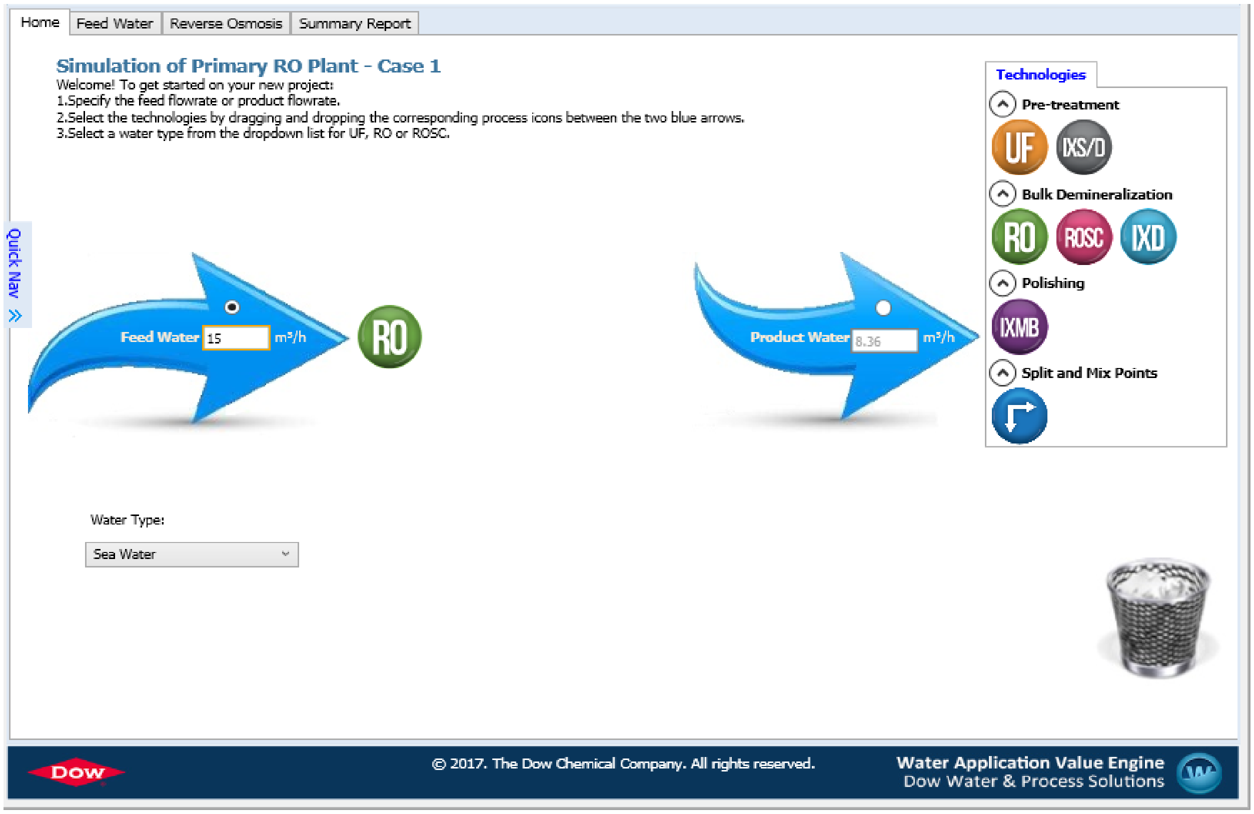
RO System Flow Diagram

#	Description	Flow (m³/h)	TDS (mg/L)	Pressure (bar)
1	Raw Feed to Pump	15.00	23,119	0.00
2	Net Feed to Pass 1	14.99	23,140	20.00
4	Total Concentrate from Pass 1	6.64	43,256	17.63
6	Total Permeate from Pass 1	8.35	7,109	0.00

Figure 11: First RO Summary Report

Feed Properties:

The feed enters the RO at the flow rate of 15 $\frac{m^3}{hr}$ and 45% of this flow goes to permeate and the remaining 55% goes to concentrate. It has a total TDS of around 23,000 $\frac{g}{L}$.



Simulation of Primary RO Plant - Case 1

Welcome! To get started on your new project:
1.Specify the feed flowrate or product flowrate.
2.Select the technologies by dragging and dropping the corresponding process icons between the two blue arrows.
3.Select a water type from the dropdown list for UF, RO or ROSC.

Feed Water 15 m^3/h

Product Water 8.36 m^3/h

Water Type: Sea Water

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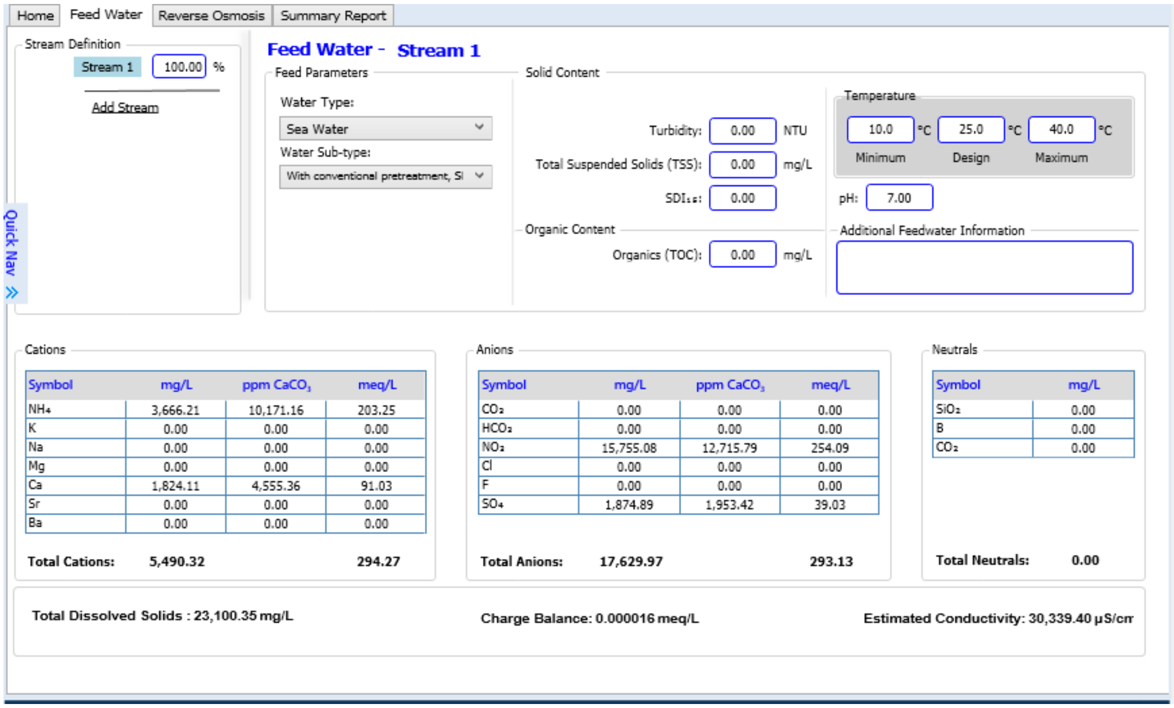


Stream Definition

Stream 1 100.00 %

Feed Water - Stream 1

Feed Parameters

Water Type: Sea Water

Water Sub-type: With conventional pretreatment, SI

Solid Content

Turbidity: 0.00 NTU

Total Suspended Solids (TSS): 0.00 mg/L

SDI_{15}: 0.00

Organic Content

Organics (TOC): 0.00 mg/L

Temperature

Minimum	Design	Maximum
10.0 °C	25.0 °C	40.0 °C

pH: 7.00

Additional Feedwater Information

Cations

Symbol	mg/L	ppm $CaCO_3$	meq/L
NH_4	3,666.21	10,171.16	203.25
K	0.00	0.00	0.00
Na	0.00	0.00	0.00
Mg	0.00	0.00	0.00
Ca	1,824.11	4,555.36	91.03
Sr	0.00	0.00	0.00
Ba	0.00	0.00	0.00
Total Cations:	**5,490.32**		**294.27**

Anions

Symbol	mg/L	ppm $CaCO_3$	meq/L
CO_3	0.00	0.00	0.00
HCO_3	0.00	0.00	0.00
NO_3	15,755.08	12,715.79	254.09
Cl	0.00	0.00	0.00
F	0.00	0.00	0.00
SO_4	1,874.89	1,953.42	39.03
Total Anions:	**17,629.97**		**293.13**

Neutrals

Symbol	mg/L
SiO_2	0.00
B	0.00
CO_2	0.00
Total Neutrals:	**0.00**

Total Dissolved Solids : 23,100.35 mg/L

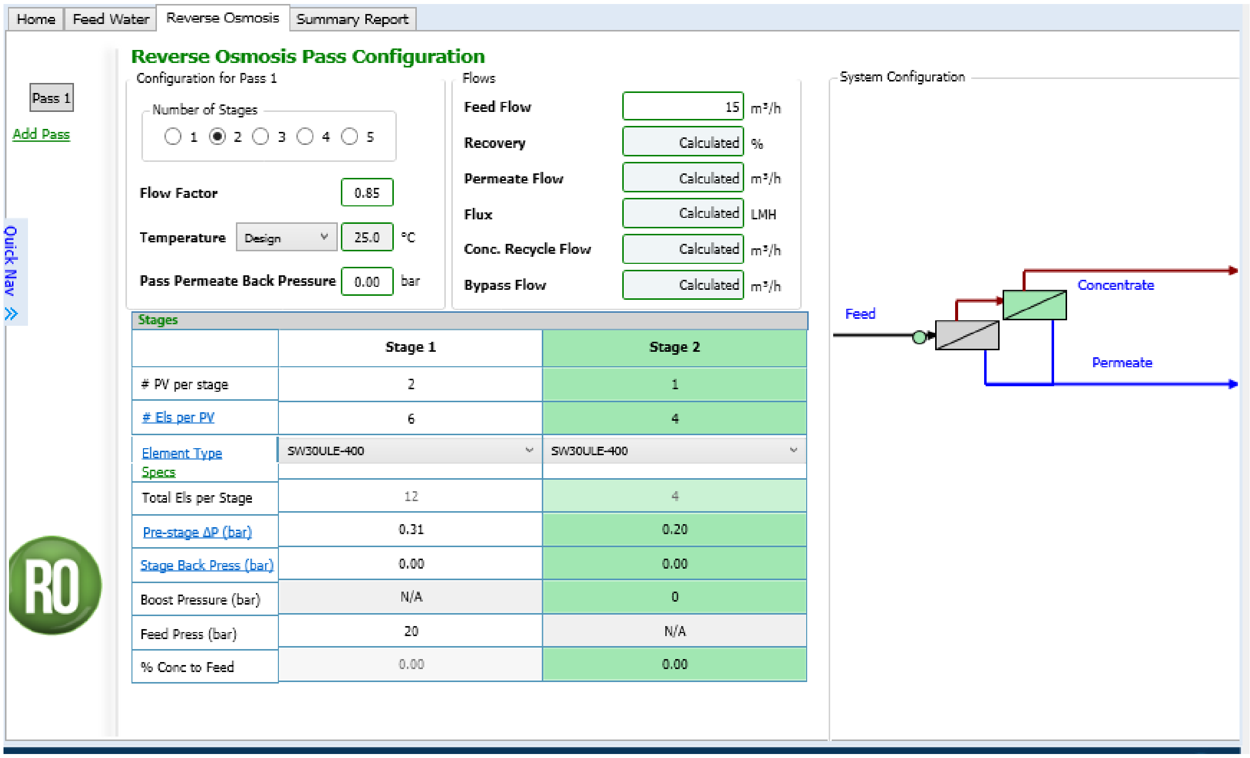
Charge Balance: 0.000016 meq/L

Estimated Conductivity: 30,339.40 µS/cm

Figure 12: First RO Feed Properties

RO Properties:

The 1st RO plant consists of 3 stages and is being operated at 20 bar pressure.



Reverse Osmosis Pass Configuration

Configuration for Pass 1

Number of Stages: ○ 1 ● 2 ○ 3 ○ 4 ○ 5

Flow Factor: 0.85

Temperature: Design 25.0 °C

Pass Permeate Back Pressure: 0.00 bar

Flows

Feed Flow	15	m³/h
Recovery	Calculated	%
Permeate Flow	Calculated	m³/h
Flux	Calculated	LMH
Conc. Recycle Flow	Calculated	m³/h
Bypass Flow	Calculated	m³/h

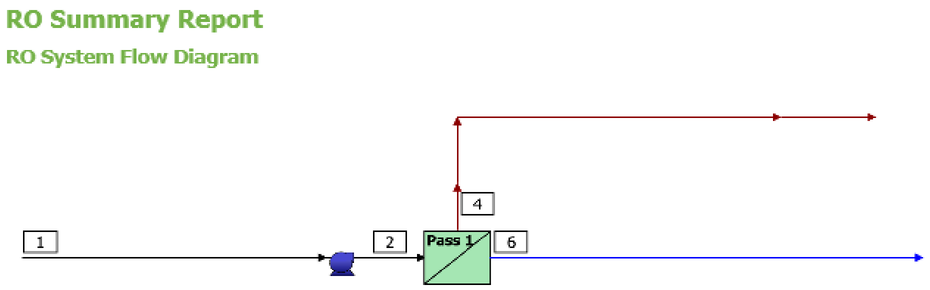
Stages

	Stage 1	Stage 2
# PV per stage	2	1
# Els per PV	6	4
Element Type Specs	SW30ULE-400	SW30ULE-400
Total Els per Stage	12	4
Pre-stage ΔP (bar)	0.31	0.20
Stage Back Press (bar)	0.00	0.00
Boost Pressure (bar)	N/A	0
Feed Press (bar)	20	N/A
% Conc to Feed	0.00	0.00

Figure 13: First RO Design Properties

4.2.2 Simulation of 2nd RO Plant:

Following is the process flow diagram of the 2nd RO SW30HRLE-400 Membrane:



RO Summary Report

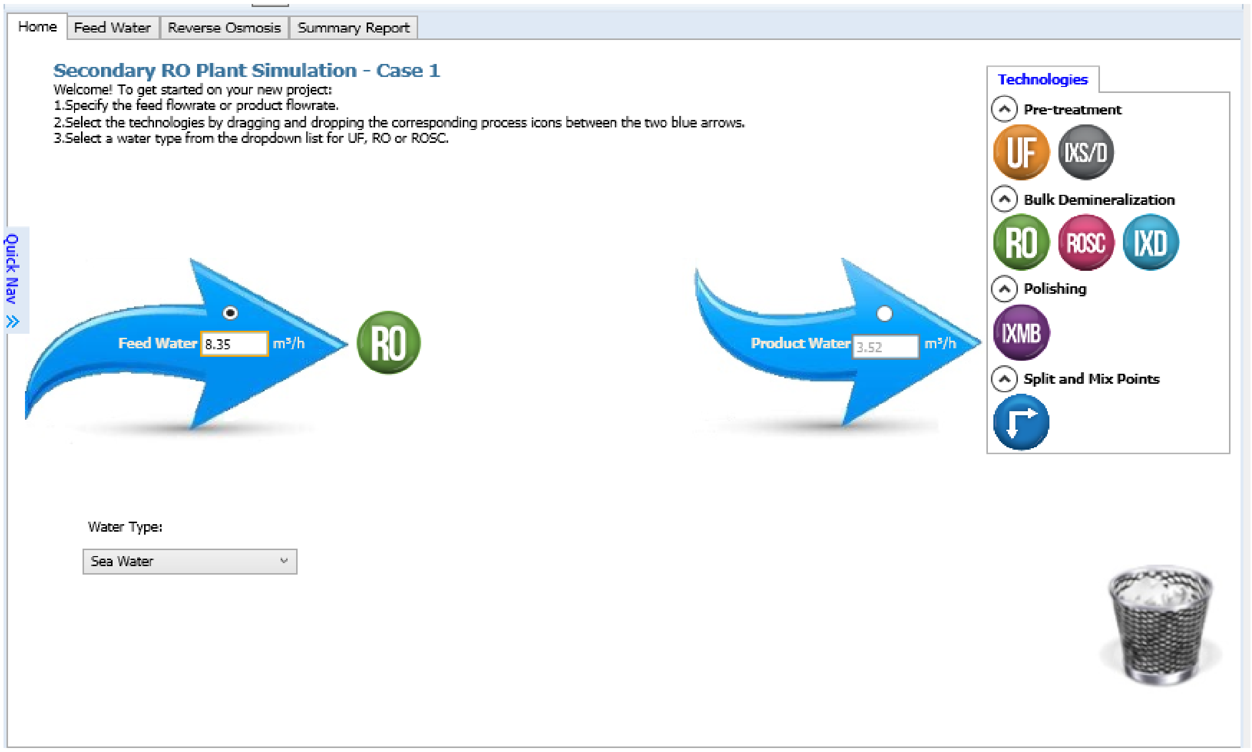
RO System Flow Diagram

#	Description	Flow (m³/h)	TDS (mg/L)	Pressure (bar)
1	Raw Feed to Pump	8.35	7,092	0.00
2	Net Feed to Pass 1	8.34	7,096	15.00
4	Total Concentrate from Pass 1	4.83	11,019	13.35
6	Total Permeate from Pass 1	3.51	1,695	0.00

Figure 14: Second RO Summary Report

Feed Properties:

The permeate of the 1st RO plant becomes the feed enters the RO at the flow rate of 8.35 $\frac{m^3}{hr}$ and 45% of this flow goes to permeate and the remaining 55% goes to concentrate. It has a total TDS of around 7,000 $\frac{g}{L}$.



Secondary RO Plant Simulation - Case 1

Welcome! To get started on your new project:

1.Specify the feed flowrate or product flowrate.

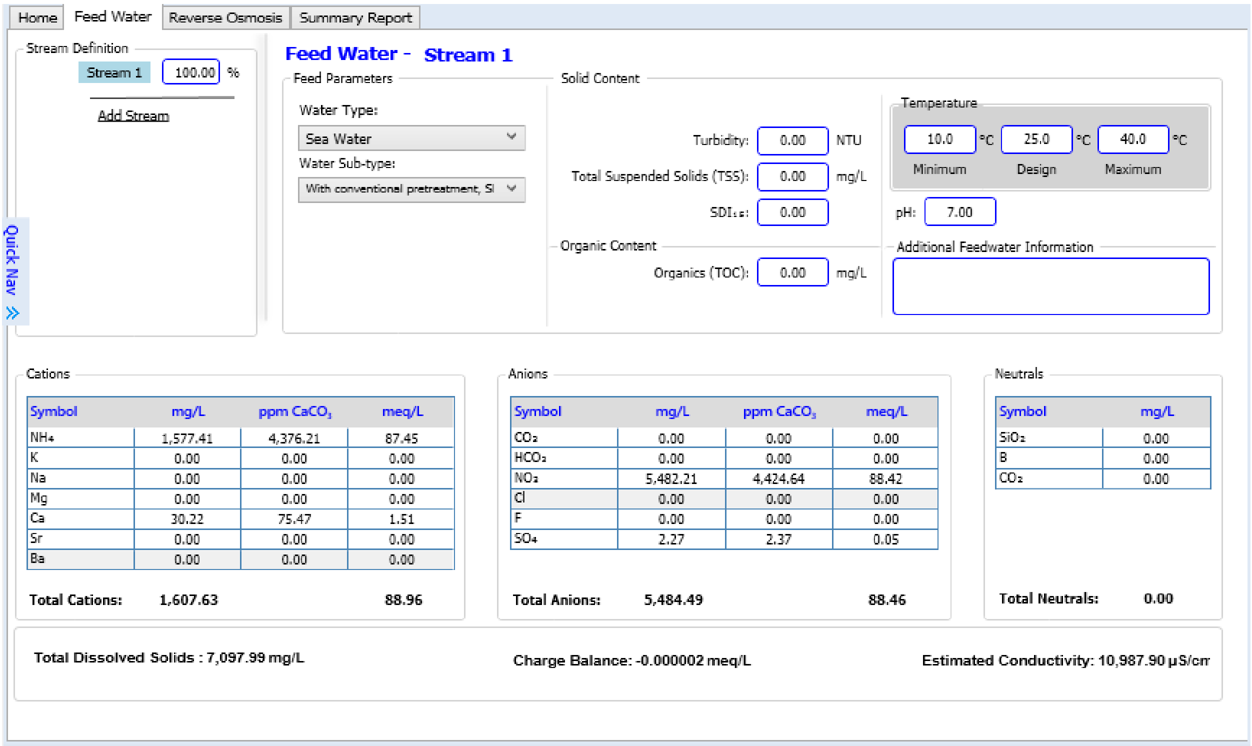
2.Select the technologies by dragging and dropping the corresponding process icons between the two blue arrows.

3.Select a water type from the dropdown list for UF, RO or ROSC.

Feed Water 8.35 m³/h

Product Water 3.52 m³/h

Water Type: Sea Water



Stream Definition

Stream 1: 100.00 %

Feed Water - Stream 1

Feed Parameters

Water Type: Sea Water

Water Sub-type: With conventional pretreatment, SI

Solid Content

Turbidity: 0.00 NTU

Total Suspended Solids (TSS): 0.00 mg/L

SDI_{15}: 0.00

Organic Content

Organics (TOC): 0.00 mg/L

Temperature

Minimum	Design	Maximum
10.0 °C	25.0 °C	40.0 °C

pH: 7.00

Additional Feedwater Information

Cations

Symbol	mg/L	ppm $CaCO_3$	meq/L
NH_4	1,577.41	4,376.21	87.45
K	0.00	0.00	0.00
Na	0.00	0.00	0.00
Mg	0.00	0.00	0.00
Ca	30.22	75.47	1.51
Sr	0.00	0.00	0.00
Ba	0.00	0.00	0.00

Total Cations: 1,607.63 88.96

Anions

Symbol	mg/L	ppm $CaCO_3$	meq/L
CO_3	0.00	0.00	0.00
HCO_3	0.00	0.00	0.00
NO_3	5,482.21	4,424.64	88.42
Cl	0.00	0.00	0.00
F	0.00	0.00	0.00
SO_4	2.27	2.37	0.05

Total Anions: 5,484.49 88.46

Neutrals

Symbol	mg/L
SiO_2	0.00
B	0.00
CO_2	0.00

Total Neutrals: 0.00

Total Dissolved Solids : 7,097.99 mg/L

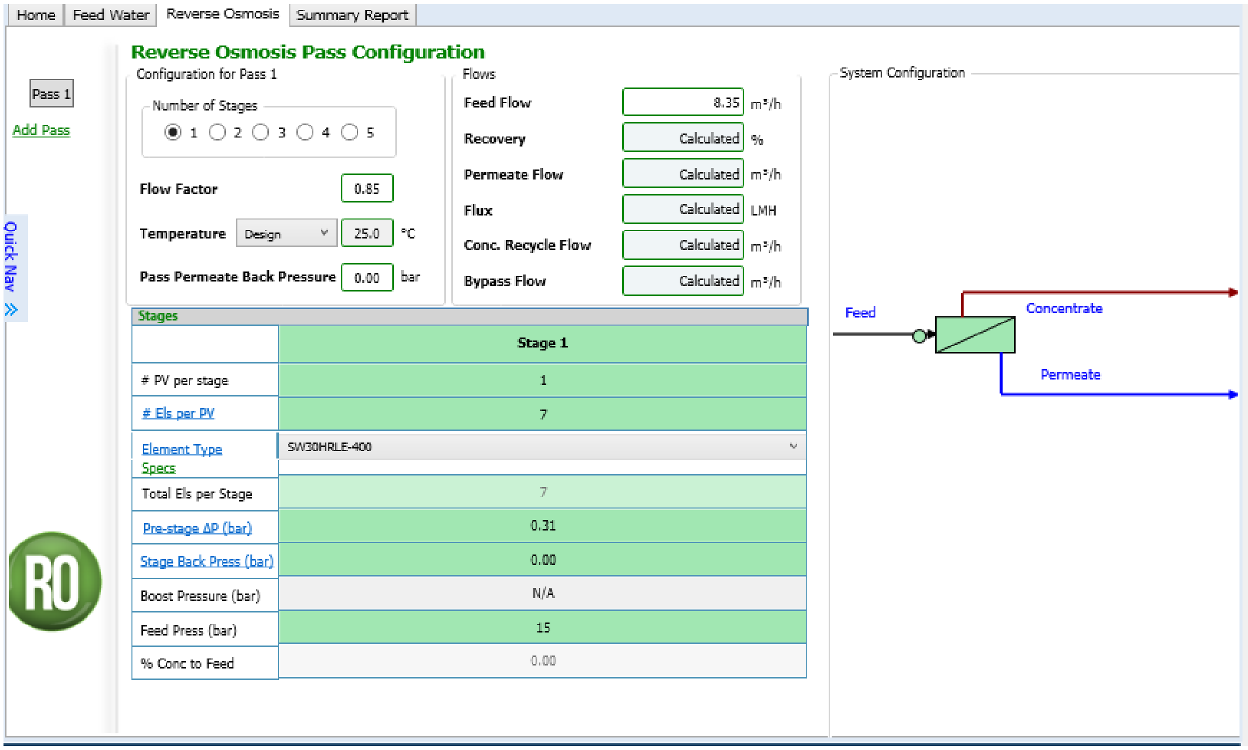
Charge Balance: -0.000002 meq/L

Estimated Conductivity: 10,987.90 µS/cm

Figure 15: Second RO Feed Properties

RO Properties:

The 2nd RO plant consists of 1 stage and is being operated at 15 bar pressure.



Reverse Osmosis Pass Configuration

Configuration for Pass 1

Number of Stages: ● 1 ○ 2 ○ 3 ○ 4 ○ 5

Flow Factor: 0.85

Temperature: Design 25.0 °C

Pass Permeate Back Pressure: 0.00 bar

Flows

Feed Flow: 8.35 m³/h

Recovery: Calculated %

Permeate Flow: Calculated m³/h

Flux: Calculated LMH

Conc. Recycle Flow: Calculated m³/h

Bypass Flow: Calculated m³/h

Stages

	Stage 1
# PV per stage	1
# Els per PV	7
Element Type Specs	SW30HRLE-400
Total Els per Stage	7
Pre-stage ΔP (bar)	0.31
Stage Back Press (bar)	0.00
Boost Pressure (bar)	N/A
Feed Press (bar)	15
% Conc to Feed	0.00

Figure 16: Second RO Design Properties

4.3 Equipment Design

The equipment to be utilized in the process was designed by the application of various research documents as well as textbooks.

4.3.1 Mixing tank

A tank will be used to mix and hold the contents of the drain channels of the CAN and NP plants. The tank's volume is determined via the daily effluent flow using:

$$Total\ hold\ up\ capacity = hourly\ flow\ \times 12\ hours$$

$$Total\ hold\ up\ capacity = 15\ m^3/hr\ \times 12\ hours$$

$$Total\ hold\ up\ capacity = 180\ m^3$$

Similar to the agitators present in the clarifiers of the effluent treatment plant, the tank will contain an overhead mounted agitator operating under a 5 kW motor.

It is worth noting that the tank is a vertical tank, as are usually used for liquid storage. The vertical orientation of the tank will also exert some degree of hydrostatic pressure into the lines before the pump, thereby reducing the pumping requirement.

4.3.2 Pumps

The pumping requirement for the reverse osmosis membrane is an essential requirement. The pump must provide a driving force contrary to the natural osmotic pressure being exerted by the solutes in the water. In order to design the pump, the first consideration is the osmotic pressure of the effluent streams entering the reverse osmosis membrane system. To begin, the equation for osmotic pressure is employed:

$$\pi = iMRT$$

$$\pi\ is\ the\ osmotic\ pressure\ (atm)$$

$$i\ is\ the\ Van't\ Hoff\ Factor$$

$$M\ is\ the\ molarity\ of\ the\ solution\ \left(\frac{mol}{L}\right)$$

$$R\ is\ the\ molar\ gas\ constant\ \left(\frac{L\ atm}{mol}\right)$$

$$T\ is\ the\ absolute\ temperature\ (Kelvin)$$

For the first pump,

$$\pi_1 = 2 \times 0.313 \times 0.082 \times 313$$

$$\pi_1 = 16\ atm$$

Therefore, the pump will operate at a value of 20 atmospheres to exceed the osmotic pressure and drive the filtration process.

The feed to the first pump is at 15 m^3/hr, which is equivalent to 0.004 m^3/s

Using the design equation, we may find the required power. This works out to be:

$$\Delta P = 19\ atm \sim 19\ bar$$

$$flowrate\ (q) = 66.04\ gpm$$

The pressure increase required dictates that the pump be designed in a multi-stage manner. We'll work with 5 stages for the pump, each increasing the pressure by 4.5 bars. The stages then work out to be:

Stage	Inlet pressure (bar)	Outlet pressure (bar)
1	1	5.5
2	5.5	10
3	10.5	14.5
4	14.5	19
5	19	23.5

Table 12: Pump Staging

Therefore, each stage must generate a head of:

$$Head = \frac{Pressure\ in\ bars}{0.0981}$$

$$Head = \frac{4.5}{0.0981}\ m$$

$$Head\ per\ stage = 45.87\ m \sim 150.5\ ft$$

Identifying a duty point with head 150.5 feet and flowrate of 66 gallons per minute on the figure:

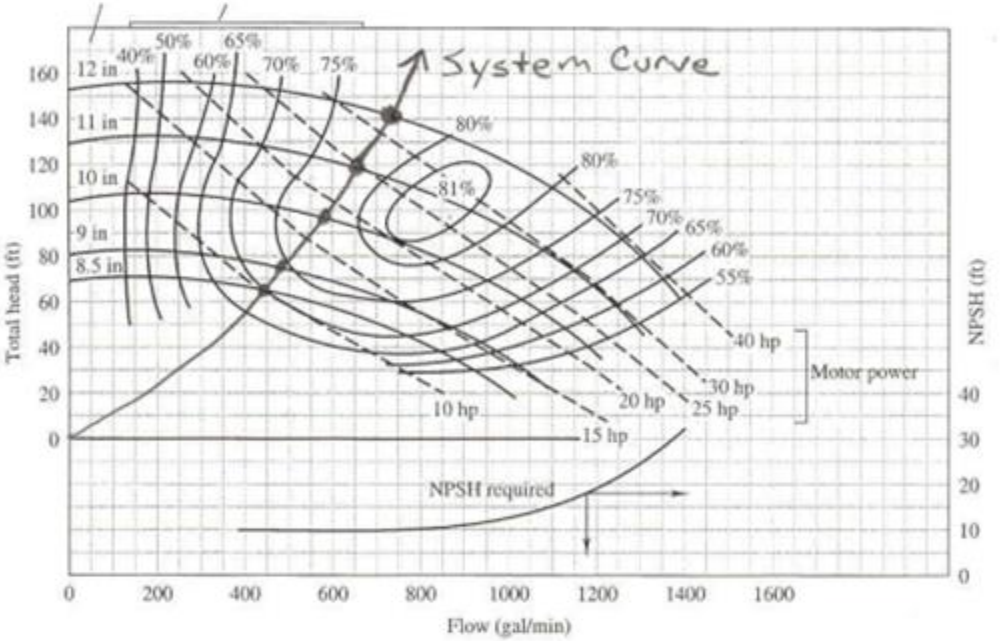


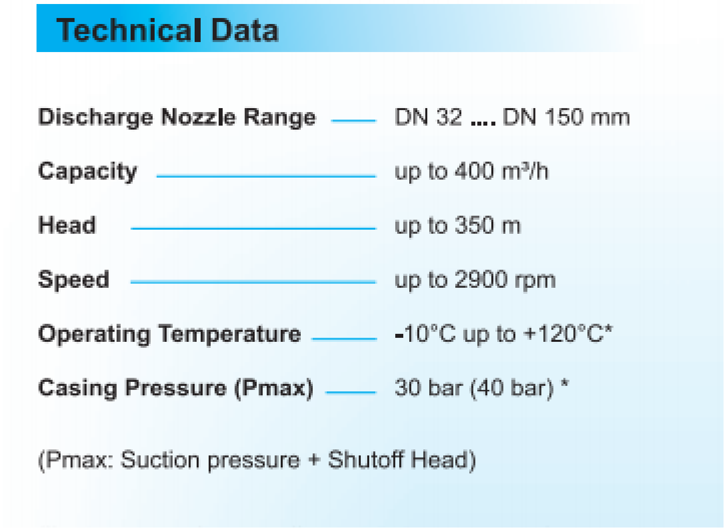
Figure 17: Multistage Pump Performance Curve

The impeller diameter will be 12 inches (304.8 mm) and will operate with an efficiency of about 30%. Moreover, the impeller will require a motor of 15 bhp.

Head (m)	45.87
Flowrate (m^3/s)	0.004
Impeller diameter (mm)	304.8
Efficiency	30%
Motor power	15 bhp

Table 13: First pump design summary

The recommended pump for this purpose is the Standart SKMH-V Vertical Multistage Centrifugal Pump by Castle Pumps. The specifications of the pump are as follows:



Technical Data

Discharge Nozzle Range	DN 32 .... DN 150 mm
Capacity	up to 400 m³/h
Head	up to 350 m
Speed	up to 2900 rpm
Operating Temperature	-10°C up to +120°C*
Casing Pressure (Pmax)	30 bar (40 bar) *

(Pmax: Suction pressure + Shutoff Head)

Figure 18: Vendor Pump Specifications

According to the figure, the pump's impeller diameter will be about 220 mm.

For the second pump,

$$\pi_2 = 2 \times 0.131 \times 0.082 \times 313$$

$$\pi_2 = 6.72 \; atm$$

Therefore, the pump will operate at a pressure of 16.5 atmospheres to exceed the osmotic pressure and drive the filtration process.

The feed to the first pump is at 8.0 m^3/hr, which is equivalent to 0.002 m^3/s

The first RO membrane will provide a pressure drop to the permeate, which can be estimated using:

$$\Delta P_{RO} = \frac{0.45}{element}$$

$$\Delta P_{RO} = 0.45 \times 13$$

$$\Delta P_{RO} = 5.85 \; bar$$

The maximum allowable pressure drop for a 6-element RO membrane is 4 bar, which works out to be 8.67 bar for our 13-element membrane. The actual pressure drop is within allowable limits.

$$P_{Pump\ feed} = 20 - 5.85$$

$$P_{Pump\ feed} = 14.15\ bar$$

$$\Delta P_{pump_2} = 16.5 - 14.15$$

$$\Delta P_{pump_2} = 1.85\ bar$$

$$Head = \frac{1.85}{0.0981}$$

$$Head = 18.85\ m$$

Using the following figure, we may identify the pump's specifications:

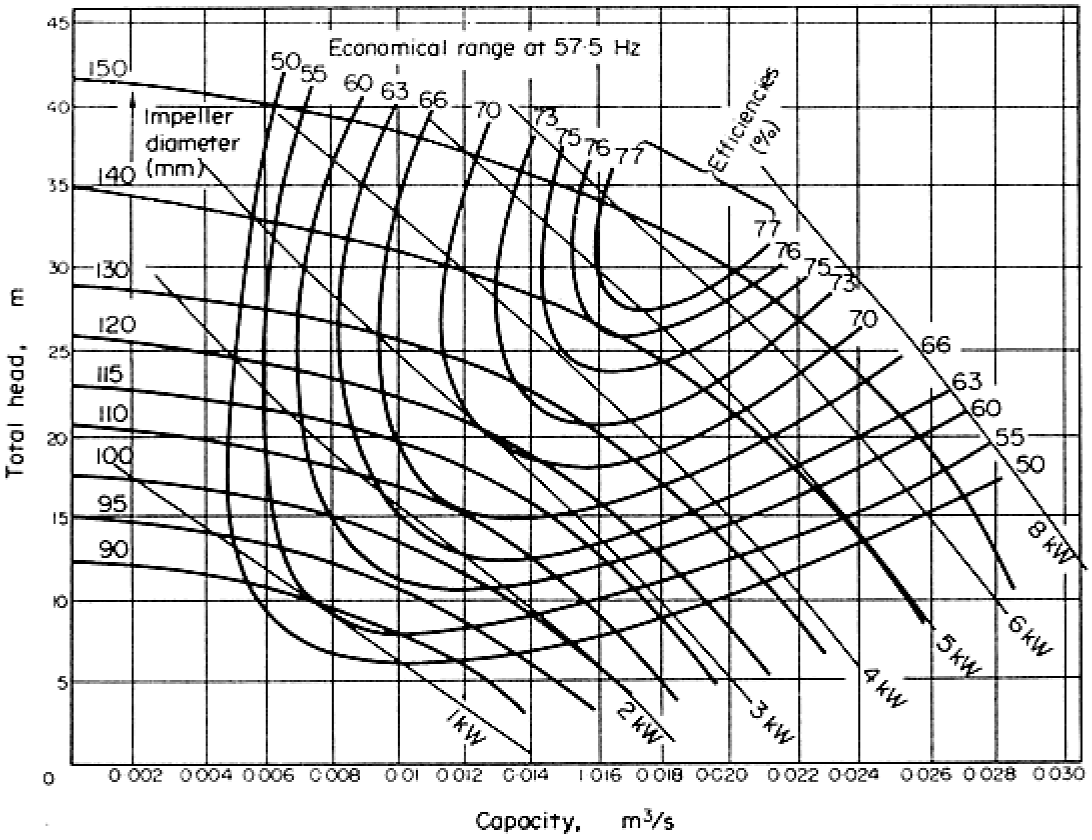


Figure 19: Pump performance curve

Head (m)	18.85
Flowrate (m^3/s)	0.002
Impeller diameter (mm)	110
Efficiency	30%
Power (kW)	1.5

RPM	3450

Table 14: Second Pump Specifications

4.3.3 RO Membrane

In order to design the reverse osmosis membrane, a method recommended by DOW Chemical Manufacturers was employed. The method is as follows:

4.3.3.1 Primary RO

Step 1: Choose Feed Water Source:

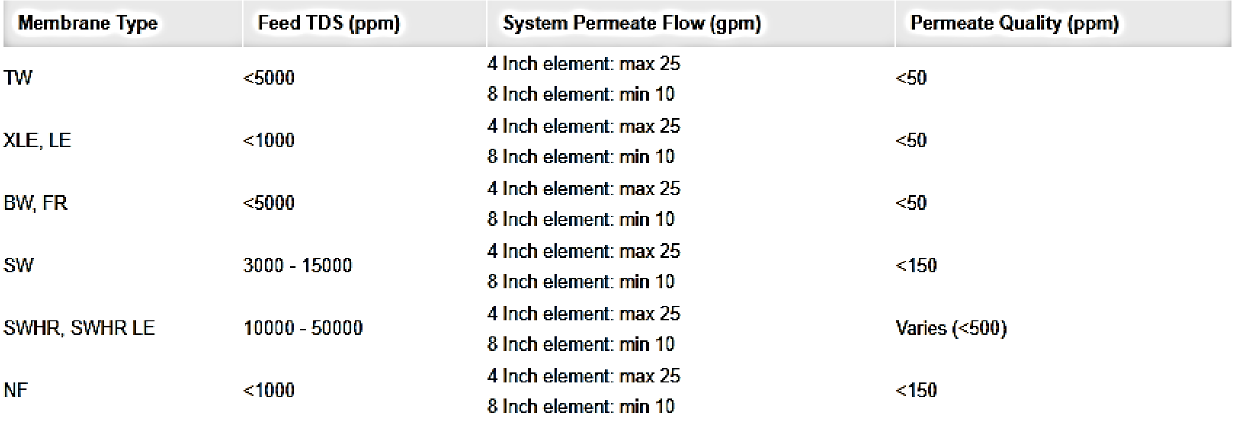
Since the TDS in our water source is greater than 5,000 $\frac{mg}{L}$ so our feed water falls in the category of sea water.

Step 2: Select the Flow Configuration and Number of Passes

The standard flow configuration for a membrane system is plug flow, where the feed volume is passed once through the system.

Step 3: Select Membrane and Element Type

Since our TDS is about 23,000 $\frac{mg}{L}$ so we will need to use the SWHR membranes as per following table. So, we will use DOW FILMTEC™ SW30HRLE-400 membrane & element type having a total area of 37 m^2 to fulfill our requirements.



Membrane Type	Feed TDS (ppm)	System Permeate Flow (gpm)	Permeate Quality (ppm)
TW	<5000	4 Inch element: max 25 8 Inch element: min 10	<50
XLE, LE	<1000	4 Inch element: max 25 8 Inch element: min 10	<50
BW, FR	<5000	4 Inch element: max 25 8 Inch element: min 10	<50
SW	3000 - 15000	4 Inch element: max 25 8 Inch element: min 10	<150
SWHR, SWHR LE	10000 - 50000	4 Inch element: max 25 8 Inch element: min 10	Varies (<500)
NF	<1000	4 Inch element: max 25 8 Inch element: min 10	<150

Figure 20: DOW membrane types

Step 4: Select Average Membrane Flux (Design Flux)

The average design flux of our RO is 14 $\frac{L}{m^2 hr}$.

Step 5: Calculate the Number of Elements Needed

$$N_E = \frac{Design\ Permeate\ Flow\ (\frac{L}{hr})}{Design\ Flux\ x\ Active\ Area}$$

$$N_E = \frac{8250\ \frac{L}{hr}}{14\ m^2\ \times\ 37\frac{L}{m^2hr}}$$

$N_E \approx$ 16 Elements

Step 6: Calculate the Number of Pressure Vessels Needed

$$N_v = \frac{Number\ of\ Elements}{Number\ of\ Elements\ in\ Pressure\ Vessel}$$

$$N_v = \frac{16}{6}$$

$$N_v = 2.67$$

$$N_v \approx 3$$

Step 7: Select the Number of Stages

No. of stages = 2 (required to meet the 45% Recovery and get the desired TDS in the Concentrate)

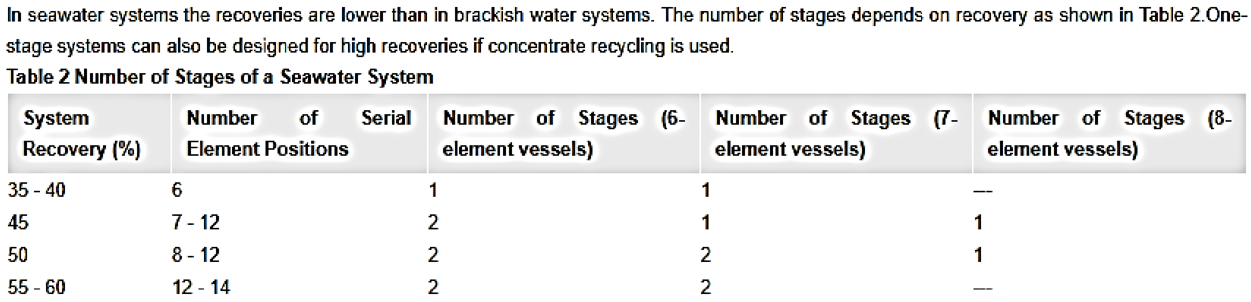

In seawater systems the recoveries are lower than in brackish water systems. The number of stages depends on recovery as shown in Table 2.One-stage systems can also be designed for high recoveries if concentrate recycling is used.

Table 2 Number of Stages of a Seawater System

System Recovery (%)	Number of Serial Element Positions	Number of Stages (6-element vessels)	Number of Stages (7-element vessels)	Number of Stages (8-element vessels)
35 - 40	6	1	1	—
45	7 - 12	2	1	1
50	8 - 12	2	2	1
55 - 60	12 - 14	2	2	—

Figure 21: Number of elements

Step 8: Select the Staging Ratio (Array Ratio)

$$R = [\frac{1}{1 - Y}]^{\frac{1}{n}}$$

Where

R = Staging Ratio

Y = Recovery in Fraction

n = Number of stages

$$R = [\frac{1}{1 - 0.45}]^{\frac{1}{2}}$$

R = 1.5

R ≈ 1.5

Or

R = 2:1

4.3.3.2 Secondary RO

Step 1: Choosing Feed Water Source:

Since the TDS in our water source is greater than 5,000 $\frac{mg}{L}$ so our feed water falls in the category of sea water.

Step 2: Selecting the Flow Configuration and Number of Passes

The standard flow configuration for a membrane system is plug flow, where the feed volume is passed once through the system.

Step 3: Selecting Membrane and Element Type

Since our TDS is about 7,000 $\frac{mg}{L}$ and the fact that simple SW membranes doesn't get us the required result so we will need to use the SWHR membrane as per following table. So, we will again use DOW FILMTEC™ SW30HRLE-400 membrane & element type having a total area of 37 m^2 to fulfill our requirements.

Step 4: Select Average Membrane Flux (Design Flux)

The average design flux of our RO is 14 $\frac{L}{m^2 hr}$.

Step 5: Calculate the Number of Elements Needed

$$N_E = \frac{Design\ Permeate\ Flow\ (\frac{L}{hr})}{Design\ Flux\ x\ Active\ Area}$$

$$N_E = \frac{3510\ \frac{L}{hr}}{14\ m^2\ \times\ 37\frac{L}{m^2 hr}}$$

$$N_E = 6.77\ Elements$$

$$N_E \approx 7\ Elements$$

Step 6: Calculate the Number of Pressure Vessels Needed

$$N_v = \frac{Number\ of\ Elements}{Number\ of\ Elements\ in\ Pressure\ Vessel}$$

$$N_v = \frac{7}{7}$$

$$N_v = 1$$

Step 7: Select the Number of Stages

No. of stages = 1 (required to meet the 45% Recovery and get the desired TDS in the Concentrate)

Step 8: Select the Staging Ratio (Array Ratio)

Since we only have 1 pressure vessel so we'll have a single stage.

4.3.3.3 Design of Primary Pressure Vessels:

Diameter of each Membrane Element, D_E = 7.9 inch

Diameter of each Vessel, D_V = D_E + Allowance

D_V = 7.9 + 1

= 8.9 inches

Total Number of Pressure Vessels = 3

Vessels with 6 Elements, N_{V2} = 2

Length of Membrane each element, L_E = 40 inches

Length of One Vessel, L_V = (L_E × No. of elements in 1 Vessel) + Allowance

= (40 × 6) + 1

= 241 inches

Volume of N_{V2} , $Vol_{N_{v2}} = \frac{\pi}{4}\ D^2\ L$

$= \frac{\pi}{4}\ 8.9^2\ \times 241$

= 14992.97 $inch^3$

= 0.246 m^3

Vessels with 4 Elements, N_{V1} = 1

Length of Membrane each element, L_E = 40 inches

Length of One Vessel, L_V = (L_E × No. of elements in 1 Vessel) + Allowance

= (40 × 4) + 1

= 161 inches

Volume of N_{V1} , $Vol_{N_{v1}} = \frac{\pi}{4}\ D^2\ L$

$= \frac{\pi}{4}\ 8.9^2\ \times 161$

= 10016.03 $inch^3$

= 0.164 m^3

4.3.3.4 Design of Secondary RO Pressure Vessels:

Diameter of each Membrane Element, D_E = 7.9 inch

Diameter of each Vessel, $D_V = D_E$ + Allowance

D_V = 7.9 + 1

= 8.9 inches

Total Number of Pressure Vessels = 1

Vessel with 7 Elements, N_{V3} = 1

Length of Membrane each element, L_E = 40 inches

Length of One Vessel, L_V = (L_E × No. of elements in 1 Vessel) + Allowance

= (40 × 7) + 1

= 281 inches

Volume of N_{V3} , $Vol_{N_{v3}} = \frac{\pi}{4}\ D^2\ L$

$$= \frac{\pi}{4}\ 8.9^2\ \times 281$$

$$= 17481.40\ inch^3$$

$$= 0.286\ m^3$$

4.3.4 Electrodialysis

The outlet of the RO system is not concentrated enough for crystallization to take place hence the need arises for further concentration. To achieve this end, an electrodialysis plant has been incorporated into the solution. The design of any ED plant starts with the determination of the required membrane area for a certain capacity. The said is calculated using the following design equation

$$\mathrm{A}_T = \frac{\eta \mathrm{F}}{\mathrm{i}\xi}$$

where η is the separation rate in mol/s, F is the Faraday constant, i is the applied current density in A/m2 and ξ is the current efficiency. This area represents the total cell area that consists of a cation and an anion exchange membrane and is the most important parameter in the designing of an electrodialysis plant.

We know the following about the feed inlet to the ED plant

- Volumetric flow rate: 11.98 m^3/hr = 3.33L /s
- Concentration: 0.974 mol /L
- Molar flow rate: 3.24 mol /s

ED plants operate above an efficiency of 90% and literature on ED plants generally assumes 90% to be the base value at which the plants operate hence the ED plant in this project has been designed to give an efficiency of 90%. This efficiency physically means that 90% of all the salts in the inlet stream are extracted by the ED plant. Using this value of efficiency and knowing the molar flow rate of the inlet stream, the value of η is calculated

$$\eta = 0.9 * 3.24 \frac{mol}{s} = 2.92 \frac{mol}{s}$$

F is the Faraday's Constant and has the following value

$$F = 96485.33289 \, \frac{C}{mol}$$

i is the applied current density. The applied current density is a parameter that can be played with to achieve desirable results however it is limited by two things

- Limiting current density
- Cost of electricity

The applied current density needs to have a value of that below the limiting current density has a value higher can cause the breakdown of water into its ions. In addition to this, the higher the current density applied, the higher the cost of electricity.

A suitable compromise between all of these was achieved with a value of 100 $\frac{A}{m^2}$

Lastly, the industry standard value of 0.9 was selected for the current efficiency and these values were incorporated into the design equation to come up with required membrane area.

$$\mathrm{A}_T = 3130.41\ m^2$$

This is the area of the membrane required for the ED plant if the said values are used in its operation. This area gives a recovery of 75 % and an efficiency of 90%

The next important parameter that needs to be found is the resistance of the ED. The cation-exchange membranes used were CR67 HMR412 (Ionics, Inc., USA), and the anion-exchange membranes AR204 SXZR 3679 (Ionics, Inc., USA). The resistances of these membranes are $0.00065\Omega\mathrm{m}^2$ and $0.00059\ \Omega\mathrm{m}^2$. The average combined resistance becomes $0.00062\ \Omega\mathrm{m}^2$. The total power required by the ED plant becomes

$$0.00062\ \Omega\mathrm{m}^2 \times\ (100\,\frac{A}{m^2})^2 = 6.2\frac{W}{m^2}$$

$$\text{Energy Consumption} = \frac{6.2W \times 3600}{1000} = 22.32\ \text{kWh}$$

4.3.5 Crystallizer

The current crystallization train consists of 36 crystallizers in series, each having a volume of 4.5 m^3. The solution overflows from one crystallizer to another, which means the crystallizers have a combined capacity of:

$$Total\ capacity = number\ of\ units\ \times volume\ of\ each\ unit$$
$$Total\ capacity = 36\ \times 4.5$$
$$Total\ capacity = 162\ m^3$$

The current feed is about 73.5 tph, which requires a coolant (brine) flowrate of 3,024 tph.

In our design, we incorporate the recovered nutrients into the existing crystallizer system, which means that 3 tph of recovered nutrients will be sent to the crystallizer. This will increase the required coolant to 3,147 tph. To summarize:

Current Flows	Proposed Flows
73.5 tph feed to crystallizers	76.5 tph feed to crystallizers
3,024 tph coolant to crystallizers	3,147 tph coolant to crystallizers

Table 15: Crystallizer modification

Chapter 5

Costing

5.1 Tank, Agitator, Pump

The capital cost for a vertical storage tank is given by the formula:

$$Cost = base\ cost\ \times size\ unit^{index}$$

The base cost is given by Coulson Chemical Engineering Volume 6, along with the index; the size unit in this case is the volume which was calculated in the previous section.

$$Cost = 2400\ \times 180^{0.65}$$

$$Cost = \$70{,}167.88$$

Similarly, the cost for the agitator driven by a 5 kW is also estimated using the equation used above. The size unit is the power of the motor. Therefore,

$$Cost = 1900\ \times 5^{0.5}$$

$$Cost = \$4{,}248.5$$

We may estimate pump costs using the following figure:

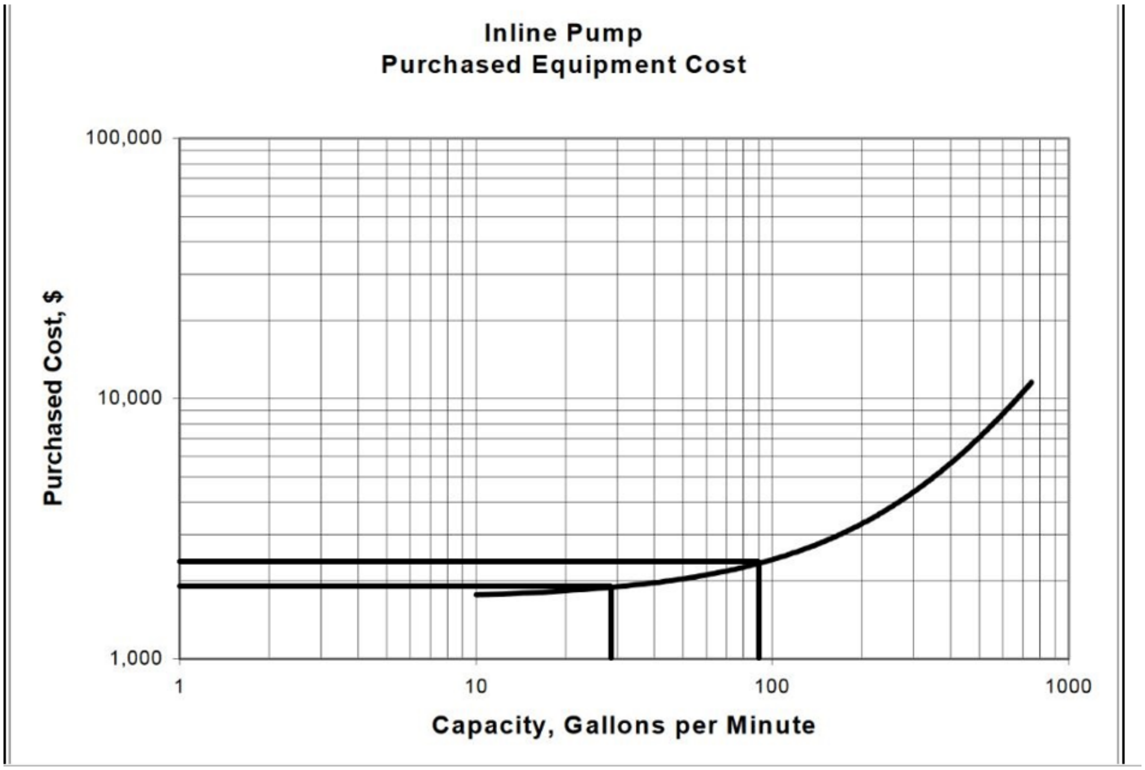
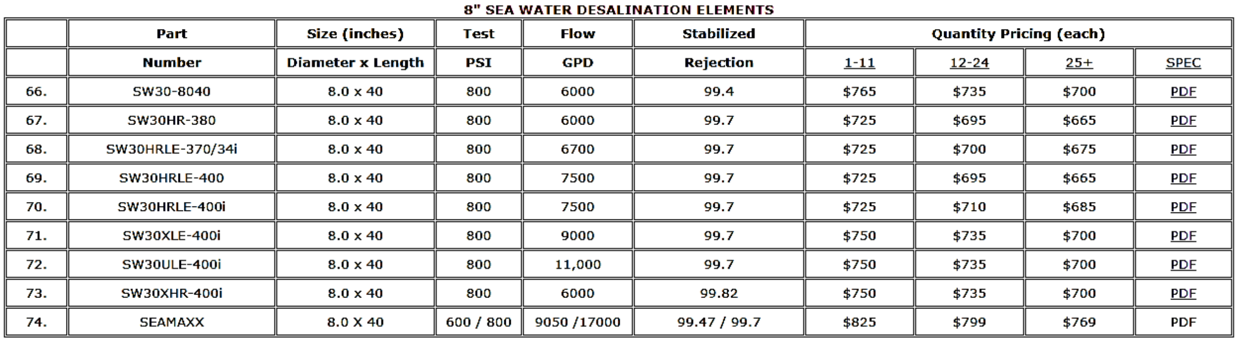


Figure 22: Pump Cost

For the first pump with a capacity of 66 gallons per minute, the cost is *$3,000*. While for the second pump, the capacity is at 33 gallons per minute, giving a cost of *$2,000*.

5.2 RO Membrane

We will be doing the costing of RO based on the following costing table of DOW FILMTEC™



8" SEA WATER DESALINATION ELEMENTS

	Part	Size (inches)	Test	Flow	Stabilized	Quantity Pricing (each)			
	Number	Diameter x Length	PSI	GPD	Rejection	1-11	12-24	25+	SPEC
66.	SW30-8040	8.0 x 40	800	6000	99.4	$765	$735	$700	PDF
67.	SW30HR-380	8.0 x 40	800	6000	99.7	$725	$695	$665	PDF
68.	SW30HRLE-370/34i	8.0 x 40	800	6700	99.7	$725	$700	$675	PDF
69.	SW30HRLE-400	8.0 x 40	800	7500	99.7	$725	$695	$665	PDF
70.	SW30HRLE-400i	8.0 x 40	800	7500	99.7	$725	$710	$685	PDF
71.	SW30XLE-400i	8.0 x 40	800	9000	99.7	$750	$735	$700	PDF
72.	SW30ULE-400i	8.0 x 40	800	11,000	99.7	$750	$735	$700	PDF
73.	SW30XHR-400i	8.0 x 40	800	6000	99.82	$750	$735	$700	PDF
74.	SEAMAXX	8.0 X 40	600 / 800	9050 /17000	99.47 / 99.7	$825	$799	$769	PDF

Figure 23: DOW FILMTEC Element Prices

<u>Costing of RO Membrane Elements:</u>

Since our DOW FILMTEC™ membrane is SW30HRLE-400. So, the above table can be written as follows:

DOW FILMTEC™ SW30HRLE-400	Quantity & Cost of Elements (each)		
	1 – 11	12 – 24	25+
	$725	$695	$665

Table 16: Cost of selected elements

Number of Elements in Primary RO = 16

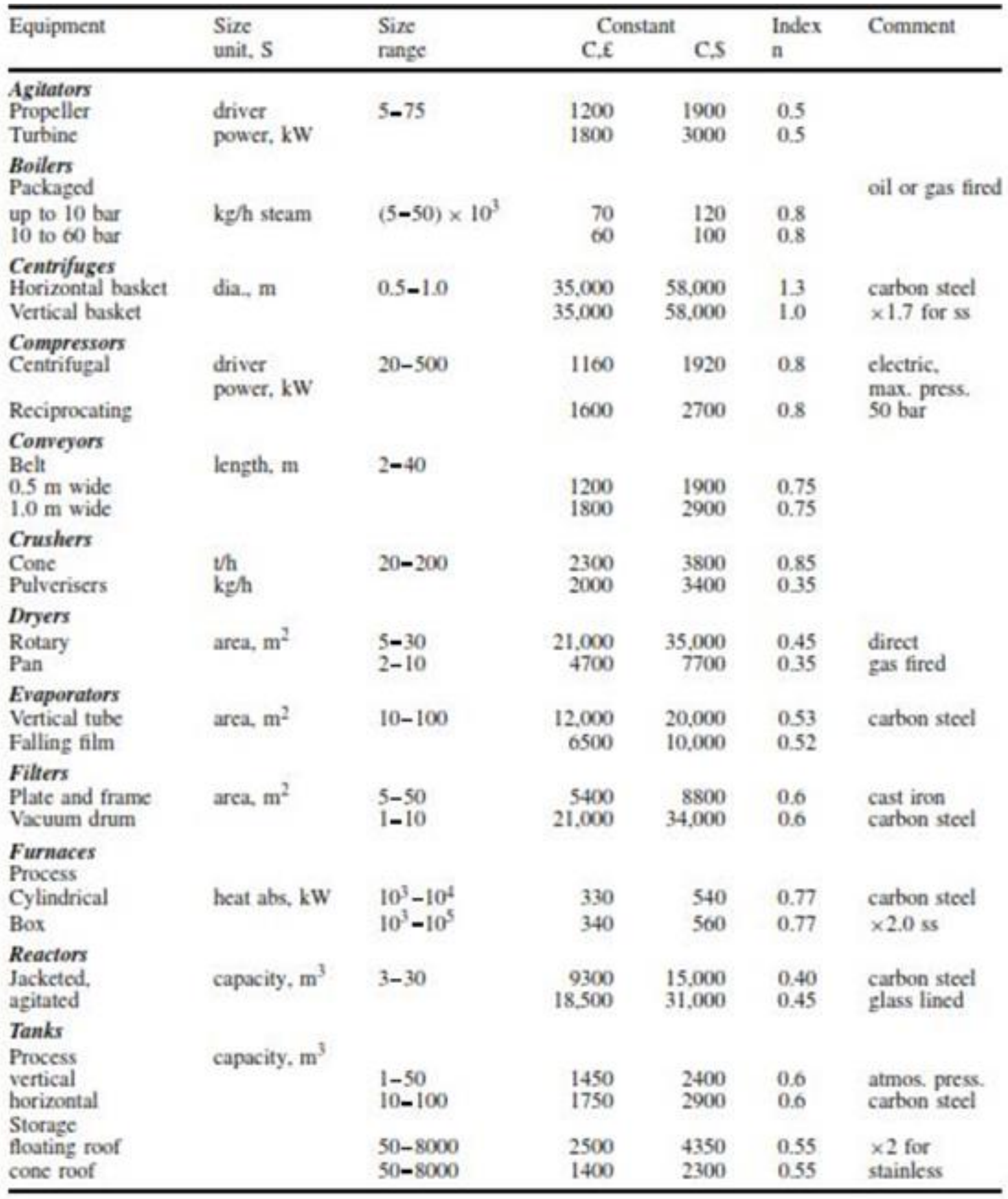
Number of Elements in Secondary RO = 7

$$\text{Total Number of Elements} = 16 + 7$$
$$= 28$$

$$\text{Cost of SW30HRLE-400 Elements} = \$665 \times 28$$
$$= \$17{,}955$$

<u>Costing of Pressure Vessels:</u>

For the Costing of Pressure Vessels, we will use the values of horizontal tanks from the following table:



Equipment	Size	Size	Constant		Index	Comment
	unit, S	range	C,£	C,$	n	
Agitators						
Propeller	driver	5–75	1200	1900	0.5	
Turbine	power, kW		1800	3000	0.5	
Boilers						
Packaged						oil or gas fired
up to 10 bar	kg/h steam	(5–50) × 10^3	70	120	0.8	
10 to 60 bar			60	100	0.8	
Centrifuges						
Horizontal basket	dia., m	0.5–1.0	35,000	58,000	1.3	carbon steel
Vertical basket			35,000	58,000	1.0	×1.7 for ss
Compressors						
Centrifugal	driver power, kW	20–500	1160	1920	0.8	electric, max. press.
Reciprocating			1600	2700	0.8	50 bar
Conveyors						
Belt	length, m	2–40				
0.5 m wide			1200	1900	0.75	
1.0 m wide			1800	2900	0.75	
Crushers						
Cone	t/h	20–200	2300	3800	0.85	
Pulverisers	kg/h		2000	3400	0.35	
Dryers						
Rotary	area, m^2	5–30	21,000	35,000	0.45	direct
Pan		2–10	4700	7700	0.35	gas fired
Evaporators						
Vertical tube	area, m^2	10–100	12,000	20,000	0.53	carbon steel
Falling film			6500	10,000	0.52	
Filters						
Plate and frame	area, m^2	5–50	5400	8800	0.6	cast iron
Vacuum drum		1–10	21,000	34,000	0.6	carbon steel
Furnaces						
Process						
Cylindrical	heat abs, kW	10^3–10^4	330	540	0.77	carbon steel
Box		10^3–10^5	340	560	0.77	×2.0 ss
Reactors						
Jacketed,	capacity, m^3	3–30	9300	15,000	0.40	carbon steel
agitated			18,500	31,000	0.45	glass lined
Tanks						
Process	capacity, m^3					
vertical		1–50	1450	2400	0.6	atmos. press.
horizontal		10–100	1750	2900	0.6	carbon steel
Storage						
floating roof		50–8000	2500	4350	0.55	×2 for
cone roof		50–8000	1400	2300	0.55	stainless

Figure 24: Pressure vessel cost parameters

Costing of N_{V2} Vessels:

Capacity of Vessel, N_{V2} = 0.246 m^3

Cost of the Vessel = $x\ CS\ Vol_{N_{v2}}{}^{n}$

Where

x = number of vessels

C = Constant (taken from the table)

n = index (taken from the above table)

Cost of the Vessels, $Cost_{N_{V_2}} = 2 \times 2900 \times 0.246^{0.6}$

= \$2500.28

Costing of N_{V1} Vessel:

Capacity of Vessel, N_{V1} = 0.164 m^3

Cost of the Vessel = $x\ CS\ Vol_{N_{v1}}{}^{n}$

Where

x = number of vessels

C = Constant (taken from the table)

n = index (taken from the above table)

Cost of the Vessels, $\mathrm{Cost}_{\mathrm{N}_{\mathrm{V}_1}} = 1 \times 2900 \times 0.164^{0.6}$

= \$980.17

Costing of N_{V3} Vessel:

Capacity of Vessel, N_{V3} = 0.286 m^3

Cost of the Vessel = $x\ CS\ Vol_{N_{v3}}{}^{n}$

Where

x = number of vessels

C = Constant (taken from the table)

n = index (taken from the above table)

Cost of the Vessels, $\mathrm{Cost}_{\mathrm{N}_{\mathrm{V}_3}} = 1 \times 2900 \times 0.286^{0.6}$

= \$1368.41

CAPEX of RO Plants

$$\text{Total capital cost} = \text{cost of elements} + \mathrm{Cost}_{\mathrm{N}_{\mathrm{V}_2}} + Cost_{N_{V_1}} + Cost_{N_{V_s}}$$

$$Total\ capital\ cost = \$17{,}855 + \$2{,}500.28 + \$980.17 + \$1368.41$$

$$Total\ capital\ cost = \$22{,}803.86$$

OPEX of RO Plants

$$Operating\ expenditure\ = 24\ \frac{US\ Cents}{m^3\ permeate\ produced}$$

$$Operating\ expenditure\ = \$0.24\ \times (8.35 + 3.75)$$

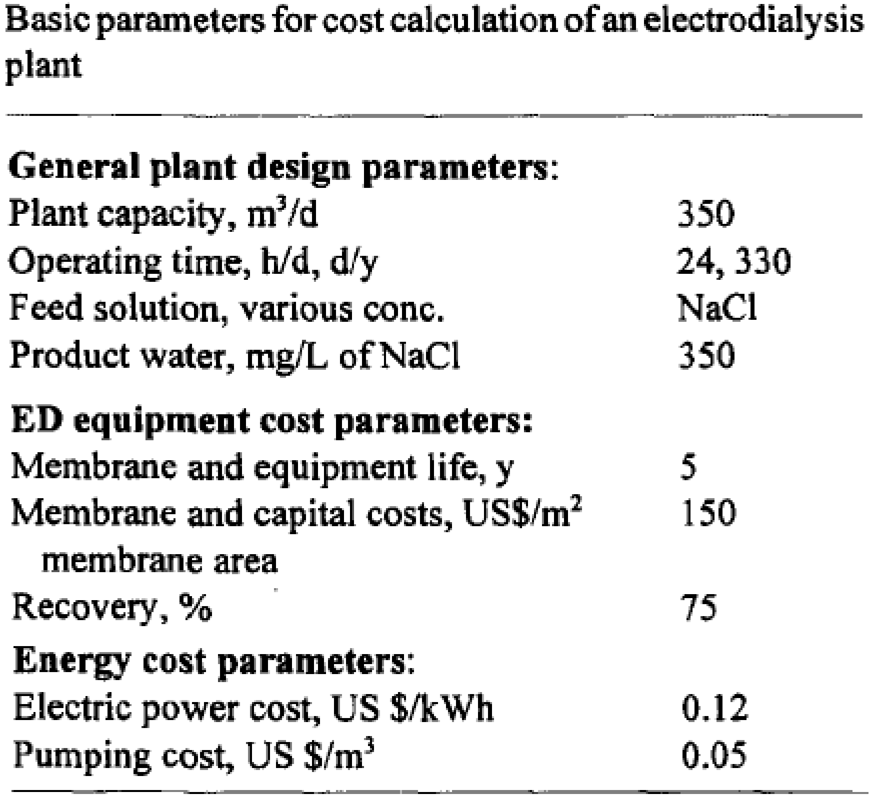
$$Operating\ expenditure = \frac{\$2.90}{hr}$$

5.3 Electrodialysis

The major cost of setting up an electrodialysis plant is associated with its size which in essence depends on the effective area of membrane used in the plant. The effective area of membrane in the ED plant designed for this project is as follows

$$\mathrm{A}_T = 3130.41\ m^2$$

The ED plant is designed to operate at a recovery rate of 75% and an efficiency of 90 %. Literature review revealed that the for a plant operating at these conditions, capital investment is a direct function of the membrane area according to the following table



Basic parameters for cost calculation of an electrodialysis plant

General plant design parameters:	
Plant capacity, m^3/d	350
Operating time, h/d, d/y	24, 330
Feed solution, various conc.	NaCl
Product water, mg/L of NaCl	350
ED equipment cost parameters:	
Membrane and equipment life, y	5
Membrane and capital costs, US\$/m^2 membrane area	150
Recovery, %	75
Energy cost parameters:	
Electric power cost, US \$/kWh	0.12
Pumping cost, US \$/m^3	0.05

The basic cost per unit area including the capital costs is estimated to be 150 US Dollars. This value has been used to calculate the cost

$$\text{Capital Cost} = 3130.41\ m^2 \times 150\frac{\$}{m^2}$$

Capital Cost = \$ 469561.5

The running cost of the electrodialysis plant can be calculated as we already know the energy consumption of the plant to $22.32\ KWh$ and the energy cost is $0.12\ \frac{\$}{KWh}$

Hence

$$\text{Running Cost} = 22.32\ kWh\ \times 0.12\ \frac{\$}{KWh} = \frac{\$2.67}{h}$$

5.4 Crystallizer

The crystallizer’s amended flowrates will increase coolant consumption

$$\Delta Coolant = 3147 - 3024$$
$$\Delta Coolant = 123\ tph$$

$$Chilled\ brine\ cost = \frac{\$0.08}{ton}$$
$$Additional\ coolant\ cost = 123\ \times 0.08$$
$$Additional\ coolant\ cost = \frac{\$9.84}{hr}$$

5.5 Overall expenditure

The total capital costs are:

Mixing Tank	\$70,167.88
Agitator	\$4,248.50
First Pump	\$3,000
Second Pump	\$2,000
RO Membrane	\$22,803.86
Electrodialysis Unit	\$469,561.50
Total	\$571,781.74

Figure 25: Total Capital Cost

$$Plant\ Physical\ Cost\ (PPC) = PCE(1 + f_1 + f_2 + f_3 + f_4)$$

f_1 *is equipment erection*

f_2 *is piping*

f_3 *is instrumentation*

f_4 *is electrical*

$$PPC = 571{,}781.74(1 + 0.4 + 0.7 + 0.2 + 0.1)$$

$$PPC = \$1{,}372{,}276.18$$

$$Fixed\ capital = PPC\left(1 + f_{design} + f_{contingcies}\right)$$

$$Fixed\ capital = \ \$1{,}372{,}276.18(1 + 0.3 + 0.1)$$

$$Fixed\ capital = \$1{,}921{,}186.65$$

Taking working capital to be 5% of the fixed capital to compensate for increased coolant flow and RO anti-scalers

$$Working\ capital = 0.05\ \times 1{,}921{,}186.65$$

$$Working\ capital = \$96{,}059.33$$

$$Investment = working\ capital + fixed\ capital$$

$$Investment = \ \$1{,}921{,}186.65 + \ \$96{,}059.33$$

$$Investment = \$2{,}017{,}245.98 \sim \$2{,}020{,}000$$

For the operating expenditures, we add the hourly expenses:

Equipment	Hourly operating cost ($)
Agitator	0.6
First Pump	1.3
Second Pump	0.18
RO Membrane	2.90
Electrodialysis	2.67
Crystallizer (increased brine flow)	9.84

Table 17: Hourly Operating Costs

The total operating cost per hour works out to be $17.49/hour.

5.6 Payback Period

To calculate the value of the recovered products, we use the equation:

$$Value = amount\ recovered\ \times price\ per\ unit$$

$$Value\ of\ Calcium\ Nitrate = \frac{121.27\ kg}{hr} \times \frac{\$200}{ton}$$

$$Value\ of\ Calcium\ Nitrate = \frac{\$24.25}{hr}$$

$$Value\ of\ Diammonium\ Phosphate = 68.01 \frac{kg}{hr} \times \frac{\$410}{ton}$$

$$Value\ of\ Diammonium\ Phosphate = \frac{\$27.88}{hr}$$

$$Value\ of\ process\ water = 12.5\ tph\ \times \frac{\$0.5}{ton}$$

$$Value\ of\ process\ water = \frac{\$6.25}{hr}$$

Calcium Nitrate	\$24.25/hr
Diammonium Phosphate	\$27.88/hr
Water	\$6.25/hr

Table 18: Quantity of Recovered nutrients

Total CAPEX	\$2,020,000
Total OPEX	\$17.49/hr
Recovered Calcium Nitrate	\$24.25/hr
Recovered Diammonium Phosphate	\$27.88/hr
Recovered process water	\$6.25/hr

Table 19: Summary of cash flows

$$Hourly\ Profit = Inflow\ from\ recovery - OPEX$$
$$Hourly\ Profit = 24.25 + 27.88 + 6.25 - 17.49$$
$$Hourly\ profit = \$40.89$$
$$Yearly\ profit = \$358{,}196.40$$

$$Payback\ period = \frac{CAPEX}{Yearly\ profit}$$

$$Payback\ period = \frac{\$2{,}020{,}000}{\$358{,}196.40}$$

$$Payback\ period = 5.64\ years$$

The installed equipment will meet its break-even point after 5 years, 7 months and 24 days.

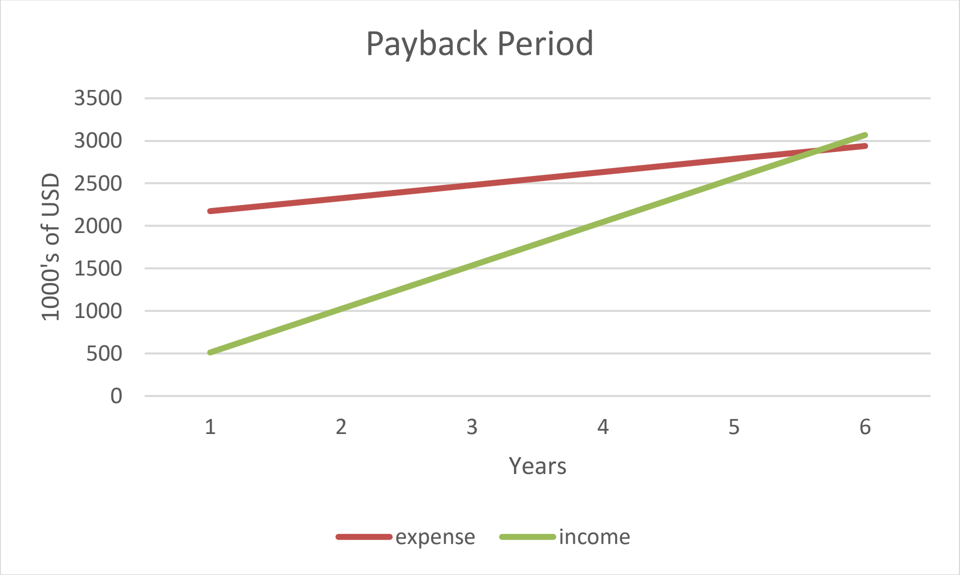


Figure 26: Payback Timeline

Chapter 6

HAZOP Analysis

Deviation	Possible Causes	Consequences	Actions Required or Recommendations
RO Fouling	Large time gaps between membrane cleanings Polarization of concentration	Loss of permeability and gradual decrease in ion rejection	Application of backwash after regular intervals Cleaning of the whole system after a month
No Pressure	1.Blockage in the outlet or inlet of the pump 2.Seepage of air in the pump 3.Pump Failure 4.Clogged pipes before the pump 5.Fouling in valves	Loss of permeate production and line tripping	1. Installation of switch on safety valves 2. Installation of auto vent on different lines 3. Prefiltration to remove suspended solids
Low Flow	1- Lack of manual valve in the outlet 2- Failure of pump to produce suction	Loss of permeate production and line tripping	1-Control of manual valves 2- Regular backwash of sand filter 3- Periodical inspection & maintenance

	3- Failure of check valves 4- Finished life of sand filters		
High Flow	1- Lack of regulatory manual valves 2- Flanges failing mechanically 3- Accidental start of backup pump	Loss of permeate production and line tripping. Pipe and membrane damage due to increased pressure	PLC to be programmed in such a way that the backup pump doesn't start
Water without chlorine	1- Failure of pump that is used for chlorine injection 2- Blockage of pipes transporting chlorine	Growth of microorganisms and algae on membranes and pipes	1- Regular checking of chlorine vessels 2- Proper maintenance of pumps
Water with additional chlorine	1-Increased injection of chlorine 2- Reduced water flow	Increase in corrosion and decrease in membrane life	1- Installation of chlorine sensor to regulate flow 2- Installing flow meter

Service failures	1- Tow phase in Acid pump in causes electrical failure 2- Acid Pump corrosion 3- Mechanical failure in Acid instrument	No unloading of Acid, Maintenance & periodical repairing diffusion of Acid on place	
Pump reversed	1-Enter error electrical phase into pump 2- Decrease on vessel level 3- No air on apparatus followed by repairing	Line Trip, and no produced permeate water	Install auto vent on routing
Increase in water hardness	1- Reduction in quality of raw water 2- Raising dust on vessel	Increased corrosion, decrease in Permeate water quality, decline in recovery, saturation of vessel	Periodical water examination, regulate recovery & pressure in RO

Abnormal Operation (failure valve)	1- Fault at PLC programming 2- Mechanical failure in valves 3- Interruption air of pneumatic valves	Damage to valves	Maintenance & periodical repairing
Increase opacity	1- Deficit silica & anthracite height in sand filter 2- Creation flood channel among sand filter 3- Inappropriate granular in sand filter 4- Running away nozzle 5- Inefficient rinse after backwash 6- Use more extra of sand filter	Quick blockage of filters	1- Install opacity tester 2- Set up diffusion water
Increase Δ P Pressure difference	1-Finished normal using time of cartridge 2- corrosion in routing	Change in recovery, passing suspended particles	Install resin catcher before cartridge

	3- Running away washer among piping		
Increase recovery	1-Decreased drainage at RO concentrate 2- RO membrane damage 3- Running away RO oaring 4- Blockage of rout and concentrate check valve	Increase Conductivity and decrease water quality also reduce in advantage using time	1- Regular flow meter calibration 2- Install recovery representative in PLC 3- install automatic regulated valve instead manual valve
Flow interruption to unloading acid pump	1-Running away stride 2-Blockage in stride	Diffuse acid in the place	Maintenance & periodical repairing
Entrance acid to alkaline line	1- Operator error in connecting routes together	Explosion	1- Full isolation acid and base route 2- labeling acid and base route
Puncturing acid vessel	1- Chemical reaction 2- Physical failure (knocking)	Sprinkling acid and environment pollution	3- using different flange for any route Install plastic curtain surrounding vessel to prevent leakage

Decrease acid concentration to below 98%	In attendance impurities like water and iron	Equipment corrosion, reduce acid potency	Periodical inspection, catching humidity in air route
Strengthen acid concentration more than 4%	1- Increase acid injection pump course 2- Low water flow in entry of Mixing Tee	Damage to resin, Equipment corrosion	1- Maintenance & periodical repairing of acid pump, valve control, 2- install flow switch high
Raised calcium and magnesium and sediment calcium sulfate	Only using water with conductivity more than 90 micro siemens	Adverse effects on membrane	1- Installation of conductivity meters on lines

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