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THÈME

**Zero Liquid Discharge Management : Optimizing Sustainable Reverse
Osmosis Desalination Practices**

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ملخص:

تقدم هذه الأطروحة مخطط تصريف منعدم السوائل (ZLD) لتحلية المياه بواسطة التناضح العكسي (RO)، مع دمج معالجة مسبقة بواسطة الترشيح الفائق والتحليل الكهربائي (ED) لتركيز المياه المالحة. يتم تقسيم المياه العادمة المالحة إلى عدة أجزاء، يتم توجيهها إلى جهاز التحليل الكهربائي والمبخر الذي يعمل بمصادر الطاقة المتجددة. تشمل النتائج البارزة قدرة محطة المعالجة على إنتاج 792 متر مكعب من المياه العذبة يوميًا، مع تخفيض تركيز الملح من 4660 جزء في المليون (ppm) إلى 30 جزء في المليون، مما يظهر فعالية التحلية. بالإضافة إلى ذلك، تعزز إعادة تدوير أجزاء من بقايا وحدة التناضح العكسي إلى مكونات مختلفة كفاءة الموارد. تبرز الدراسة إنتاج 2269.27 كجم من الهيدروجين يوميًا، مع استهلاك كهرباء قليل يبلغ 74885.91 كيلو واط في الساعة، مما يحسن الكفاءة الطاقوية الشاملة. علاوة على ذلك، يقلل استخدام الطاقة الشمسية من الاعتماد على الوقود الأحفوري، مما يعزز الاستدامة و حماية البيئة. وبالتركيز على الحفاظ على البيئة والأمن المائي، يشير تركيز ملح المياه المالحة في التناضح العكسي بمقدار 13648 جزء في المليون ومؤشر بنسبة 2.7% إلى أهمية أنظمة ZLD في ممارسات التحلية المستدامة. عرض النموذج انخفاضًا كبيرًا في استخراج المياه قليلة الملوحة من 1200 متر مكعب يوميًا إلى 871.52 متر مكعب يوميًا، مما يشكل انخفاضًا ملحوظًا بنسبة 27%. تسلط هذه النتائج الضوء على فعالية مخطط ZLD المقترح في تعزيز كفاءة معالجة المياه العكرة، مما يظهر قدرته على تقليل الطلب على موارد المياه العذبة بشكل كبير مع تحقيق ممارسات تحلية مستدامة. تم استيراد محطة معالجة المياه والبيانات المستخدمة في الحسابات من مصنع عدوان للكيماويات، الواقع في منطقة فرناكة الصناعية بولاية مستغانم، الجزائر.

الكلمات المفتاحية: معالجة المياه، التناضح العكسي، تصريف منعدم السوائل، المياه العادمة، الاستدامة.

Abstract:

This study introduces a Zero Liquid Discharge (ZLD) scheme for Reverse Osmosis (RO) desalination, integrating ultra-filtration pretreatment and Electrodialysis (ED) for brine concentration. The scheme divides brine reject into fractions, directing them to an electrolyser and evaporator powered by renewable energy sources. Notable findings include the treatment plant's capability to produce 792 cubic meters of fresh water daily, while decreasing salt concentration from 4,660 ppm to 30 ppm, showcasing efficient desalination. Additionally, recycling fractions of RO unit waste to various components enhances resource efficiency. The study highlights the daily production of 2,269.27 kg of hydrogen, coupled with minimal electricity consumption of 74,885.91 kWh, thereby improving overall energy efficiency. Furthermore, the utilization of solar energy, reduces reliance on fossil fuels, promoting sustainability. Emphasizing environmental preservation and water security, the RO brine salt concentration of 13,648 ppm and ZLD index of 2.7% underscore the importance of ZLD systems in sustainable desalination practices. The model showcased a significant decrease in brackish water extraction from 1,200 cubic meters per day to 871.52 cubic meters per day, marking a notable 27% reduction. These results highlight the promising effectiveness of the proposed ZLD scheme in enhancing the efficiency of brackish water treatment, demonstrating its potential to significantly reduce the demand for fresh water resources while achieving sustainable desalination practices. The water treatment plant and the data used for the calculations were sourced from the Adwan Chemicals factory, located in the Fornaka industrial zone in the Wilaya of Mostaganem, Algeria.

Keywords: Water treatment, reverse osmosis, zero liquid discharge (ZLD), wastewater, sustainability.

Résumé :

Cette étude propose un schéma de zéro décharge de liquide (ZLD) pour le dessalement par osmose inverse (RO), intégrant un prétraitement par ultrafiltration et une électrodialyse (ED) pour la concentration de la saumure. Le schéma divise le rejet de saumure en fractions, les dirigeant vers un électrolyseur et un évaporateur alimenté par des sources d'énergie renouvelables. Parmi les résultats notables, on trouve la capacité de l'usine de traitement à produire 792 mètres cubes d'eau douce par jour, tout en réduisant la concentration en sel de 4,660 ppm à 30 ppm, démontrant un dessalement efficace. De plus, le recyclage des fractions de déchets de l'unité RO vers divers composants améliore l'efficacité des ressources. L'étude met en évidence la production quotidienne de 2,269.27 kg d'hydrogène, couplée à une consommation électrique minimale de 74,885.91 kWh, améliorant ainsi l'efficacité énergétique globale. En outre, l'utilisation de l'énergie solaire réduit la dépendance aux combustibles fossiles, favorisant la durabilité. En mettant l'accent sur la préservation de l'environnement et la sécurité de l'eau, la concentration de sel de la saumure RO de 13,648 ppm et l'indice ZLD de 2.7% soulignent l'importance des systèmes ZLD dans les pratiques de dessalement durable. Le modèle a montré une diminution significative de l'extraction d'eau saumâtre, passant de 1,200 mètres cubes par jour à 871.52 mètres cubes par jour, soit une réduction notable de 27 %. Ces résultats mettent en évidence l'efficacité prometteuse du schéma ZLD proposé pour améliorer le traitement de l'eau saumâtre, démontrant son potentiel à réduire considérablement la demande en ressources d'eau douce tout en réalisant des pratiques de dessalement durables. L'usine de traitement de l'eau et les données utilisées pour les calculs proviennent de l'usine de produits chimiques Adwan Chemicals, située dans la zone industrielle de Fornaka, dans la Wilaya de Mostaganem, en Algérie.

Mots clés : Traitement de l'eau, osmose inverse, décharge liquide zéro (ZLD), eaux usées, durabilité.

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Dedications

We dedicate this work to our dear parents, whose unwavering and boundless support has been the cornerstone of our journey. Your endless sacrifices have provided us with everything we needed to become who we are today. May God protect you, and may success always be within our reach, allowing us to fill your lives with happiness.

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Abbreviations

Abbreviation

Definition

AWWA	American Water Works Association
BW	Brackish Water
BWRO	Brackish Water Reverse Osmosis
Ca ²⁺	Calcium ion
CIP	Cleaning In Place
Cl ⁻	Chloride ion
CO ₃	Carbon trioxide
CO ₃ ⁻	Carbon trioxide ion
DEG	Diethylene Glycol
ED	Electrodialysis
EDR	Electrodialysis Reversal
H ₂	Hydrogen
H ₂ O	Water
HCO ₃	Bicarbonate
HCO ₃ ⁻	Bicarbonate ion
IMSDesign	Membrane projection software
ISO	International Organization for Standardization
K ⁺	Potassium ion
KCl	Potassium chloride
KMgCl ₃ ·6(H ₂ O)	Carnallite
m_{brc}	The mass flow rate of brine concentrate from the evaporator
m_{ev}	The mass flow rate of brine feed to evaporator
Mg ²⁺	Magnesium ion
m_{H_2}	The mass flow rate of hydrogen produced
M_{H_2}	The molecular mass of hydrogen
m_{H_2O}	The mass flow rate of brackish water fraction from brine reject of RO
M_{H_2O}	The molecular mass of water
MLD	Minimal Liquid Discharge
m_{wv}	The mass flow rate of water vapor produced in the

	evaporator
Na ⁺	Sodium ion
NALCO	Water compnay
NaOCl	Sodium hypochlorite
n_{cell}	The number of cells
NF	Nanofiltration
NH ₄	Ammonium
NH ₄ ⁺	Ammonium ion
NO ₂	Nitrogen dioxide
NO ₂ ⁻	Nitrogen dioxide ion
NO ₃	Nitrate
NO ₃ ⁻	Nitrate ion
O ₂	Oxygen
OH	Hydroxide
P_{cell}	Power produced from each PV cell
PFD	Process Flow Diagram
PO ₄ ³⁻	Phosphates
PO ₄ ³⁻	Phosphates ion
PV	Photovoltaic
PVC	Polyvinyl Chloride
R_{ev}	The evaporation rate fraction achieved in the evaporator leading to pure water vapor.
RO	Reverse Osmosis
SEC	Specific Energy Consumption
SiO ₂	Silicon dioxide
SO ₄ ²⁻	Sulfate ion
SWRO	Sea Water Reverse Osmosis
TDS	Total Dissolved Solids
V_{br}	The volumetric flow rate
V_{bw}	The volumetric flow rate of saline brackish water source feed
V_{fw}	The volumetric flow rate of fresh water
V_{sc}	The volumetric flow rate of the saline combined feed to

RO

X_{br}	Salt concentration of brine reject
X_{bw}	Salt concentration in the brackish water feed stream
X_{fw}	Salt concentration of fresh water
ZLD	Zero Liquid Discharge
ΔE_{el}	Typical energy demand for electrolysis
θ_{sun}	The sunny hours per day
ρ_{fw}	Density of fresh water
ρ_{bw}	Density of brackish water
X_{sl}	Salt concentration in the brine concentrate leaving the evaporator

Introduction

In an era marked by escalating concerns over freshwater scarcity and the pressing need for sustainable water management solutions, the application of advanced technologies becomes vital. Among these technologies, reverse osmosis (RO) stands out as a promising method for addressing the challenges of water purification and resource conservation. [1]

To understand how the process of Reverse Osmosis exactly works, one must first understand the naturally occurring process of Osmosis.

Osmosis is a naturally occurring phenomenon and one of the most important processes in nature. It is a process where a weaker saline solution will tend to migrate to a strong saline solution. Examples of osmosis are when plant roots absorb water from the soil and our kidneys absorb water from our blood. [2]

Jean-Antoine Nollet used the bladder of a pig as a semi-permeable membrane in a lab setting to study the process of osmosis for the first time in 1748. Through the process of natural osmotic pressure, he demonstrated how a solvent may selectively pass through a semi-permeable membrane [3]. The solvent will continue to enter through the cell membrane until dynamic equilibrium is attained on both sides of the bladder.

Osmosis was a phenomenon that was only seen in lab settings over the following two centuries. osmosis and semi-permeable membranes were originally investigated by the University of California, Los Angeles in 1949 as a potential method of extracting salt from seawater. In the middle of the 1950s, researchers from the Universities of Florida and California successfully produced fresh water from seawater, but the flow was too low to be economically feasible [3].

Furthermore, reverse osmosis is essentially the opposite of osmosis. While osmosis happens spontaneously without any energy input, reverse osmosis requires energy to force water through a semi-permeable membrane against its natural flow. This membrane selectively allows water molecules to pass through while blocking the majority of dissolved salts, organic compounds, and bacteria. To achieve this, pressure greater than the natural osmotic pressure is applied to the saline solution, effectively desalinating (or demineralizing/deionizing) the water by separating pure water from contaminants. [4]

In 1977, Cape Coral, Florida became the first city in the United States to use reverse osmosis on a large scale with an initial operating capacity of more than 11 thousand cubic meters per day. By 1985, due to the rapid growth in population of Cape Coral, the city had the largest low-pressure reverse-osmosis plant in the world, capable of producing almost 57 thousand cubic meters per day. [5]

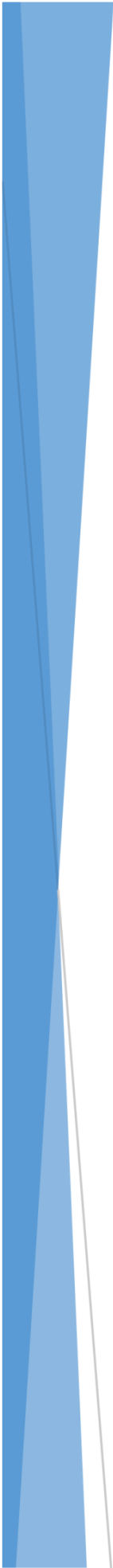
By 2019, approximately 16,000 desalination plants operated around the world, producing around 95 million cubic meters per day, around the world, around half of this capacity was in the Middle East and North Africa. Algeria, for example, already runs 23 desalination plants and has plans for 14 more, to meet 60 per cent of its water needs by 2030. [6]

Reverse osmosis stands out for its remarkable ability to eliminate a broad spectrum of contaminants from water, boasting the capacity to filter out ions and molecules as small as 0.1 nm, this makes it an ideal technology for the production of fresh, potable, and process water [7]. Its application extends to treating water from diverse sources, ranging from wells to seawater. However, while reverse osmosis effectively purifies water, it also removes minerals, including beneficial ones like calcium and magnesium, which requires additional treatment steps to re-mineralize the water for optimal health benefits [8]. Additionally, the reverse osmosis process yields a considerable volume of wastewater due to the concentration of contaminants. This can lead to elevated water consumption compared to alternative filtration methods [9]. The resulting global desalination brine was estimated at 129 million m³/d [10].

Nevertheless, efforts are underway to address this challenge, driven by the increasing scarcity and value of water, coupled with growing populations. One such promising solution is zero liquid discharge (ZLD), a technology that eliminates wastewater entirely turning it into solid waste, this new technology can make water 99% reusable which will be the central point of our thesis [11].

Implementing Zero Liquid Discharge (ZLD) in industrial operations offers numerous benefits. It reduces waste volumes, thereby lowering associated costs and environmental impact. On-site water recycling decreases water acquisition expenses and treatment needs for compliance with discharge standards. Moreover, ZLD minimizes reliance on off-site wastewater disposal, reducing greenhouse gas emissions and road incident risks. Additionally, it enhances environmental performance and regulatory compliance, potentially yielding valuable resources such as ammonium sulfate fertilizer or sodium chloride salt [12].

This thesis will present a detailed yet a simple description of reverse osmosis and ZLD, how do they correlate and how these two technologies represent the future of water treatment.



Chapter I

Bibliography

I. Bibliography

I.1. Adwan Chemicals factory presentation

Adwan Chemicals Algeria was established on May 19, 2004, as part of the strategic expansion of its parent company's operations, which is headquartered in Saudi Arabia. This establishment marks a significant extension of the parent company's industrial footprint, leveraging Algerian resources and market opportunities. Adwan Chemicals Algeria operates as a wholly Saudi-owned entity under Algerian law and is situated in the west of Algeria, in the commune of Fornaka, within the Wilaya of Mostaganem.

The company's core activities revolve around the production and commercialization of a wide range of inorganic chemical products. Its expansive facility covers an area of 70,000 square meters, with a substantial capital investment of 3.7 billion dinars. The company plays a crucial role in the local economy by providing 280 direct jobs, thereby supporting regional employment and economic stability.

Adwan Chemicals Algeria is committed to maintaining high standards of quality, environmental responsibility, and occupational health and safety. This commitment is demonstrated through its adherence to internationally recognized standards, holding ISO 9001:2015 certification for its Quality Management System, ISO 14001:2015 certification for its Environmental Management System, and ISO 45001:2018 certification for its Occupational Health and Safety Management System.

The company's production capabilities are organized into several specialized units. These include a plant for treated sand and its derivatives, a chlorine production plant and its derivatives, and a calcium chloride production plant. Within the chlorine production unit, the company has significant annual production capacities: 22,300 tons of liquid chlorine, 24,000 tons of caustic soda, 42,000 tons of sodium hypochlorite, 35,600 tons of hydrochloric acid, and 30,000 tons of ferric chloride.

The products manufactured by Adwan Chemicals Algeria have diverse and essential applications across various industries. Liquid chlorine is primarily used for water treatment purposes. Sodium hypochlorite is utilized in the manufacturing of detergents and also for water treatment. Caustic soda finds applications in the food industry, particularly for cleaning-in-place (CIP) processes, as

well as in the production of detergents and surface cleaning products. Hydrochloric acid is used extensively in the oil and gas sector, the production of chemicals and pharmaceuticals, the food industry, and metallurgical industries. Ferric chloride is essential for wastewater treatment processes.

The presence of Adwan Chemicals Algeria as a major industrial player in the region significantly contributes to the local economic development. The company's primary mission is to ensure the supply of high-quality chemical products to both local and international markets, thereby enhancing the industrial capabilities and economic resilience of the region. Through its operations, Adwan Chemicals Algeria not only supports regional economic growth but also upholds stringent standards of environmental sustainability and workplace safety, aligning with global best practices in the chemical manufacturing industry.

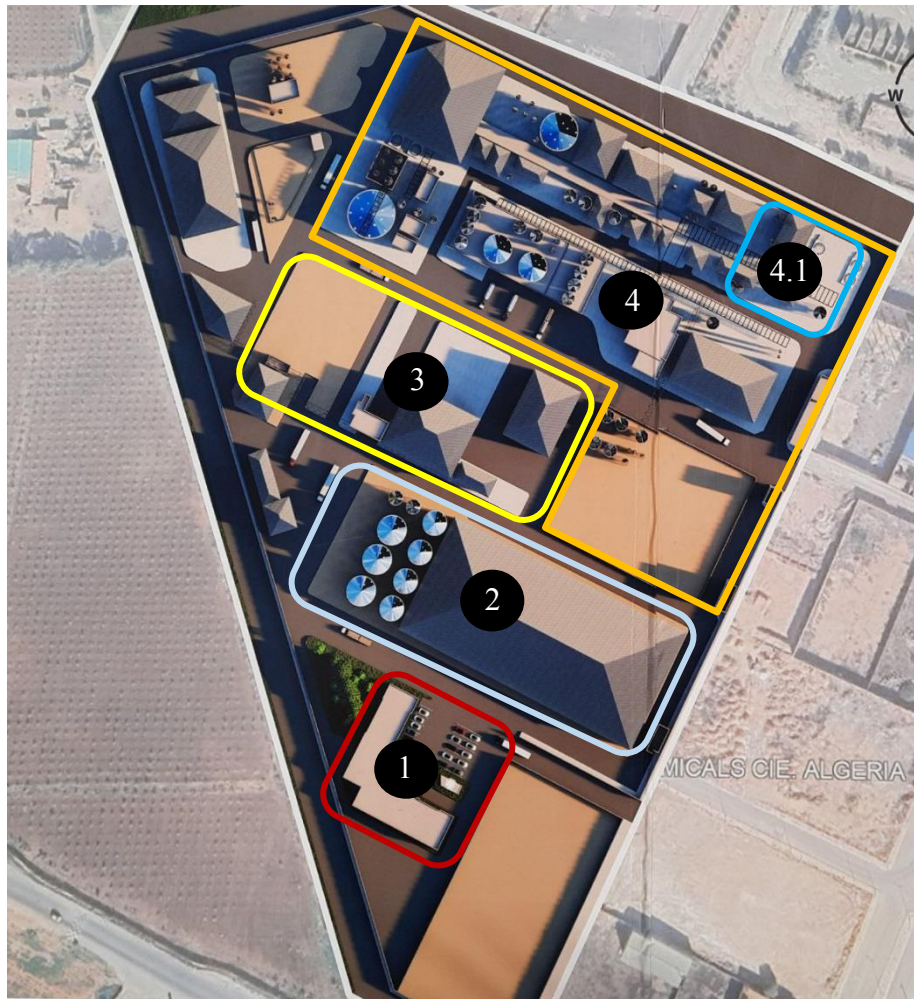


Figure 1: Graphical presentation of zones by domain at Adwan Chemicals.

Zone 1 : Administration

Zone 2 : Treated Sand Production Unit

Zone 3 : Ferric Chloride Production Unit

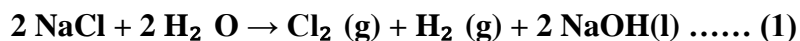
Zone 4 : Chlorine and Derivatives Production Unit

Zone 4.1 : Water treatment plant.

I.1.1. Overview of the Chlorine and Derivatives Manufacturing Process

Chlorine (Cl), with atomic number 17, is the most common halogen and is abundant in nature, primarily as sodium chloride (NaCl). Chlorine, in its diatomic form (Cl₂), is a yellow-green gas, 2.5 times denser than air, with a pungent odor and extreme toxicity. While commonly referred to as "chlorinated," bleach contains hypochlorite ions, not chlorine gas, a frequent source of confusion.

Chlorine is only found in combination with other elements, notably as NaCl, carnallite (KMgCl₃·6(H₂O)), and sylvite (KCl). The primary method for chlorine production is the chlor-alkali process, which involves the electrolysis of aqueous sodium chloride. This process yields chlorine gas at the anode, and hydrogen gas and sodium hydroxide at the cathode. The overall chemical reaction is:



The process includes five main sections: brine purification, electrolysis, chlorine processing, 50% caustic soda production, and hydrogen processing. There are three main electrolysis methods: the mercury cell process, diaphragm cell process, and membrane cell process, which account for over 90% of chlorine production. Other methods include the electrolysis of hydrochloric acid and catalytic oxidation of gaseous HCl.

Chlorine is widely used to manufacture common items and products, including as a biocide for water purification and pool treatment, in solid forms like chlorinated isocyanurates, for bleaching paper, and in the production of antiseptics, dyes, insecticides, paints, petroleum products, plastics (such as PVC), pharmaceuticals, textiles, solvents, and many other consumer products.

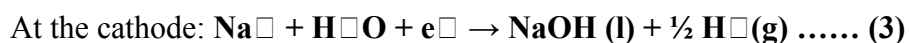
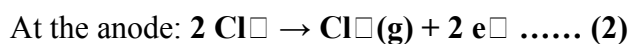
I.1.2. Chlorine Production Unit

The chlorine production process involves using raw salt (NaCl), water, and electricity. Pure water is essential and is achieved through sand filters, microfiltration (10μ, 5μ, 1μ), and reverse osmosis, along with chemical treatments like bleach injection, antiscalant for membrane protection, and metabisulfite to remove sodium hypochlorite.



Figure 2: Sand filters at Adwan Chemicals' water treatment plant

Raw salt, transported from El Oued with 98% concentration, is chemically and physically treated to remove impurities like SO_4^{2-} , Mg^{2+} , and Ca^{2+} . This involves saturation, precipitation, filtration, and ion exchange to ensure high purity. The brine undergoes membrane electrolysis, separating NaCl into chlorine gas (Cl_2) at the anode and sodium hydroxide (NaOH) and hydrogen gas (H_2) at the cathode. The overall reactions are:



Used brine is recovered and recirculated, with secondary chlorine products removed before re-entering the water treatment stage. Material selection is crucial to handle abrasion and corrosion from chlorine compounds. This process ensures the efficient and sustainable production of chlorine and its derivatives, maintaining high quality and minimizing environmental impact.

I.1.3. Chlorine derivatives production

I.1.1. Sodium hypochlorite

Sodium hypochlorite production involves reacting chlorine gas (Cl_2) with sodium hydroxide (NaOH) according to the equation:



In the hypo-reactor, chlorine gas and sodium hydroxide are combined to produce sodium hypochlorite. The resulting solution is then cooled to around 19°C in an exchange system before being sent to storage tanks. From there, it undergoes further cooling and recycling until it reaches the required level. Once the desired level is achieved, the sodium hypochlorite is automatically transferred to sealed storage tanks. These tanks are kept in a cool, dry place away from direct sunlight and heat and can store the product for up to a week before packaging for sale.

I.1.2. Liquid Chlorine

- **Cooling and Drying Chlorine:**

The chlorine gas evacuated from the electrolyser is cooled by iced water to a temperature of around 15°C. The wet chlorine is separated from water in the chlorine dimer. The cooled chlorine gas is split into four streams: one goes to neutralization, the second to hypochlorite production, the third to the HCl synthesis unit under constant pressure, and the fourth to the drying tower. The drying tower has two operators: C-161, circulating 83% H₂ SO₄ with low-pressure pumps, and C-162, circulating 96% H₂ SO₄ with high-pressure pumps. Due to the heat generated by sulfuric acid, it is cooled by iced water through an acid cooler to maintain a temperature below 30°C in the first tower (C-161).

- **Chlorine Compression:**

The dry chlorine gas is first compressed using a liquid ring compressor with 96% H₂ SO₄, creating a two-phase mixture of compressed chlorine gas and sulfuric gas. It is then sent to the first separator, where it is separated from the sulfuric acid and discharged after passing through an unmolding element at a pressure of 3.5 bar. Next, it goes to the second separator, where the sulfuric acid is recycled into the cooler, which removes the compression energy.

- **Chlorine Liquefaction**

The objective of chlorine liquefaction is to reduce its volume for transportation over long distances. It is also used to store some of the gas in liquid form during periods of low consumption and vaporize it when demand is high. To liquefy chlorine, towing cooling units are used to produce refrigerated brine and collect iced brine, which is then pumped to the cooling unit at 12°C.

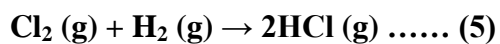
Dry and compressed to a pressure of about 3.5 bar, the chlorine gas enters the liquefier, where it is cooled and liquefied using a diethylene glycol (DEG) solution in a shell-and-tube heat exchanger. It is then transferred by gravity to the separator, where the two-phase mixture of gaseous/liquid chlorine is separated.



Figure 3: Separator at Adwan Chemicals

I.1.3. Hydrochloric Acid

Hydrogen chloride (HCl) is produced according to the reaction:



The production of hydrochloric acid can be done directly in torches, in a 5,000°C flame, after the liquefaction of HCl by water absorption.

I.1.4. Sodium Hydroxide

32% of sodium hydroxide is produced by the electrolysis of a sodium chloride solution (NaCl):



To increase the concentration of sodium hydroxide to 52%, evaporation is used to remove water through heat exchangers.

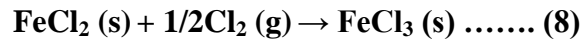
I.1.5. Ferric chloride

Ferric chloride is an iron salt with the chemical formula FeCl_3 , appearing as a brown acidic solution. This corrosive liquid is used for treating wastewater and potable water. It is also employed for metallographic etching on copper alloys and stainless steel. Ferric chloride is produced in a reactor through the following process:

1. Solid iron reacts with hydrochloric acid:

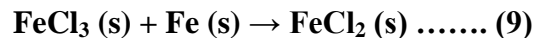


The resulting FeCl_2 is then elevated using a pump for the second reaction with chlorine gas:



The production of ferric chloride begins at 75°C with a concentration of 39% to 40%. Some of the ferric chloride is stored in storage tanks, while another portion is reused instead of using HCl.

2. The remaining FeCl_3 reacts with solid iron:



We can notice the usage of water in almost every step during the production process. Water treatment is crucial in industries to ensure the availability of clean water for various processes, maintain product quality, and protect equipment from damage due to contaminants. Effective water treatment systems enhance operational efficiency and sustainability. Reverse osmosis, a widely used water purification method within these systems, is particularly beneficial as it removes a broad spectrum of impurities, ensuring high water quality for industrial applications.

I.2. Overview of reverse osmosis in industrial complexes

Reverse osmosis (RO) is a widely employed water treatment method in industries for purifying water. It involves passing water through a semi-permeable membrane under pressure, separating contaminants from the pure solvent. In industrial settings, RO systems efficiently remove various impurities, including salts, minerals, organic compounds, and microorganisms, ensuring high-quality water for diverse applications such as manufacturing, food and beverage production, pharmaceuticals, and power generation. RO technology offers several advantages, including high efficiency, scalability, and the ability to customize treatment processes to meet specific industrial needs. As a result, reverse osmosis plays a vital role in ensuring reliable access to clean water for industrial processes, contributing to operational efficiency, product quality, and environmental sustainability.

However, reverse osmosis also has its drawbacks. RO systems are energy-intensive due to the significant energy input required for high-pressure pump operation. Additionally, RO generates a concentrated brine or reject stream that necessitates proper disposal or treatment to avoid environmental impact, posing challenges for waste management. Moreover, membrane fouling, caused by the accumulation of contaminants on the membrane surface, can reduce filtration efficiency over time, leading to increased operating costs and the need for frequent membrane cleaning or replacement.

I.3. Overview of reverse osmosis Adwan chemicals and its problematic facets

The water treated at Adwan chemicals comes from a nearby well, the water treatment plant is composed of sand filters, microfilters and a reverse osmosis unit, it also uses various chemical products for the chemical processing part which we will address later. The RO unit was initially processing water at a rate of 35 m³ per hour of permeate, and 15 m³ of concentrate per hour. However, due to various factors such as time and the effects of scaling and fouling on the membranes, these values have decreased to 33 m³/h for permeate and 17 m³/h for concentrate, that means 408 cubic meters of waste water per day 148,920 per year when the unit is working at full capacity.

This issue is inevitable and the rate of brine reject will continue to rise over time until the membranes are replaced. This causes several environmental issues such as possible inappropriate waste disposal and excessive usage of drinkable water which is becoming scarce every year.



Figure 4: Reverse osmosis unit at Adwan Chemicals

As mentioned before, the water treatment phase is essential in almost every industry, therefore it is impossible to stop these plants from working and an alternative and solid solutions must be found and applied. One promising solution is the Zero Liquid Discharge (ZLD) system, which can be installed in almost every water treatment system, it works by separating waste water into a fresh and reusable water and turning the harmful particles into solid.

To test the efficiency of the ZLD system, we will try to install it on Adwan chemicals water treatment plant, we'll use mathematical equations and a software program to affirm our calculations and results, which is the latest version of Hydraulics membrane projection software the IMSDesign (Integrated Membrane Solutions Design), an advanced sizing tool created to meet the most demanding needs of the membrane industry professional.

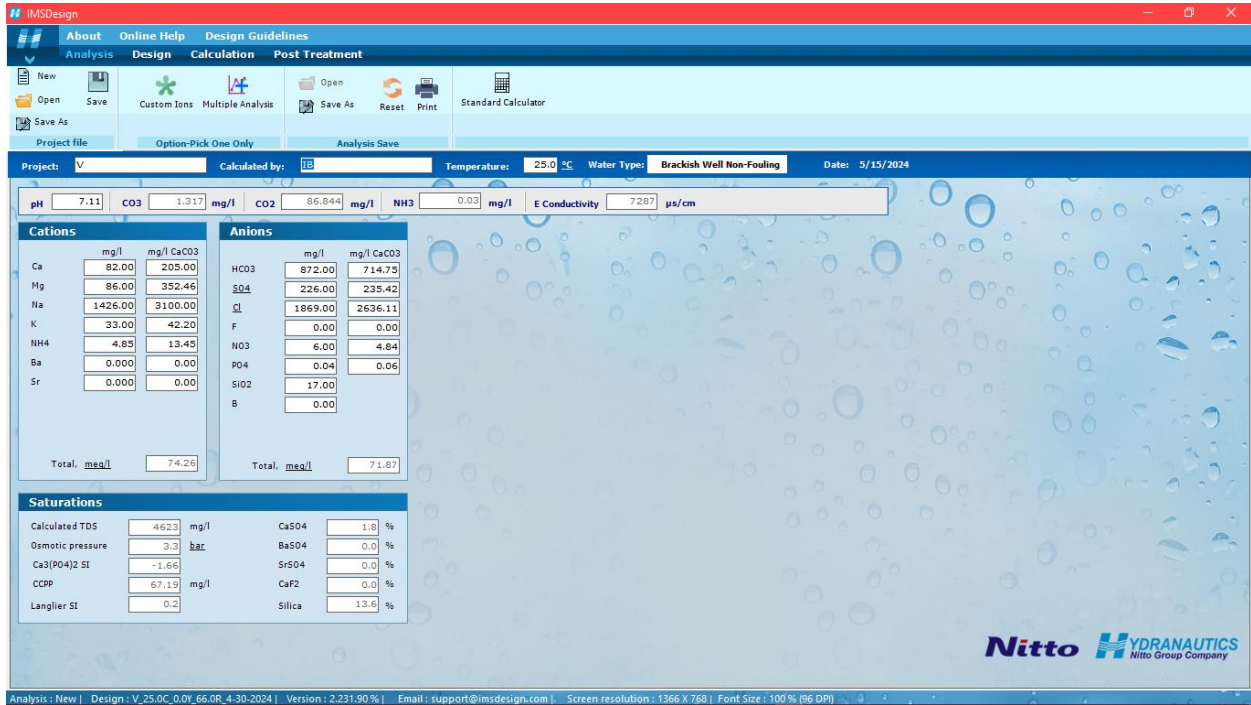


Figure 5: Screenshot from IMSDesign software



Chapter II

Materiel and methodology

II. Materiel and methodology

II.1. Methodology:

The proposed method outlined in this study aims to address the environmental concerns associated with the disposal of brine reject from RO desalination units, which can be quite problematic. This approach, termed Zero Liquid Discharge (ZLD), suggests dividing the brine reject into multiple fractions, typically three splits. **Figure 6** illustrates a Process Flow Diagram (PFD) depicting the ZLD approach.

II.1.1. Conceptual model description

This study proposes modifying BWRO desalination units to implement ZLD. The brine reject is divided into three fractions. One fraction is used in an electrolyser powered by renewable energy to produce hydrogen, which can be utilized for various applications, including providing heat to thermal storage. The second fraction enters an evaporation system powered by solar energy and hydrogen heat to produce fresh water and concentrate the brine further. The fresh water is recycled to the RO module, reducing the salinity of the brine feed and minimizing the volume of water drawn from wells. The third fraction is recycled with the saline source water before entering the RO unit. The concentrated brine can be disposed of by reinjection into surface water or deep wells, depending on environmental costs. The conceptual process results in fresh water,

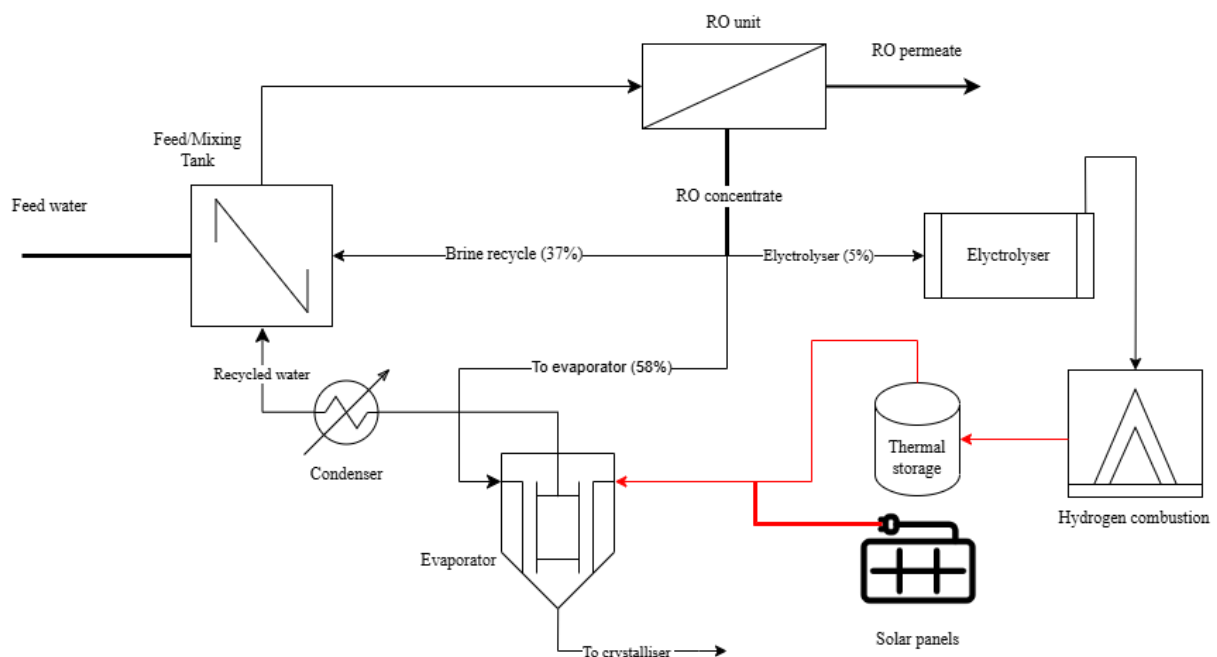


Figure 6: Conceptual model process flow diagram for a BWRO system implementing a ZLD approach.

hydrogen, and salts, achieving zero liquid discharge.

II.1.2. Conceptual model equations:

- *RO membrane unit*

The conceptual model involves equations for mass and energy balance, as well as salt concentration balances around individual units as shown in **Figure 6**. Apart from these balance equations, the model also incorporates the characteristic performance of each piece of equipment. An essential component in the model is the Reverse Osmosis (RO) module, which is responsible for producing a fresh water stream from the brackish water feed stream at a recovery rate (R) based on the volume of the brine/saline source water. The salt concentration of the brine reject is calculated using a salt balance around the RO unit, assuming that the salinities of the brackish water and the fresh water are provided. The equation representing this balance is:

$$X_{br} \times V_{br} \times \rho_{br} = X_{bw} \times V_{bw} \times \rho_{bw} - X_{fw} \times V_{fw} \times \rho_{fw} \dots\dots (10)$$

Where V_{br} is the volumetric flow rate (in liters per day, L/d) of the brine reject from the RO unit, V_{bw} is the volumetric flow rate (in liters per day, L/d) of the saline brackish water source feed, V_{fw} is the volumetric flow rate (in liters per day, L/d) of the fresh water, ρ_{bw} is the density of brackish water (1015 kg/m³), ρ_{fw} is the density of fresh water, X_{bw} , X_{br} , and X_{fw} are the salt concentrations (in parts per million, ppm) in the brackish water feed, brine reject stream, and fresh water stream produced, respectively

The mass balance and salt balance calculations around the RO unit are determined according to the following equation:

$$V_{sc} \times \rho_{bw} = V_{br} \times \rho_{bw} + V_{fw} \times \rho_{fw} \dots\dots (11)$$

Where V_{sc} represents the volumetric flow rate (in liters per day, L/d) of the saline combined feed to the RO unit.

The volumetric flow rate (V_{sc}) and salt concentration of the combined stream, utilized in reverse osmosis (RO), are determined by the mixing tank equilibrium, represented by the equations below:

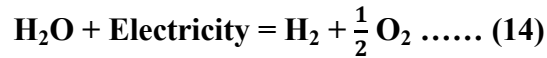
$$V_{sc} \times \rho_{bw} = V_{bw} \times \rho_{bw} + V_{br} \times (1 - r_{el} - r_{ev}) \times \rho_{bw} + V_{br} \times r_{ev} \times R_{ev} \times \rho_{fw} \dots\dots (12)$$

$$X_{sc} \times V_{sc} \times \rho_{bw} = X_{bw} \times V_{bw} \times \rho_{bw} + X_{br} \times V_{br} \times (1 - r_{el} - r_{ev}) \times \rho_{bw} \dots\dots (13)$$

Here, R_{ev} denotes the evaporation rate fraction achieved in the evaporator, resulting in pure water vapor. It's important to note that the salt concentration of the water vapor leaving the evaporator is zero.

• *Electrolyser*

Electrolysis stands as a vital method for hydrogen generation from saline water sources like seawater or brackish water. However, challenges arise due to chlorine and oxygen evolution at the anode. Brine water's diverse ions, such as Na^+ , Cl^- , Mg^{2+} , Ca^{2+} , complicate seawater electrolysis, with high Cl^- concentrations leading to chloride evolution. Additionally, Ca^{2+} and Mg^{2+} may precipitate, forming $Ca(OH)_2$ and $Mg(OH)_2$ at the cathode. Hydrogen evolution diminishes with rising OH^- concentration, while oxygen evolution is bolstered by Cl^- presence. The chlorine produced can be sold or utilized for various purposes, including bromine ion oxidation. Unlike desalination processes, electrolysis directly splits water into hydrogen and oxygen. Electricity for this technology can be sourced from renewables like photovoltaic cells or wind, or from the conventional grid. The fundamental electrolysis equation is:



This suggests that for every mole of water electrolyzed, 1 mole of hydrogen is produced while a half mole of oxygen is released. Consequently, a mass balance on the electrolyser yields the following equations:

$$m_{H_2} = \frac{m_{H_2O}}{M_{H_2}} \times M_{H_2} \dots\dots (15)$$

$$m_{H_2O} = (1 - X_{br}) \times V_{br} \times r_{el} \times \rho_{bw} \dots\dots (16)$$

Here, m_{H_2O} represents the mass flow rate of brackish water fraction from brine reject of RO, m_{H_2} represents the mass flow rate of hydrogen produced, M_{H_2O} and M_{H_2} are the molecular masses of water and hydrogen respectively. The typical energy demand (ΔE_{el}) for electrolysis ranges from 33 to 56 kWh/kg of hydrogen produced. As of 2022, commercial electrolysis requires around 53 kWh of electricity to produce one kg of hydrogen, which holds 39.4 kWh of energy. Therefore, the total energy required (ΔE_{tot}) for procuring hydrogen with a mass flow rate m_{H_2} can be determined by:

$$\Delta E_{tot} = m_{H_2} \times \Delta E_{el} \dots\dots (17)$$

If this energy is provided by solar photovoltaic cells, the number of cells (n_{cell}) is calculated using the power produced from each PV cell (P_{cell}) and the sunny hours per day (θ_{sun}), according to the following equation:

$$n_{cell} = 1P_{cell} \times 1\theta_{sun} \times \Delta E_{tot} \quad (18)$$

It's important to note that the electrolyser is used to provide hydrogen necessary as a heat source for evaporation. In cases where a large fraction of brine reject is directed to the electrolyser, the hydrogen produced may exceed the necessity of evaporation. Consequently, the surplus hydrogen can be sold or utilized in fuel cells for other purposes.

- **Evaporator**

Evaporation equipment can function either as a single effect or multiple effects. Heat is applied to convert a brine solution or salty water into water vapor. In a single-effect evaporator, supplying a kilogram of steam can generate approximately 0.9 Kg of water vapor or steam from a kilogram of water (as noted by Kern). The remaining 0.1 Kg of water retains the majority of the salt. The produced water vapor is condensed and recycled back to the RO unit to diminish the salt content of the brackish water source, while the concentrated brine is directed to crystallizers or evaporation ponds. The evaporator model is delineated by the equations below:

$$m_{ev} = V_{br} \times r_{ev} \times \rho_{bw} \quad (19)$$

$$m_{wv} = m_{ev} \times R_{ev} \quad (20)$$

$$m_{brc} = m_{ev} - m_{wv} \quad (21)$$

$$X_{sl} = m_{ev} \times X_{br} / m_{brc} \quad (22)$$

In these equations, m_{ev} represents the mass flow rate of brine feed to the evaporator, m_{wv} represents the mass flow rate of water vapor produced in the evaporator, m_{brc} represents the mass flow rate of brine concentrate from the evaporator, and X_{sl} represents the salt concentration in the brine concentrate leaving the evaporator.

- **ZLD performance**

The proposed ZLD flowsheet introduces a new parameter called pZLD, which is defined as the ratio of the brine reject from the entire plant to the fresh brackish water drawn from the wells. This parameter, calculated using the formula $pZLD = m_{brc} / (V_{bw} \times \rho_{bw})$, serves as a measure of the modified unit's performance in achieving zero liquid discharge (ZLD). While an absolute

value of zero for pZLD indicates ideal performance, it's important to note that this value may not always represent the optimal condition. Assessing the effectiveness of the modified RO desalination unit involves analyzing its cost implications and the resulting profit from the modifications.

II.2. Study Area

The theoretical model is put to the test by simulating the desalination process of brackish water containing 4,660 ppm TDS, withdrawn from a nearby well at Adwan Chemicals factory located in Fornaka Industrial Zone, Mostaganem where we conducted our internship that lasted for a full month.

Adwan Chemicals similar to many industries, rely on reverse osmosis for water treatment purposes. RO systems are used to purify process water, boiler feedwater, cooling water and other water sources required in manufacturing processes. By removing impurities such as minerals, chemicals, and dissolved solids, reverse osmosis ensures that water used in industrial operations

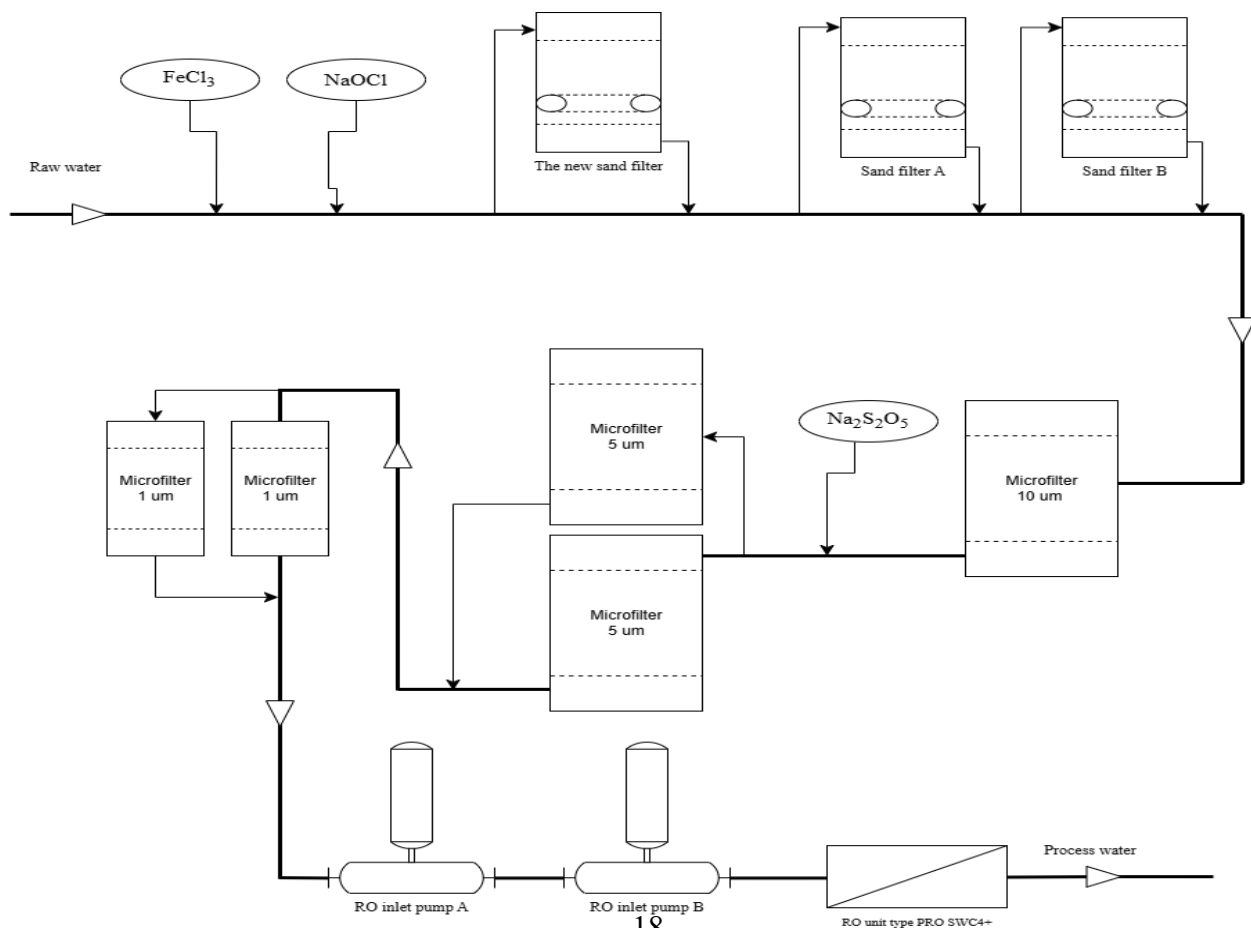


Figure 7: Flow scheme of the water treatment plant

meets the required quality standards. This helps prevent equipment corrosion, scaling, and fouling, ensuring efficient and reliable manufacturing processes.

The RO unit at Adwan Chemicals is part of a larger water treatment plant, that ensures the production of process water with less than 30 ppm TDS. To achieve this, the brackish water drawn from a well goes through several treatment steps, which can be divided into two types of treatment, chemical treatment and physical treatment.

In the full treatment process, the initial step involves dosing flocculant (FeCl_3) to facilitate the aggregation of suspended particles, enabling their efficient removal through filtration. Concurrently, a carefully measured amount of disinfectant (NaOCl) is introduced to the system to preemptively counteract bacterial proliferation. Subsequently, the water undergoes filtration over a sand layer, effectively eliminating physical impurities. Following this, a reducing chemical ($\text{Na}_2\text{S}_2\text{O}_5$) is administered to neutralize any residual free chlorine, ensuring the water's safety for consumption. To prevent the precipitation of sparingly soluble salts on reverse osmosis membranes, a scaling inhibitor (PermaTreat NALCO) is introduced. The core of the treatment lies in the reverse osmosis unit, where feed water is subjected to desalination, rendering it purified and suitable for use. Lastly, another dose of disinfectant is administered to maintain prophylactic safety against bacterial growth throughout the system, guaranteeing the delivery of clean and potable water [24] [25].

II.3. From raw water to process water

II.3.1. Flocculant

This is the first step in this water treatment plant, the purpose of dosing flocculant into the raw water is to coagulate colloidal matter. The particles in a colloid suspension mainly are negatively charged. The flocculant helps to reduce the repulsion forces and to link the particles. This so-called coagulation process produces during a certain exposure time filterable particles. These particles reach sizes up to 100 μm , which will allow to remove them by a filtration step downstream.

As a typical flocculant a solution of iron-III-chloride (FeCl_3) is used. The dosing amount is related to the treated flow rate and to the content of colloidal matter in the raw water. The impact on the removal of colloidal matter has to be determined by a laboratory research [24].

As a thumb rule for the dosing amount a content in the range of 5 - 20 mg/l FeCl_3 in the raw water can be adjusted.

II.3.2. Chlorination

The purpose of dosing disinfectant into the raw water is to avoid bacteria growth in the equipment downstream.

As a typical disinfectant chemical a diluted solution of sodium hypochlorite (NaOCl) is used. The dosing amount is related to the treated flow rate and to the kind and number of bacteria in the permeate water [24]. The impact on the bacteria has to be determined by laboratory research.

Typical values for disinfection by sodium hypochlorite are as follows:

- Active component: 12 % (weight) of chlorine = 150 mg/ml chlorine
- Dosing amount: 0.5 mg/l (content in the raw water)

II.3.3. Sand filter

The sand filter plays a pivotal role in physical water treatment, particularly as a pre-treatment for systems like reverse osmosis, aiming for a maximum amount of solid matter at 50 ppm while colloidal matter will not be treated.

Structurally, it comprises two layers of gravel: a supportive bottom layer with grain sizes ranging from 1 to 2 mm, and an upper layer with grain sizes between 0.7 and 1.2 mm [24]. As water flows from top to bottom during filtration, particles adhere to the gravel. Over time, this accumulation increases pressure drop across the filter layer, a backwash process has to be executed typically at a pressure threshold of 0.5 bar. During backwashing, flow direction reverses from bottom to top, expelling trapped particles, with a flow rate boosted to approximately 1.5 to 2 times that of filtration, ensuring thorough cleaning.

Originally there were only one sand filtration step composed of two filters that works alternatively. A new sand filter was added before the original ones to help filter out maximum amount of particles, to provide a better protection the micro filters and the reverse osmosis



Figure 8: Newly added sand filter at Adwan Chemicals water treatment plant

membranes.

II.3.4. De-chlorination

De-chlorination of raw water aims to eliminate residual free chlorine, typically injected during disinfection to combat bacteria and oxidize inorganic compounds. Maintaining a controlled level of free chlorine post-treatment is essential for preventing contamination [24]. However, free chlorine can harm reverse osmosis membranes due to their sensitivity to oxidizing agents.

Therefore, it is necessary to remove free residual chlorine by injecting a chemical deoxidizing matter.

As a typical reducing agent a diluted solution of sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) is used.

II.3.5. Scaling inhibitor

The purpose of dosing scaling inhibitor into raw water is to prevent the precipitation of sparingly soluble salts, such as carbonates of alkaloids of soil (e.g. CaCO_3 , MgCO_3), and oxides of iron, manganese, and alumina. This inhibition is crucial to maintain membrane integrity within the RO unit, ensuring consistent permeate flow and applied pressure according to design specifications. A common scaling inhibitor used is an undiluted solution of “PermaTreat” supplied by Nalco [24].

II.3.6. Microfiltration

Originally, the water would go through filters of 5 microns and 1 micro meter before entering the reverse osmosis unit, with each filter having a secondary unit in case of maintenance or a malfunction. A 10 microns filter was added to protect the RO membranes after the ground team discovered an increase in pressure and the membranes regenerative periods decreased.

II.3.7. Reverse osmosis unit

The reverse osmosis (RO) unit is the main component of the water treatment plant. This unit consists of 35 polyamide membranes housed within 7 pressure vessels, with each vessel containing 5 membranes. A high-pressure pump is used to increase the pressure on the salt side of the RO unit to above 32 bar, which forces the water to flow across the semi-permeable membrane. This process leaves behind most of the dissolved salts (approximately 95%-99%).

Within the membrane system, the feed water is separated into a low-saline product, known as permeate, and a high-saline solution, referred to as concentrate, brine or reject stream. Initially, the permeate exited the RO unit at a rate of 35 m³/h, and the concentrate at 15 m³/h. However, due to various factors such as time and the effects of scaling and fouling on the membranes, these values have decreased to 33 m³/h for permeate and 17 m³/h for concentrate.

The processed water is stored in a 1000 cubic meter underground storage tank and is subsequently utilized in various processes throughout the factory. The brine, which does not pose environmental risks, is typically disposed of in remote, uninhabited areas.

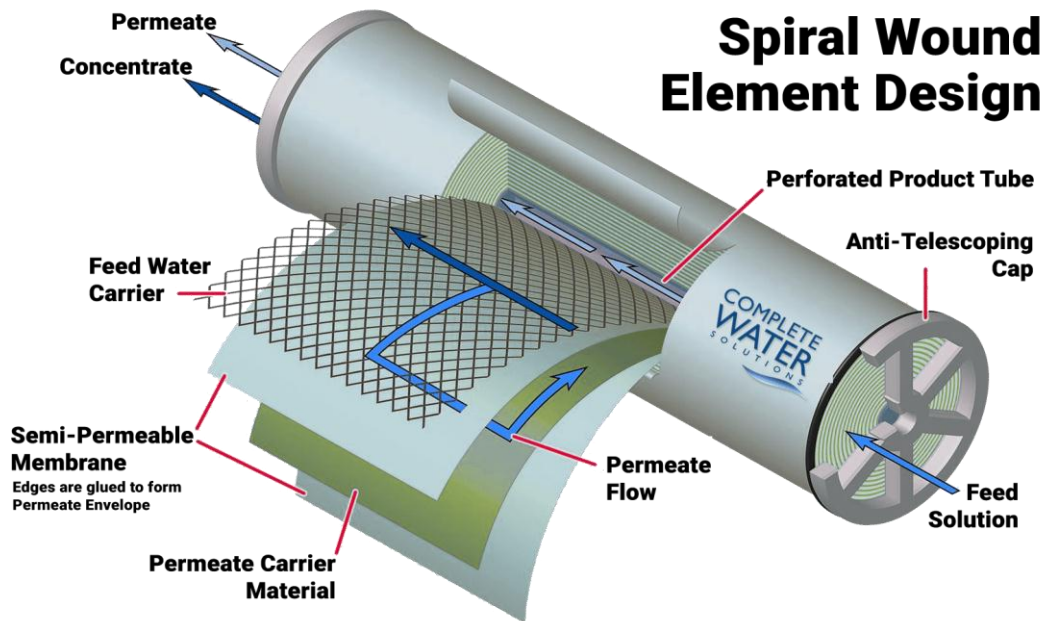


Figure 9: Illustrative diagram of an RO membrane

II.4. Problematic Aspects of Reverse Osmosis in Water Treatment

Reverse osmosis is one of the most effective forms of water filtration because unlike chemical or carbon filtration systems, which use certain materials to attract or directly target the contaminants in the water, reverse osmosis works by pushing water through a semi-permeable membrane with pores around 0.0001 microns, allowing only water molecules to pass while trapping contaminants, organic materials, and salts. Initially developed for seawater desalination and reducing heavy metals, reverse osmosis is now widely used in government, commercial, military, and residential applications.

One of the biggest disadvantages to reverse osmosis water systems is wasted water. Studies show various reverse osmosis systems can waste between 3 and 20 times as much water as they produce [10]. There are numerous ongoing efforts such as ZLD systems to address this issue in the near future, driven by concerns over water scarcity and climate change.



Chapter III

Results and discussion

III. Results and discussion

III.1. Validation of the Conceptual Model

To test the practicality of our conceptual model, we used data obtained from Adwan Chemicals' water treatment plant and the latest version of Hydranautics' membrane projection software, IMSDesign (Integrated Membrane Solutions Design). This advanced sizing tool allows for quick and accurate design and analysis of membrane-based systems such as RO/NF systems. We compared our conceptual model calculations with those made by IMSDesign.

In our case, we primarily verified the salt concentrations in the brine reject stream (Xbr) because they are used in almost every equation and determine the performance of our proposed ZLD system.

III.2. Case Study Description

The theoretical model was tested for the treatment of brackish water with a Total Dissolved Solids (TDS) concentration of 4,660 ppm. A water treatment plant capable of producing 792 cubic meters per day of fresh water with a salt concentration of 30 ppm was utilized for this study. This plant, representing a water processing system, is located at Adwan Chemicals in Algeria. The recovery rate of the RO unit was set at 66%.

The feed water compositions used at Adwan Chemicals are detailed in Table 1.

Compound	Concentrations/Value
Calcium (Ca_2^+)	$\leq 82 \text{ mg/ l}$
Magnesium (Mg_2^+)	$\leq 86 \text{ mg/ l}$
Sodium (Na^+)	$\leq 1.426 \text{ mg/ l}$
Potassium (K^+)	$\leq 33 \text{ mg/ l}$
Chloride (Cl^-)	$\leq 1.869 \text{ mg/ l}$
Sulphate (SO_4^{2-})	$\leq 226 \text{ mg/ l}$
Carbonate (CO_3^-)	$\leq 0 \text{ mg/ l}$

Alkalinity (HCO ₃ ⁻)	≤ 872 mg/ l
Nitrate (NO ₃ ⁻)	≤ 6 mg/ l
Nitrite (NO ₂ ⁻)	≤ 4,6 mg/ l
Ammonia (NH ₄ ⁺)	≤ 4,85 mg/ l
Phosphates (PO ₄ ³⁻)	≤ 0,04 mg/ l
Silicate (SiO ₂)	≤ 17 mg/ l
pH value	≤ 7,11
raw water TDS	≤ 4.621,9 mg/l

III.2.1. Modeling Results with IMSDesign

The data presented in **Table 1**: The feed water compositions used at Adwan Chemicals was entered into the IMSDesign software in order to simulate the performance of the reverse osmosis (RO) system and validate the theoretical model. This software enables precise calculations to be made and the expected results to be analysed as a function of the input parameters.

After inserting the above data into the IMSDesign software, we obtained almost identical results for the RO brine salt concentration, which was approximately 13,369 ppm, as shown in **Figure 10**: Screenshot from IMSDesign software below:

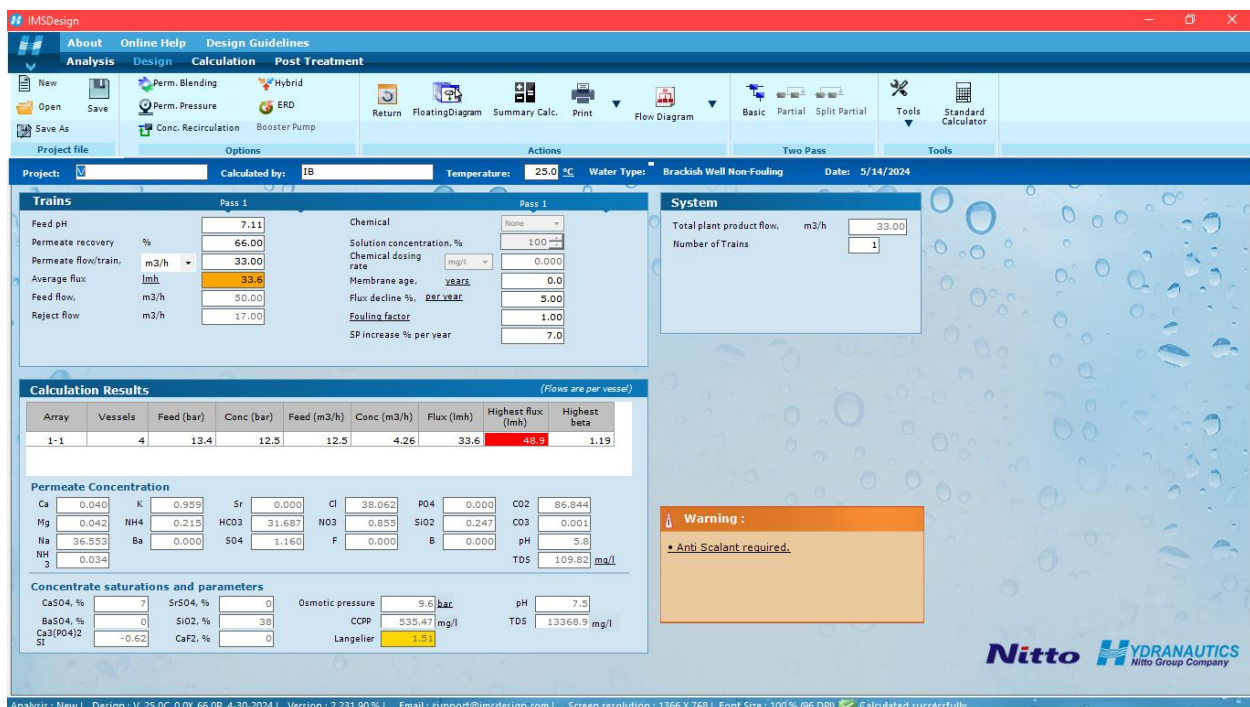


Figure 10: Screenshot from IMSDesign software

The close correlation between the software's output and our theoretical predictions strengthens the reliability of our conceptual model. The slight variations observed can be attributed to the

inherent assumptions and approximations in both the theoretical model and the software's algorithms.

III.3. Performance of the ZLD System

III.3.1. Performance Before ZLD Implementation

Before modifications to adopt the Zero Liquid Discharge (ZLD) concept, the conventional unit consumed 1,200 cubic meters per day of brackish water from a well to achieve the maximum production capacity of 792 cubic meters per day of fresh water. The following results were obtained:

- Water drawn from well: 1,200 m³/d
- Wastewater produced: 408 m³/d
- Salt concentration of final brine: 13,648 ppm

III.3.2. Performance After ZLD Implementation

The application of the ZLD model equations yielded the following results:

- Water drawn from well = 871.52 m³/d
- Fraction of RO reject to electrolyser = 5% of total reject from RO unit.
- Fraction of RO reject to evaporator = 58% of total reject from RO unit.
- Fraction of RO reject recycled to feed/mixing tank = 37% of total reject from RO unit.
- Recycled salt concentration = 4,660 ppm
- RO mixed feed flow rate = 1,200 m³/d
- H₂ produced = 2,269.27 kg/d
- Electricity required = 74,885.91 kWh (Minimum)
- Solar energy = 4 kW (solar energy period = 8.18 h)
- Salt concentration of RO brine = 13,648 ppm

	Before the installment of the ZLD system	After the installment of the ZLD system
Water drawn from well (m³/d)	1200	871.52
H₂ produced (kg/d)	0	2,269.27
Waste water produced (m³/d)	408	0

Salt concentration of final brine (ppm)	13,648	54,592
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- pZLD = 4.9%

Table 2: The impact of the proposed ZLD system on the water treatment plant

III.4. Analysis of ZLD System Performance

Reduction in Water Consumption

Implementing the ZLD system significantly reduced the water drawn from the well, from 1,200 m³/d to 871.52 m³/d, representing a reduction of approximately 27.4%. This reduction is due to the reuse and recycling of reject water.

Hydrogen Production

The ZLD system also enabled the production of 2,269.27 kg/d of hydrogen, providing a renewable and potentially profitable energy source.

Wastewater Elimination

The ZLD system successfully eliminated wastewater production, reducing environmental impact and associated waste treatment costs.

Energy Consumption and Production

The implementation of the ZLD system requires a minimum electrical consumption of 74,885.91 kWh per day. By integrating renewable energy sources, particularly solar energy with a capacity of 4 kW per cell and a solar energy period of 8.18 hours per day, it is possible to reduce dependence on fossil fuels and lower operational costs.

III.5. Optimization of the ZLD Scheme

Potential Improvements

- **Enhanced Pretreatment:** Adding new pretreatment processes, such as adsorption or coagulation, could improve feed water quality and extend the lifespan of RO membranes.

- **Integration of Renewable Energy Sources:** A deeper analysis of integrating solar and wind energy could demonstrate a more significant reduction in fossil fuel dependence and enhance system sustainability.

Life Cycle Analysis (LCA)

Conducting a full LCA of the proposed ZLD system would quantify the environmental impacts across the entire life cycle, from raw material extraction to waste management.

Economic Evaluation

A detailed economic analysis, including installation, operation, and maintenance costs, as well as savings from hydrogen production and reduced waste treatment costs, would provide a comprehensive view of the system's viability.

III.6. Future Perspectives

Emerging Technologies

Exploring the integration of emerging technologies, such as low-fouling membranes or membrane distillation processes, could offer substantial improvements.

Scalability

Studying the scalability of the system for larger treatment capacities or other types of brackish water could demonstrate the flexibility and adaptability of the proposed scheme.

IV. Conclusion

In this study, a conceptual Zero Liquid Discharge (ZLD) scheme has been proposed for the treatment of brackish water using a Reverse Osmosis (RO) membrane unit. The model incorporates splitting the brine reject from the RO unit into an electrolyser and an evaporator, thereby reducing the salt concentration of the recycle streams returning to the RO unit. Model equations have been developed to describe the performance of individual components within the ZLD scheme. This conceptual model can be utilized to analyze the sensitivity of the scheme's performance to various operational parameters.

The model was tested on an RO system capable of producing 792 cubic meters per day of fresh water from brackish water with a salt concentration of 4,660 ppm, with an RO recovery rate of 66%, the model demonstrated a reduction in the brackish water withdrawn from the well, decreasing from 1,200 cubic meters per day to 871.52 cubic meters per day, which represents a 27% reduction. These findings indicate the potential effectiveness of the proposed ZLD scheme in improving the efficiency of brackish water treatment.

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