PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH BLIDA 1 UNIVERSITY

FACULTY OF TECHNOLOGY

DEPARTMENT OF PROCESS ENGINEERING



Thesis To obtain the Master's degree in Process Engineering

Specialty: Chemical Engineering

Theme

Modeling and optimization of desalination technologies used in refineries.

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Acknowledgements

This thesis isn't merely the product of academic effort, but a reflection of a journey filled with perseverance, growth, and silent battles that I have overcome.

First and foremost, I offer my deepest gratitude to **Allah**, who supported me with His guidance and strength in every moment of doubt and uncertainty. Without this silent presence, I would not have made it this far.

To my supervisor, **Dr. DADOU.S**, and to the engineer who oversaw my work at the Algiers refinery, **Mr. RECHIDI.Y**, thank you for your support, insightful guidance, and patience. Your trust in my abilities gave me the space to explore, learn, and push beyond limits.

I extend my sincere thanks and appreciation to all my professors at the university, who played a vital role in both my academic and personal journey. From you, I learned more than just academic lessons. I learned values of commitment, diligence, and a love for knowledge. Thank you for all your efforts, your support, and your constant encouragement. You have my deepest respect and appreciation.

All my gratitude goes to the best teacher - the one who made me love mathematics. You didn't just teach me the subject, but also offered me valuable lessons in life. Professor **KHEMACHE.F**, I am forever grateful to you.

Thank you to the one who helped me learn the language and opened doors to understanding and communication. Your support made a difference in my journey and personal growth. You have my heartfelt thanks.

To my parents - thank you for your sacrifices, your prayers, and your belief in me. To my mom **ABBAD.K**, your quiet strength and patience have taught me more than words ever could.

To my beloved dad M, my first teacher and steadfast supporter - your warmth and encouragement were my refuge in moments of fear. Your words and advice continue to light my path.

To my sister **N**, who has been a second mother and a close friend - your love has always been a source of comfort and peace. To those who have stood by me when life felt uncertain, and to those who were my safe haven when the world felt heavy - **My siblings** and small, cherished family - you are a precious gift fromAllah. For every kind word, every piece of advice, and every moment of patience and love... thank you from the bottom of my heart. I pray that Allah protects you and keeps us united in love and goodness.

To those who doubted me, and to the challenges that nearly broke me - thank you. You helped shape a stronger, wiser, and more determined version of myself.

To **my friends** - thank you for being part of my days, in joy and sorrow, in exhaustion and success. Thank you for every laugh we shared, every moment of honesty and loyalty. You hold a permanent place in my heart and a fond memory that will never fade. I pray that our bond remains strong and that we are always united in goodness.

And finally, to the younger version of myself - the one who felt lost, afraid, and not enough - you made it. You turned pain into purpose, fear into passion, and dreams into reality. This thesis is dedicated not only to knowledge but to the soul behind the struggle - to you, \mathbf{H} .

ملخص

تقع وحدة إزالة الأملاح أمام برج التقطير. تُعد إزالة أملاح النفط الخام عملية معالجة أولية بالغة الأهمية في نكرير البترول. وتهدف إلى تقليل محتوى الأملاح والشوائب المصاحبة لها لمنع التأكل والتلوث وتعطيل المحفز في وحدات التكرير. يركز هذا البحث على نمذجة وتحسين تقنيات إزالة الأملاح. وقد تم تطبيق منهجية إحصائية تستند إلى تصميم بوكسب بيهنكين باستخدام برنامج 13 JMP لفحص تأثير ثلاثة عوامل: انخفاض الضغط عبر صمام الخلط، ومستوى واجهة الزيت والماء، ومعدل تغذية النفط الخام. وأظهرت النتائج أن معدل تغذية النفط الخام كان العامل الأكثر تأثيرًا، بقيمة احتمالية قدر ها 20,0002. وتم تحقيق أقصى كفاءة لإزالة الأملاح بنسبة 95.56% عند أدنى معدل تغذية النفط الخام (460) مثر مكعب/ساعة)، وأعلى مستوى لواجهة الزيت والماء (46%)، وأقل انخفاض للضغط عبر صمام الخلط (0.1 بار). وتسمح هذه النتائج باقتراح ظروف تشغيل مثالية لتحسين جودة النفط الخام المعالج وإطالة عمر المعدات اللاحقة.

الكلمات المفتاحية: محتوى الملح، تحلية، النفط الخام، المستحلب، التآكل.

Abstract

The desalting unit is located in front of the distillation tower. Crude oil desalting is a critical pretreatment process in petroleum refining. It aims to reduce the content of salts and associated impurities to prevent corrosion, fouling, and catalyst deactivation in refining units. This research focuses on modeling and optimizing desalting techniques. A statistical methodology based on the Box-Behnken design was applied using JMP13 software to examine the influence of three factors: pressure drop across the mixing valve, oil-water interface level, and crude oil feed rate. The results showed that the crude oil feed rate was the most influential factor, with a p-value of 0.00002. The maximum desalting efficiency of 95.76% was achieved at the lowest crude oil feed rate (460 m³/h), the highest oil-water interface level (46%), and the lowest pressure drop across the mixing valve (0.1 bar). These results allow for the proposal of optimal operating conditions to improve the quality of the processed crude oil and extend the life of subsequent equipment.

Keywords: Salt content, Crude oil, Desalting, Emulsion, Corrosion.

Résumé

L'unité de dessalage est située devant la tour de distillation. Le dessalage du pétrole brut est un procédé de prétraitement essentiel dans le raffinage du pétrole. Il vise à réduire la teneur en sels et impuretés associées afin de prévenir la corrosion, l'encrassement et la désactivation des catalyseurs dans les unités de raffinage. Cette recherche se concentre sur la modélisation et l'optimisation des techniques de dessalage. Une méthodologie statistique basée sur le modèle Box-Behnken a été appliquée à l'aide du logiciel JMP13 pour examiner l'influence de trois facteurs : la perte de charge à la vanne de mélange, le niveau de l'interface huile-eau et le débit d'alimentation en pétrole brut. Les résultats ont montré que le débit d'alimentation en pétrole brut était le facteur le plus influent, avec une valeur-P de 0,00002. L'efficacité maximale du dessalage de 95,76 % a été atteinte au débit d'alimentation en pétrole brut le plus faible (460 m³/h), au niveau de l'interface huile-eau le plus élevé (46 %) et à la perte de charge la plus faible à la vanne de mélange (0,1 bar). Ces résultats permettent de proposer des conditions de fonctionnement optimales pour améliorer la qualité du pétrole brut traité et prolonger la durée de vie des équipements ultérieurs.

Mots clés: Teneur en sel, Dessalage, Pétrole brut, Émulsion, Corrosion.

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List of abbreviations

AC: Alternating Current.

ADU: Atmospheric Distillation Unit.

ANOVA: ANalysis Of VAriance.

API: American Petroleum Institute.

ASTM: American Society for Testing and Materials.

BBD: Box-Behnken Design.

BFW: Boiler Feed Water.

BS&W: Basic Sediment and Water.

CD: Direct Current.

CFR: Cooperative Fuel Research.

Cp: Capacity.

CPP: Clean Production Plant.

CPU: Condensate Polishing Unit.

ECS: Electrical Control System.

ETP: Effluent Treatment Plant.

GTG: Gas Turbine Generator.

ppm: Parts Per Million.

Psi: Pound per Square Inch.

PTB: Pounds of salt per Thousand Barrels of crude oil.

RMSE: Root Mean Square Error.

RSM: Response Surface Methodology.

RVP: Reid Vapor Pressure.

STG: Steam Turbine Generator.

Introduction

Introduction

Petroleum refining is a heavy industry that transforms crude oil into a range of energy products such as fuels and combustibles, and non-energy products such as petrochemical feedstocks, paint solvents, oils, greases, paraffins, waxes, and bitumens. A refinery consists of several production units. These devices employ physical or chemical methods that fall into three distinct categories: separation, transformation, and refining. A refinery also includes support units such as utilities, electricity, steam, and hydrogen. Global energy demand is increasing year after year, primarily due to economic and demographic growth. This has led to the world's near-total dependence on its primary energy source, oil. Crude oil must undergo appropriate processing to deliver oil that meets required standards and minimize its impact on oil facilities.

Among the units of the ALGIERS refinery (RA1G), we are interested in our work at the desalter which is located in front of the distillation tower. Desalting is a key pretreatment stage in crude oil refining, and improving this process has become a key area of technological research and development. Its goal is to remove inorganic salts, water, suspended solids, and metals from crude oil before further refining. These contaminants, particularly salts such as sodium chloride, calcium, and magnesium chloride dissolved in water-based emulsions within crude oil, pose significant risks. Efficient desalting ensures equipment protection, reduces corrosion, fouling, and catalyst poisoning, and contributes to overall product quality.

Desalting typically involves mixing heated crude oil with wash water and chemical demulsifiers to loosen and break up the emulsions. This is followed by applying an electric field to coalesce the water droplets, which then gravity separate from the oil. This process can be performed in single-stage or two-stage units. Two-stage desalting provides higher desalting efficiency to meet stringent refinery specifications, often reducing the salt content to less than one PTB.

This project focuses on modeling and optimizing desalting technology, investigating the key variables and mechanisms governing the separation of water and salts from crude oil. The study explores both conventional methods (electrostatic fusion and chemical demulsification) and advanced approaches that integrate process control, energy optimization, and environmental considerations. Particular attention is paid to the influence of operating parameters, such as temperature, wash water dosage, crude oil feed, emulsifier concentration, pressure drop, and oil-water interface level, all of which play critical roles in desalination efficiency.

Introduction

This thesis consists of two main sections: a review of the scientific literature on the one hand, and a statistical analysis of the influencing factors, modeling, and optimization of the desalination process, which leads to energy savings, improved separation efficiency, and reduced environmental footprint, on the other.

We conclude this work with a general conclusion and general perspectives.

PART I
General Overview of the Algiers Refinery and Crude
Oil Desalting Processes

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

I.1. Presentation of the Algiers refinery field

The Algiers refinery is located in Sidi-Arcine near Baraki 5 km from El Harrach and 20 km east of Algiers, nicknamed the dean of Algerian refineries, it was erected on an area of 182 hectares. This location was followed by a floor study and discovering a water table which is necessary for the supply of cooling systems. In addition, the choice of the Algerian region emanated from what was presented as a future pole in industrial development, in addition, it has the advantage of being the largest consumption center with a share of 40% to 50% of domestic demand, and it clearly appears that production from Algiers will be less than coming from other refineries.

Its construction and start -up were carried out by the French company Foster Wheeler, and commissioned in 1964 with:

- ➤ Starting in February of the atmospheric distillation unit with a capacity of 2.7 tons of crude per year.
- > Starting in March of the catalytic reforming unit.

An extension was carried out to be able to reach up to 3.6 million tons of gross treatment per year, meet market demand, and increase the refrigeration capacity of certain equipment.



Figure I.1. Algiers RA1G refinery.

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

The purpose of this filter is the treatment of crude oil from HASSI-MESSOUAD alone or mixed with capacitors from the HASSI-R'MEL fields, in order to obtain oil cuts.

The ability of the treatment of the Algeria refinery increased after rehabilitation. This table will represent the quantities of products expressed in tons per year:

Table I.1: Annual production capacity of the Algiers refinery.

Product	Annual production (tonnes)
Reformat	603333
Isomerate	364333
Naphta (export)	76000
Fuel oil	60000
Propane	69333
Butane	209667
Normal essence	600000
Super essence	757000
RFCC petrol	376000
Kerosene	620666
Diesel	1261667

I.1.1. Main Refinery Facilities

The main installations of the Algiers refinery are

I.1.1.1 Atmospheric Topping Distillation Unit (U100)

Intended to separate the various petroleum products contained in crude oil, it is the mother unit of the refinery (U 100).

I.1.1.2. Liquefied Gas Separation Unit (U300)

The liquefied gas separation and treatment unit for the treatment of the liquid product from the head of the head of the distillation and the repair unit has been dismantled in order to obtain final liquid products: propane and butane. The latter will cross the purification systems that contain a molecular sieve in order to rid them of all the effects of moisture and sulfur products.

I.1.1.3. NHT Naphtha Hydrotreatment Unit (U500)

A naphtha hydrotreating unit allows obtaining different fractions of naphtha free of various compounds such as water, halogens, sulfides, nitrogen, olefins, diolefins, mercury, arsenic, etc Which may affect the efficiency of the catalysts used in the downstream units for the isomerization and CCR reforming process.

I.1.1.4. Naphtha Isomerization Unit (U510)

This unit is used for the isomerization of naphthas, i.e. the transformation of C5 and C6 into their isomers, in order to obtain a high-octane product used in the blending sections to obtain the commercial gasolines produced by the refinery.

I.1.1.5. CCR Catalytic Reforming Unit (U520)

The reforming unit was installed to replace the catalytic reforming unit, as it provides higher efficiency and a high-octane product. Using a catalyst, this unit produces high-octane naphtha for blending into high-octane gasoline.

I.1.1.6. RFCC Catalytic Cracking Unit (U530)

This unit is designed to process one million tons per year from the atmospheric residue obtained in the atmospheric distillation unit (unit 100) using a high-temperature catalytic cracking process.

I.1.7. Block Sulphide Section.

Comprises four units:

- Acid gas treatment unit (fuel gas) with Amine (U560).
- Acid water stripping unit (U570).
- Amine regeneration unit (U580).
- > Sulfur recovery unit (U590).

I.1.1.8. Utilities

Consist of the following units:

Raw water unit (U 701)

This unit receives raw water from drilling wells located within the refinery and can be supplied with SEAL water through a pipeline. Raw water unit 701 distributes water to the various refinery users.

➢ Cooling Towers (U 710/711)

This unit supplies cooling water to users within the refinery and is fed by raw water unit 701.

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

> Demineralized Water Unit (U 720)

This unit receives raw water from raw water unit 701 located within the refinery and treats this water to convert it into demineralized water.

> Firefighting Water Unit (U 741).

➤ Unit 751

The steam and boiler feed water systems are part of the new facilities for the Algiers refinery and are designated CPP 751 (clean production plant, or power plant dedicated to the production of electricity for own consumption). This unit is designed to supply steam to consumers in the process unit facilities and to produce high-quality boiler feed water (BFW) used internally by the new boilers and supplied as high-pressure (HP) BFP to various units in the refinery. In addition, the complex is equipped with a gas turbine generator (GTG) and a steam turbine generator (STG), connected to the electrical control system (ECS), which cover the electrical needs of the entire refinery.

> Air Production Unit (U 781)

Compressed air is required in the refinery for multiple purposes, such as operating the instruments used in the facility and purging certain control panels. And as compressed air for fire hydrants, catalytic regeneration, furnace decoking, etc.

> Flare (U 791)

The flare system safely collects and removes gaseous hydrocarbon discharge streams from the Algiers refinery, as well as any liquids entrained or condensed within the flare lines.

➤ Nitrogen Production Unit (U 810)

This unit consists of a gaseous and liquid nitrogen production unit with associated liquid nitrogen storage and vaporization facilities.

Condensate Polishing Unit (U 830)

Installed within the new fluids units of the Algiers refinery, it consists of a centralized treatment facility for polluted condensates generated by various refinery-processing units. The purified condensate from the CPU unit (U 830) is returned downstream to the deaerator of the new CPP unit (U 751).

Caustic Soda and Hydrochloric Acid Unit (U 840)

The caustic soda system is designed to meet the refinery's requirements.

➤ Effluent Treatment Unit (U 850)

The purpose of this unit is to treat all wastewater generated by refinery operations in the new Effluent Treatment Plant (ETP).

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

I.1.1.9. Storage Park

Comprising 53 cylindrical tanks with a total capacity of 474,500 m³ for the storage of various products and 9 spherical tanks with a capacity of 15,106 m³ for the storage of propane and butane.

I.1.1.10. Laboratory

The laboratory conducts a series of standard tests on various intermediate and finished products to ensure compliance with petroleum product specifications according to applicable standards. It also plays a key role in detecting process anomalies and optimizing operating parameters. The laboratory belongs to the Technical Sub-Directorate and is composed of two departments:

> Shift control department

Is responsible, as its name suggests, for monitoring product quality during operations. It performs several types of analyses, including distillation (to determine the initial and final boiling points of petroleum cuts), density measurement, and verification of the freezing point, cloud point, and flash point of diesel, kerosene, and/or Jet A-1. It also measures the conductivity of kerosene and/or Jet A-1, verifies the color of certain products, and determines the fuel index using a Cooperative Fuel Research (CFR) engine.

> Finished products department

Is in charge of conducting qualitative and quantitative analyses on various finished products as well as on process water.

I.1.2. Refinery's distillation unit

The Atmospheric Distillation Unit (ADU) in a refinery is the parent unit that performs the primary separation of crude oil to produce direct distillate blends (after appropriate downstream processing) and feedstocks for other downstream processing units.

The products of the distillation unit are:

- Light ends (off-gas and LPG) for feeding the gas plant unit.
- Total naphtha for feeding the naphtha hydrotreating (NHT) unit.
- ➤ Kerosene for storage.
- Light gas oil for storage.
- ➤ Heavy gas oil and atmospheric residue for feeding the unit.

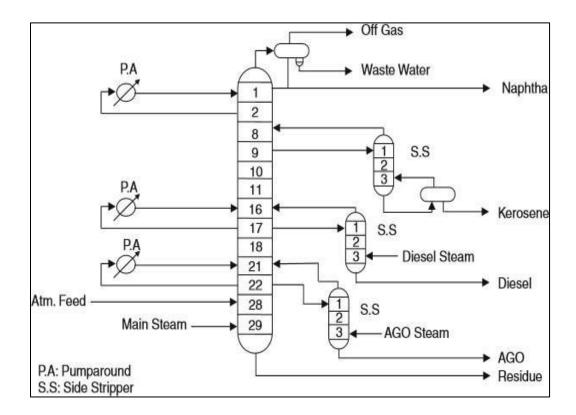


Figure I.2. Schematic of the atmospheric distillation process.

The Atmospheric Distillation Unit (ADU) includes various stages, such as preheating, evaporation, and fractionation. This study will not cover the entire distillation process in detail, but will focus on the desalting unit and the stage immediately preceding it, the first section of the preheating train, as it is directly related to the goal of improving desalting of crude oil.

Crude Feed and Preheat Train I

Crude oil from off-site storage is received at the Atmospheric Distillation Unit (ADU) plant zone boundary at atmospheric pressure and 27°C at the crude feed pump suctions in the zone boundary (100-P-101 A/B/C/D), where the crude oil is pumped to the desalter under pressure control. Pressure control at the desalter outlet maintains the crude oil with free water in the liquid phase at operating temperature. Crude Preheat Train I consists of 100-E-501 A/B crude overhead/pre-vaporizer exchangers (two jackets in parallel) and 100-E-101 A-F crude/top RC exchangers with two x three jackets in series. The preheated crude is sent to the desalter to remove salts and water. The purpose of the initial heat exchanger is to heat the crude stream (to reduce its viscosity) to the desired desalter inlet temperature of approximately 101°C.

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

> Desalter

The desalter tank (100-M-101) is designed to remove salts and water from crude oil to the desired level. The desalter tank is designed to handle an inlet salt content of 72 ppmw with a water-soluble chloride removal efficiency of 95% to obtain 3.6 ppmw of salt in the desalted crude. According to the design performance, the insoluble aqueous phase (water and basic sediment) in the desalted crude oil, at operating temperature, will not exceed 0.2% by volume (predicted <0.1% by volume). The principle of the desalter operation requires mixing the preheated wash water and the preheated crude in the mixing valve (enabling homogeneous emulsification of the oil/water mixture) and extracting impurities. The degree of emulsion is adjusted and controlled by means of differential pressure control. The water/crude mixture is then decomposed by coalescence in a high-voltage electric field and then separated in the desalter. Sufficient pressure is maintained at the desalter to ensure that the crude oil remains in the liquid phase and that no vaporization takes place. For this purpose, a pressure control valve is placed at the discharge of the crude feed pump (100-P 101 A/B/C/D). And to promote the dehydration and salt removal efficiency of the desalter and improve the oil content in the water effluent, a demulsifying chemical is pumped through 100-P-125 A into the drum 100-D-115 and is injected at the suction of 100-P-101 A/B/C/D.

I.2. Overview of crude oil

Crude oil is a liquid composed primarily of hydrocarbons and water, and contains organic compounds such as sulfur, oxygen, and nitrogen. It also contains varying amounts of inorganic salts, such as sodium chloride, calcium chloride, and magnesium chloride. The salinity of the latter is limited to 40 mg/L, and basic sediment and water (BS&W) is less than 1%. These salts can cause various challenges during crude oil processing, including corrosion, equipment clogging and fouling, and catalyst poisoning in processing units. For this reason, advanced technologies and ongoing research are being used to remove salts and water from crude oil. The goal is to save processing facilities and improve the selling price per barrel. To achieve this goal, these contaminants must first be removed through desalination (dehydration), which involves washing the crude oil with clean water and then removing the water, resulting in dry, low-salt crude oil.

I.2.1. Composition of crude oils

Crude oil, also known as hydrocarbons, is classified into two groups: hydrogen and carbon, which are the essential components of all crude oils.

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

Their contents range from 83% to 87% for carbon and from 11% to 14% for hydrogen. These two elements form the three main hydrocarbon families:

- Aliphatic.
- Cyclic.
- Mixed Hydrocarbons.

Crude oil also contains other elements, more or less harmful for its processing or the use of finished petroleum fractions. These elements are oxygen, sulfur, and nitrogen (up to 6% to 7%) in the form of compounds. In addition, the presence of other compounds such as Cl, I, P, As, Si, Na, and Iron has been detected by hydrocarbon ash analysis.

I.2.2. Physicochemical properties of Algerian Crude Oil

> Density

Density is defined as the ratio of the mass of a body to the volume it occupies.

For petroleum products, Density varies depending on the specific crude sample; heavier crude oils show higher density. Algerian light crude from Hassi-Messaoud has an API gravity of 45°, corresponding to a specific gravity of approximately 0.80 g/cm³ [1].

Viscosity

Algerian crude oils exhibit non-Newtonian pseudoplastic behavior with viscosity decreasing significantly with temperature [2]. It is determined by measuring the flow time of crude oil in the capillary tube of given length, at a well-defined temperature [3], and it's About 2.23 Cp at 40 °C, showing relatively low viscosity suitable for easier flow [2]. Viscosity is sensitive to shear rate and temperature, with heavier components like asphaltenes and waxes contributing to higher viscosity at lower temperatures [2].

➤ Reid Vapor Pressure (RVP)

It's the vapor pressure produced at 100°F (37.8°C) by a specific volume of crude oil. The measurement of Ried vapor pressure (RVP) is standardized (NF M07-007 or ASTM D323), and its value is given in either PSI or g/cm2. The light hydrocarbon content of crude oils can be estimated by measuring their Ried vapor pressure (RVP).

> Pour point

The lowest temperature at which a crude oil flows (remains fluid) under test conditions is known as its pour point. This test's objective is to determine how much petroleum wax, or long-chain paraffinics, is present in the crude oil. Crude oils typically have a pour point between -60° C and $+30^{\circ}$ C.

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Note: knowing the pour point is important for determining crude oil pumping conditions in winter [5].

> Sulfur content

With its unpleasant odor, sulfur is a pollutant that refiners must remove; therefore, the presence of sulfur in petroleum decreases its value [5]. Determining the sulfur content of petroleum products is governed by three methods: - Combustion sulfur determination method: ASTM D 129. - Hydrogenation sulfur determination method: ASTM D 4045. - Fluorescence sulfur determination method [4].

> Salt content

This indicates how much salt is dissolved in the water in the crude oil and is measured in milligrams of sodium chloride (NaCl) per liter of crude oil or pounds/barrel of crude oil. Serious corrosion issues are caused by crude oil's high salt content. Desalting is usually necessary when the NaCl level is greater than 10 lb/1000 barrels or greater than 28.6 mg/L. (1 barrel = 159 liters, 1 pound = $4.54.10^{-1}$ kg) [5].

➤ Content of Basic Sediment and Water (BS&W)

Fine sand particles, drilling mud, rock fragments, and metal ores like copper, lead, nickel, vanadium, etc. are examples of sediments that can be detected in crude oil. Operators and refiners must be aware of the water and sediment content in crude oils to prevent equipment damage (corrosion, erosion, deposits, clogging, etc.). By measuring the amount of water and sediment that is removed from the crude oil through centrifugation, a standardized method (NF M07-020; ASTM D 96 and D 1796) is used to determine BS&W content of crude oils [4].

I.3. Fundamentals related to desalting

I.3.1. General Overview of salts

Salt comes from two main sources: seawater, and the sodium chloride mineral halite (also known as rock salt). Rock salt occurs in vast beds of sedimentary evaporite minerals that result from the drying up of enclosed lakes, playas, and seas [6]. In chemistry, a salt is an ionic compound of cations and anions forming a neutral product with no net electric charge. The most common type of salt is sodium chloride (NaCl), which is composed of positively charged sodium ions (Na+) and negatively charged chloride (mineral) ions (Cl⁻).

Other examples of salts include potassium chloride (KCl), calcium chloride (CaCl $_2$), and magnesium sulfate (MgSO $_4$) [7].

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

The salt present in crude oil usually exists as salt crystals dissolved in the water that is emulsified within the oil, with the primary components being sodium calcium and magnesium chlorides [8]. The presence of these salts during the transformation of crude oil causes certain problems, such as corrosion problems, plugs and connection and equipment deposit [10]. The hydrolysis of magnesium and calcium chloride salts at high temperatures (over 110°C) produces hydrochloric acid (HCl), which is what causes corrosion in heat exchangers and distillation columns. Additionally, this corrosion becomes extremely hazardous when hydrogen sulfide (H₂S) is present. The following steps provide a summary of the primary reactions:

Hydrolysis of salts

$$CaCl2 + 2H2O \rightarrow Ca(OH)2 + 2HCl$$
 (eq I.1)

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$
 (eq I.2)

Corrosion

Corrosion caused by the condensation of HCl vapors (HCl in aqueous solution) especially at the top of the column and in the head condensers where the iron is attacked by these vapors as follows:

$$2HCl + Fe \rightarrow Fe^{2^{+}} + 2Cl^{-} + H_{2}$$
 (eq I.3)

Presence of (H₂S)

This corrosion becomes even more significant.

$$H_2S + Fe \rightarrow FeS + H_2$$
 (eq I.4)

In presence of (H_2S) , (HCl) produced by (eq I.1) and/or (eq I.2) reacts with (FeS) formed by (eq I.4) as follows:

$$2HCl + FeS \rightarrow Fe^{2+} + 2Cl^{-} + H_2S$$
 (eq: I.5)

Reproducing (H₂S) by reaction (eq: I.5) feed's reaction (eq I.4) and increases corrosion [11].

General Overview of the Algiers Refinery and Crude Oil Desalting Processes



Figure I.3. Salt crystal magnified [6].

I.3.2. General overview of emulsions

Emulsion plays a role in oil-water mixtures, especially in crude oil, and is a major obstacle to the separation process [12]. An emulsion is a heterogeneous liquid system consisting of two immiscible liquids, where one liquid is intimately dispersed as droplets in the other (diameter generally bigger than $0.1~\mu m$). In the context of the petroleum industry, emulsions typically involve crude oil and water or brine. The most common type of emulsion encountered in crude oil production is the water-in-oil emulsion, also known as a "normal" emulsion [13], where water droplets are dispersed in the continuous oil phase. While oil-in-water (O/W) emulsions, inverse emulsions, are less common [14][15].

***** Types of emulsions

One of the main challenges that are often faced during the production and transportation of crude oil in the petroleum industries is the formation of very complex and stable emulsions with salt water. There are three main types of emulsions. A two-phase emulsion consists of one continuous phase and one dispersed phase, whereas a three-phase emulsion includes one continuous phase and two dispersed phases.

1. Water-in-oil (W/O)

Emulsion characterized by water droplets dispersed in an oil phase [16].

2. Oil-in-water (O/W)

Emulsion that consists of oil droplets dispersed in an aqueous phase [16].

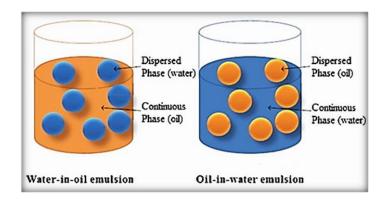


Figure I.4: Water in Oil and Oil in Water [44].

3. Multiple phases

Comprise three phases [16]

3.a. Oil-in-water-in-oil (O/W/O)

Emulsions are recommended for fuel preparation.

3.b. Water-in-oil-in-water (W/O/W)

Emulsions are recommended for pharmaceutical field.

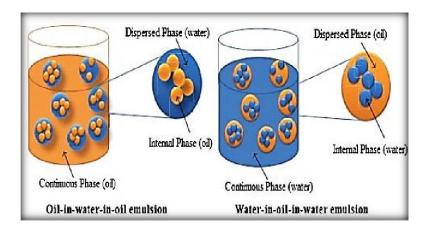


Figure I.5: Multiple phases [16].

A major challenge in the petroleum industry is the high-water content that accompanies crude oil extraction, compounded by water injection during processes like desalting and steam treatment. Schubert and Armbruster identified three main reasons for emulsion formation:

- > Interaction of immiscible fluids.
- > Presence of emulsifying agents.
- > Diffusion of one liquid into another due to turbulence [12][17].

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

***** Consequences of emulsion formation

- ➤ Raise transportation and pumping costs.
- ➤ Cause corrosion, and damage processing plant catalysts.
- > Increase fluid viscosity.
- ➤ Complicate separation processes, and affect the overall efficiency of oil production and transportation [18].

❖ Three key conditions for stable emulsions formation

- Interaction between two immiscible fluids, for example, oil and water.
- Existence of emulsifying agents inside the crude oil such as asphaltenes and resins, and organic acids.
- > Sufficient turbulence flow and energy for dispersion.

These agents form a barrier at the water in oil interface, preventing droplet coalescence [19].

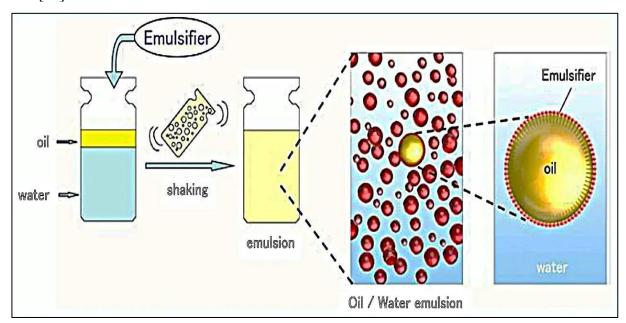


Figure I.6: Process of forming an emulsion [20].

❖ The role of emulsions in crude oil processing

a. Stabilizes the mixture

- Normally, oil and water separate quickly due to differences in density [21].
- Asphaltenes, resins and naphthenic acids in crude oil work as emulsion factors, stabilize the tiny water droplets and preventing them from coalescing and settling out [21].

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

b. Makes separation harder

- This stable emulsion prevents efficient gravity-based separation [21].
- ➤ It increases the residence time and energy requirements in separation equipment such as desalinates and electrostatic treatments [21].

c. Increases processing cost

Emulsions can cause corrosion, scaling, and fouling in downstream equipment [21].

d. Affects quality

- Residual water or salt in the oil (due to poor separation) can affect refinery efficiency and product quality [21].
- In order to remove them, the use of emulsifying chemicals, heat, or electrostatic fields is required [21].

❖ Techniques for breaking emulsions in crude oil

As previously mentioned, the presence of water in crude oil causes significant damage to equipment used in refining processes [20]. To separate water from crude oil, the emulsion must be destabilized. This is accomplished using a combination of Chemical, Electrical, Mechanical, and Thermal techniques [22]. We combine demulsifier chemical and an electrical system. Using a chemical agent capable of breaking the emulsion (A proper demulsifier chemical program is to be implemented and optimised by field-testing) [11]. In another process, we also apply a high-voltage electrical system (The Electrical System for each Desalter is composed of three (3) Power Units, each sized at 50kV with primary power of 380V– Single Phase 120 (Phase to Phase) - 50Hz. The Total Power Installed per desalter vessel is 3 x 50kVA = 150kV) [23], by which small adjacent water droplets converge to form larger droplets that settle under the effect of gravity. [20]. Temperature plays a role in this. When the temperature rises, the viscosity of the oil decreases, which helps accelerate the droplet collision and coalescence. Since the two resulting liquid phases are immiscible, the oil phase, having the lower specific gravity or density, rises to the top of the tank whereas the water being of higher density gravitates towards the bottom of the tank. Therefore, separation of the two liquids after de-emulsification is generally readily accomplished [24].

I.4. Desalination of crude oil

Raw oil contains different impurities, including inorganic salts, water, water and suspended solid materials, which constitute great operational challenges such as corrosion, pollution, and expansion of the stove strainer equipment.

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

These pollutants should be removed before treatment by a separation step known as desalination. Desalination can be performed in one stage or two phases, depending on the requirements of the process. Drought efficiency is usually inspired by 95 % in one stage and up to 99 % in two phases. In general, this invention device includes a stable vessel typically for cylindrical or spherical [23].

I.4.1. Purpose of desalination of crude oil

The primary purpose of desalination of crude oil as mentioned earlier is to remove salt and other impurities from oil before it is subject to more refining operations. Here are the main reasons that make desalination of water important:

I.4.1.1. Protection of equipment

Exhaustion and salts in crude oil contain materials that lead to erosion and damage to equipment, such as pipelines, pumps and refining units. The oil desalination process contributes to maintaining these valuable assets by removing corrosion elements [25][26].

I.4.1.2. Refinery efficiency

The presence of salt and impurities can disrupt the refining process, resulting in operational challenges and decreased efficiency. Desalination enhances the quality of crude oil before it enters the refining units, facilitating smoother operations and increasing the yield of refined products [25][27].

I.4.1.3. Product quality

Desalination enhances the quality of refined products. Sodium in atmospheric residue poisons catalysts in downstream units (e.g., fluid catalytic crackers) [28], and the quality and performance of fuels, lubricants, and other petroleum products. By eliminating salt and impurities, desalination improves the specifications and performance attributes of the final product. Failure to meet commercial specifications (BS&W <1%, salinity <40 mg/L) incurs penalties and limits marketability [29][25].

I.4.1.4. Environmental considerations

Desalination lowers the salt concentration in the wastewater produced during the refining process, making it safer for disposal or treatment [31]. Overall, desalination plays a crucial role in ensuring the integrity of equipment, optimizing refinery operations, improving product quality, and minimizing environmental impacts associated with crude oil refining [25][30].

I.4.1.5. Fouling and Corrosion

Salts like Ca, Mg, and NaCl hydrolyze in distillation columns, forming corrosive hydrochloric acid (HCl) that damages overhead systems [32].

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

Suspended solids and salts deposit in heat exchangers and furnaces, reducing thermal efficiency and increasing maintenance costs [25][33].

I.4.1.6. Hydrocarbon entrainment in wastewater

Inefficient dehydration causes oil-in-water emulsions, resulting in hydrocarbon losses (environmental contamination) and higher wastewater treatment costs [25].



Figure I.7: Example of corrosion on a refinery distillation tray [34].

I.4.2. Process of desalination

The crude oil desalination process depends on three main stages:

I.4.2.1. Salt Diffusion: Transfer of salts from the crude to the wash water

The first step involves promoting the migration of dissolved salt crystals present in the crude oil into the wash water. The objective is to maximize the solubilization of all the salts contained in the oil. To achieve this, the crude oil is thoroughly mixed with water via a mixing valve located at the inlet of the desalter. This intensified contact is often assisted by the controlled injection of additional water [35].

I.4.2.2. Coalescence of micro-water droplets

Water droplets are very fine, ranging in diameter from 1 to 10 μ m, which prevents them from settling under gravity. Coalescence produces larger droplets that can be settled under gravity. This is achieved under the influence of an intense electrostatic field. The aligning of the dipoles of the water molecules promotes the gradual coalescence of the droplets.

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The attractive force \mathbf{F} between two droplets in a continuous non-conductive hydrocarbon phase (crude oil) is expressed by the formula [35][23]:

$$\mathbf{F} = \frac{KE^2r^6}{d^4} \tag{eq I.6}$$

Where

r: Diameter of droplets (dependent on the degree of mixing).

d: Distance between 2 droplets (dependent on the degree of mixing and quantity of water added)

E: Potential gradient between electrodes.

K: Proportional factor.

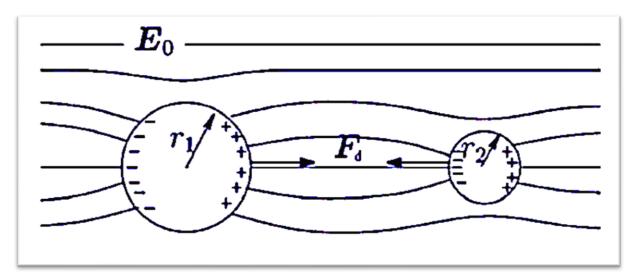


Figure I.8: The attractive force F between two droplets [36].

It follows that coalescence is influenced by:

- > The electric field strength.
- > The injected wash water rate.
- > The temperature of the desalting process.

I.4.2.3. Settling phase

According to Stock's law the settling rate of the water droplets after coalescence is given by [39]

Settling rate =
$$\frac{k(\rho eau - \rho oil)d^2}{\mu oil}$$
 (eq I. 7)

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

Where

 ρ : the density.

 μ : the viscosity.

d: the droplet diameter.

K: a constant.

I.5. Desalting technologies

Crude oil desalting technologies are critical for removing salts and impurities from crude oil before refining. There are several methods used for crude oil desalination. Below is an overview of key desalting methods [40].

I.5.1. Chemical desalting

Chemical demulsifiers are added to destabilize water-oil emulsions, facilitating the separation of water droplets from crude oil. It is effective to break stable emulsions, particularly in heavy or waxy rocks. High chemical use increases operational costs, as well as liquid waste that contains chemicals that require additional treatment before disposing of them [25][41].

I.5.2. Thermal desalting

Crude oil is heated to reduce its viscosity and improve the dissolution of salts in wash water. Effective for treating heavy crudes with high impurity levels. But it consumes a lot of energy due to the high temperature requirements (100-150°C) [25][41].

I.5.3. Two stage desalting systems

Crude oil undergoes two successive desalting stages to improve the desalting process (salt levels less than 0.3 PTB). Its advantages include superior desalting efficiency compared to single-stage systems and reduced corrosion risks in subsequent equipment caused by residual salts. However, it consumes high energy due to heating requirements (approximately 120-150°C), in addition to increased complexity and maintenance requirements [25].

I.5.4. Steam-Assisted desalting

Steam is injected into the crude oil-water mixture to improve salt dissolution and separation efficiency. Its advantages include: Effective in removing hard-to-recover salts from heavy crude oil. It also reduces residual salt content at minimal additional cost when integrated into existing systems. However, the process is energy-intensive and requires high-pressure steam systems (e.g., 100 psi) [25].

I.5.5. Electrostatic desalting

An electric field (Alternating Current (AC) or Direct Current (DC)) is applied to a crude oilwater emulsion to promote droplet coalescence and separation.

Electrostatic forces polarize the water droplets, causing them to coalesce into larger droplets that settle by gravity. This technique requires precise control of electrical conductivity and field strength to achieve optimal performance. It is highly efficient at separating fine water droplets ($<10~\mu m$). It also reduces reliance on chemical demulsifiers compared to chemical desalting alone. A drawback is that it is susceptible to coarse film formation, which can disrupt processes [25].

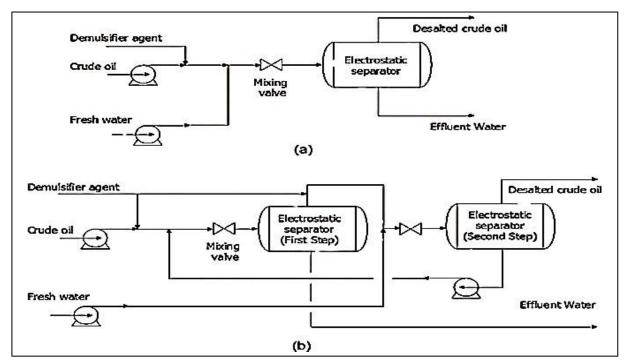


Figure I.9: Desalting process flow diagrams: (a) one-step and (b) two-step [39].

I.6. Electrostatic desalting process

Technically, the desalting process operates by injecting washing water and a chemical (demulsifier) into the crude oil stream, followed by electrostatic coalescence by using electrical desalting vessel, which promotes the agglomeration and separation of water droplets containing dissolved salts like chlorides, sulfates, and carbonates.

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

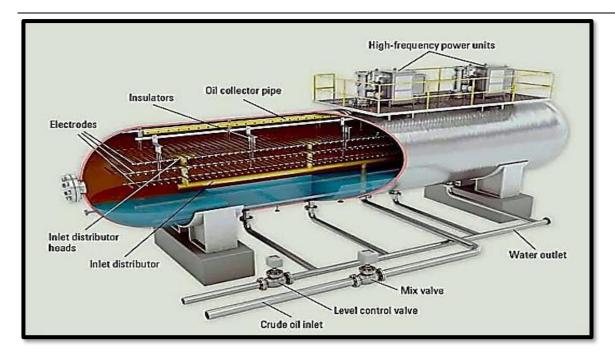


Figure I.10: Main components of an electrostatic desalter system [36].

I.6.1. Process Steps

Electrical desalter is the typical method of crude oil desalting. After separation by gravity settling, crude oil can be desalted by following the steps:

1. Preheating crude oil

Crude oil is preheated to temperatures between 98 - 130°C to reduce viscosity and surface tension, improving fluidity and phase separation. High preheating also destabilizes water-in-oil emulsions and increases their reactivity, facilitating subsequent steps.

2. Mixing crude oil with wash water and a demulsifier

Typically, 2.5-12% by volume of fresh water is injected to dilute the brine and dissolve the salts. In addition to the wash water, a chemical demulsifier (e.g. a surfactant) is injected to destabilize the emulsion by reducing the interfacial tension between the oil and water phases (disrupting the stable film around the water droplets and allowing them to coalesce and aggregate).

3. Emulsion formation

The mixture is passed through a mixing valve to form a homogeneous water-in-oil emulsion, ensuring contact between the wash water and the loaded salts.

4. Electrical coalescence in the desalter

The emulsion is introduced into an electrical desalter, where an AC or DC electric field typically ranging from 500 to 1,000V is applied.

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This electric field facilitates the separation process through two key mechanisms:

a. Droplet polarization

The electric field induces polarization of the water droplets, causing them to align and attract oppositely charged neighbors. This results in the formation of larger coalesced droplets.

b. Electrophoretic migration

Water droplets are also driven toward the electrodes due to their charge, promoting further collisions and coalescence.

5. Gravity separation (Settling)

Coalesced water droplets, being denser, settle at the bottom as brine under the influence of gravity, while the lighter desalted oil rises to the top.

6. Discharge and post-treatment

a. Desalted oil

Exits the desalter unit with a significantly reduced salt content, typically less than 3 mg/L, making it suitable for downstream refining processes.

b. Brine wastewater

Withdrawn from the bottom of the desalter, this stream contains removed salts, residual hydrocarbons, and suspended solids. It is directed to appropriate treatment systems for purification and safe disposal or reuse.

I.6.2. Electrical desalter unit elements

Main components of a single-stage electrolytic desalting unit and their functions, based on technical specifications from refining systems [25].

➤ High-Frequency Power Unit

This power-transforming unit, which is affixed on top of the desalter, generates a high-frequency voltage in the water-oil mélange to facilitate waterdrop coalescence.

Oil Collector Pipe

Following the separation of water and oil. On top of the emulsion, a distinct layer of oil develops and is collected by an oil collection pipe. It is situated in the desalter's uppermost section.

> Insulators

These desalter pieces shield electrodes from other desalter components.

Electrodes

An oil-water mixture's electrodes distribute the power that is transmitted from the transformer.

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> Inlet distributor

The main header pipe connected to the Inlet distributor heads.

> Inlet distributor heads

These are branches that distribute oil water emulsion into the desalter tank from the inlet distributor header.

> Crude oil inlet

This is the piping system that allows crude to enter in the Inlet distributor header.

➢ Mix Valve

This valve makes it possible to combine water, emulsifying agent, and crude oil.

> Water Outlet

This is the desalter vessel's drainage, which permits water to leave the desalter system.

> Level control valve

This valve regulates the water level within the desalter vessel and is coupled to a water outflow piping system.

Desalter Feed Pump

This pump transfers crude oil from the preheating train to the desalter by sucking it.

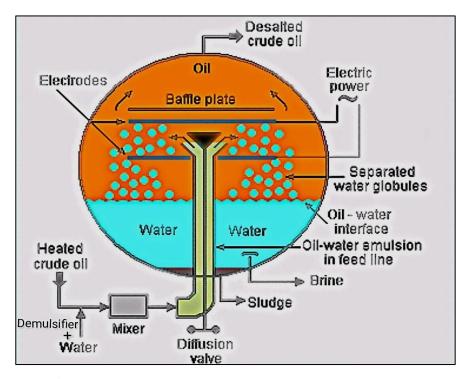


Figure I.11: Cross-sectional view diagram of a horizontal, cylindrical crude oil desalter.

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I.7. Key parameters in crude oil desalting

Crude oil desalting efficiency relies on several interdependent parameters that affect water, salt, and impurity separation. Optimizing these factors ensures high desalting performance while reducing costs and risks. Key parameters are outlined below:

I.7.1. Temperature

Increasing temperatures have a beneficial effect on the desalting process because they lower the viscosity of crude oil, which makes it easier for water droplets to settle, promotes salt dissolving, and increases phase density differences, which improve oil-water separation. Depending on the particulars of the crude oil, the ideal temperature range for efficient desalting is usually between 98 and 130 °C. But there are drawbacks to working at greater temperatures, namely the possibility of equipment damage and reduced separation effectiveness from vaporization. Furthermore, high temperatures have the potential to decrease desalting efficiency and need changes in voltage frequency due to a rise in crude oil conductivity, which weakens the electrostatic forces necessary for coalescence [41][36].

I.7.2. Wash water rate

By lowering interfacial tension and diluting brine microdroplets, wash water is essential for improving desalting efficiency and promoting the mass transfer of salt ions from the crude oil to the aqueous phase. This range guarantees adequate desalting without encouraging the development of stable emulsions, which might impede phase separation due to enhanced emulsion conductivity. To attain the best results, the dose of wash water should be carefully regulated within 2.5–12 vol% of the crude feed. Beyond this ideal range, separation becomes unstable and the amount of entrained water in the desalted crude increases, which has an adverse effect on downstream processing and the quality of the final product [41].

I.7.3. Emulsifying rate and injection points

Demulsifiers function by adsorbing at the water—oil interface, thereby lowering interfacial tension and destabilizing the emulsion. This facilitates the coalescence of dispersed water droplets, enhancing phase separation efficiency. The concentrations effective contingent upon the physicochemical properties of the crude oil, such as asphaltene content, API gravity, and emulsion stability. Excessive demulsifier dosage can lead to the formation of a stable interfacial rag layer, which impairs electrostatic coalescence and compromises the efficiency of downstream desalting operations [41][36].

General Overview of the Algiers Refinery and Crude Oil Desalting Processes

I.7.4. Differential pressure (ΔP) across mix valve

The differential pressure (ΔP) across the mixing valve directly governs the turbulence intensity and shear forces during the contact of wash water with crude oil. This interaction critically affects emulsion formation dynamics and the efficiency of salt dissolution from the crude matrix. Operating range is Approximately $1.5 \text{Kg/cm}^2 \text{g}$ for light crude oils. Heavier crude blends typically necessitate higher ΔP values to achieve adequate mixing and desalter efficiency. Excessive ΔP may lead to over-shearing, potentially destabilizing emulsions post-desalting and accelerating mechanical wear on the mixing infrastructure [41].

I.7.5. Oil-Water interface level

Accurate regulation of the oil-water interface within the desalter vessel is critical to preventing the formation of emulsified rag layers and ensuring efficient phase disengagement. any variation in the water level disturbs the primary field which is governed by the law [35]:

$$\mathbf{E1} = \frac{\mathbf{U}}{\mathbf{h}} \tag{eq I.8}$$

Where

E1: Primary field (V/cm).

U: Voltage between the electrodes (V).

h: Distance between the interface and the lower electrode (m).

- ➤ If the water level is too high, the electric field increases and the settling time decreases and there will be water entrainment in the desalinated crude, thus disrupting the stabilization.
- ➤ If the water level is too low, the crude will not have sufficient washing time, hence reducing the desalination efficiency and entrainment of the crude.

So, we must maintain a constant level to have good.

I.8. Conclusion

In conclusion, these desalter techniques are essential to reduce the salts and water impact from the crude oil. As this process is based on several factors that control the efficiency. the second part will delve into statistical analysis of this factors and modeling and optimization of the desalination process.

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Part II

Description of the Desalination Process at RA1G

This part aims to analyze and explain the most important operational parameters affecting the performance of crude oil desalination units in refining operations. As mentioned in the first section, crude oil desalination is a critical processing stage in oil refineries. Based on my review of the literature, I highlight the benefits of removing dissolved inorganic salts, suspended matter, and free water from incoming crude oil prior to processing in refineries. Despite its apparent simplicity, desalination is a highly complex process involving hundreds of physical and chemical interactions, including water droplet formation, emulsion stabilization, interference phenomena, and electrostatic effects. These interactions directly impact the performance of the desalination unit, which in turn impacts the safety, performance, and emissions of the entire refinery.

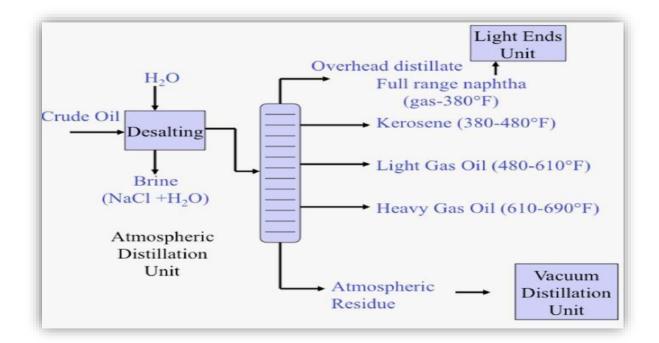
The procedure followed in this work can be divided into two parts: the first, statistical analysis of the influencing parameters, and the second, modeling and optimization of the desalination process. An initial set of histograms is dedicated to each of the key variables affecting desalination efficiency. Following statistical analysis, a modeling framework will be developed to describe the behavior of the desalination process as a function of the specified parameters. This model will form the basis for the optimization phase, where process conditions will be fine-tuned to maximize desalination efficiency while minimizing water and energy consumption, effluent discharge, and the use of chemical demulsifiers.

II.1. Description of the Desalting Process for Crude Oil

Crude oil often contains fine saline water droplets, salt crystals, suspended solids and traces of metals. Large amounts of dissolved salts can affect the crude refining process quite significantly. Although distillation is usually known as the first process in petroleum refineries, in many cases, desalting should take place before distillation (FigureII.1). Salt dissolved in water (brine) enters the crude stream as a contaminant during the production or transportation of oil to refineries. If salt is not removed from crude oil, serious damage can result, especially in the heater tubes, due to corrosion caused by the presence of Cl. Salt in crude oil also causes reduction in heat transfer rates in heat exchangers and furnaces.

The three stages of desalting are:

- 1. Adding dilution water to crude.
- 2. Mixing dilution water with crude by a mixer.
- 3. Dehydration of crude in a settling tank to separate crude and sediment and water (S&W).



FigureII.1: Desalting and fractional distillation of crude oil. [23]

II.1.1. Desalting Vessel (100-M-101)

The desalting vessel (100-M-101) is designed to remove salts from crude oil to a desired level. It is engineered to handle an inlet salt content of 20 PTB (approximately 72 ppm), with a water-soluble chloride removal efficiency of 95%, thereby reducing the salt content in the desalted crude to 1 PTB (approximately 3.6 ppm).

According to design performance, the insoluble aqueous phase (water and basic sediments) remaining in the desalted crude oil at operating temperature will not exceed 0.2% by volume, with an expected value of less than 0.1% vol.

The desalting operation involves mixing preheated wash water with preheated crude oil in a mixing valve, which emulsifies the oil/water mixture uniformly to facilitate the removal of impurities. The degree of emulsion is adjusted and controlled using differential pressure regulation.

II.1.2. Principle of the Desalting Operation

The crude/water emulsion is then broken by coalescence in a high-voltage electric field, and the phases are separated within the desalter vessel. Sufficient pressure is maintained in the desalter to ensure that the crude oil remains in the liquid phase and no vaporization occurs. To achieve this, a pressure control valve is installed at the discharge of the crude charge pump (100-P-101 A/B/C/D).

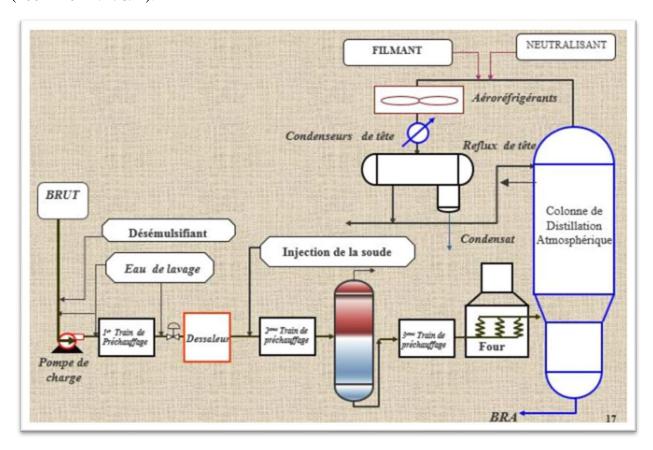


Figure II.2: Schematic Diagram of the Atmospheric Distillation Unit (Topping Unit). [23]

II.1.3. Wash water injection and heating

A sufficient quantity of wash water is mixed with the crude oil upstream of the desalter to dissolve the salts present in the crude. Typically, rectified sour water from the sour water stripper is used for this purpose. Provisions are also made to use treated water or demineralized water as an alternative.

The injection flow rate of rectified sour water, treated water, or demineralized water is controlled based on the lower liquid level in the sour water drum (100-D-114).

The wash water is pumped from the 100-D-114 drum by the desalter water charge pumps (100-P-160 A/B), with flow regulation, to the desalter/brine water heat exchanger (100-E-164 A/B).

The water is heated to a temperature of 80–85 °C before being mixed with the incoming crude oil in the desalter (100-M-101). The crude/water mixing is enhanced by mixing valves located at the inlet of the desalter.

II.2. Factors affecting desalting performance

First, in Hassi Messaoud, they pre-treat the crude oil using a magnetic field to remove salt, water, gas, and clay (large quantities). They then send it to us (Algiers Refinery). In addition, here we do the One of the most important analysis is determining the amount of salt in the oil (Electrometric method) before and after desalination by a Salinometer. This apparatus must consist of a unit capable of producing and displaying multiple voltage levels to apply a stress to a set of electrodes suspended in a beaker containing a test solution. The apparatus must be capable of measuring and displaying the current (mA) conducted through the test solution between the electrodes at each voltage level.

In a flask, we put 10 ml of crude oil with 40 ml of chemical product (Xylene) - toxic product; it has an affinity for salts (capture) - with 50 ml of Alcoholic solvent mixture: mix 63 ml of 1-Butanol and 37 ml of absolute (anhydrous) Methyl Alcohol. Then, we mix well, after a few seconds towards the bicher, and then by the device, which mentions the quantity of salts per (g/m^3) .



Figure II.3: Salinometer.

It is important to remember that the desalination process is complex. These six histograms illustrate how salt removal efficiency varies across operating parameters.

We can observe the following:

II.2.1. Temperature effect

Heat causes a decrease in viscosity, thickness, and cohesion of the film surrounding water drops. Heat also reduces the continuous phase (oil) viscosity, helping water drops to move freely and faster for coalescing. Controlling the temperature during operations is a very delicate job. Any excessive heat might lead to evaporation, which results in a loss of oil volume. Liquid density and viscosity usually decrease with temperature. This means that increasing operation temperature will raise settling rate and therefore, improve separation. In a given desalted, separation improvement means that a larger quantity of oil can be desalted at the same time. This would suggest that a higher temperature is more convenient. However, crude oil conductivity increases with temperature and so does the power requirement of the process. Additionally, higher temperatures imply an increase in heating costs. Given these opposing facts, it is expected that there is an optimum temperature. In the case of Iranian heavy crude oil feedstock, it was necessary to know the dependence of effective parameters on the temperature to determine if an optimum temperature exists. Temperature plays a critical role in the desalination process. Higher temperatures generally reduce the density and viscosity of crude oil, which improves mixing and droplet coalescence, Increase the solubility of salts in the wash water, Enhance the mass transfer rate of salts from the oil to the water. However, excessively high temperatures can also increase the evaporation of lighter components (related to TVR) and may stabilize emulsions, negating their benefits. The data in (Figure II.4) indicates that the temperature remains generally high across the different efficiency levels, most of them are around (90°C). The highest efficiency (about 84.69%) corresponds to a slightly lower temperature (about 88°C) than some other high-efficiency points, but the optimal point for efficiency depend on the other factors.

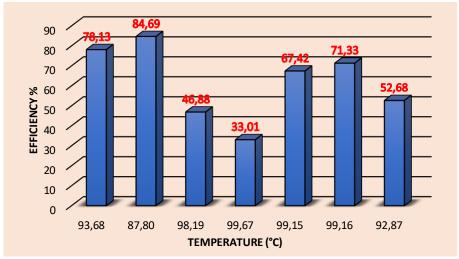


Figure II.4: Distribution of Temperature (°C) data.

II.2.2. Dilution with freshwater effect

It is obvious that salt removal from crude oil is directly proportional to the amount of wash water although the lower values of demulsifier amount and operational temperature [11]. Salts in emulsion sometimes come in solid crystalline form. So, the need for freshwater to dissolve these crystal salts arises, and dilution with freshwater has become a necessity in desalting/dehydration processes. Freshwater is usually injected before heat exchangers to increase the mixing efficiency and to prevent scaling inside pipes and heating tubes. Freshwater is injected so that water drops in emulsions can be washed out and then drained off. Hence the term "wash water." The quantity/ratio of freshwater injected depends on the API gravity of the crude, but, generally, the injection rate is 3-10% of the total crude flow. To improve the efficiency of W/O, the wash water injection must be operated at the optimum point. Beyond that point, experience has shown that excessive water may lead to deterioration in the pH range of the water volume as a whole. Ranges of pH above or below seven, may cause severe problems in emulsion breaking and precipitation of hydrocarbon solids (e.g., naphthalene) into the continuous water phase [42].

Wash Water Flow Rate (m³/h); A sufficient amount of wash water is needed to dissolve the salts. Too little water may leave the salts undissolved, while too much can lead to increased energy consumption for heating and separation. (Figure II.5) shows the variation in wash water flow rates across efficiency levels. The highest efficiency (84.69%) is associated with a moderate wash water flow rate (21 m³/h). The highest wash water flow rate (approximately 27m³/h at approximately 46.88% efficiency) does not correspond to the highest efficiency. The optimum wash water rate is related to the initial salt content. As we can see in (Figure II.6), when the efficiency was (78.13%), it corresponded to a high initial salt content (12.80 g/l), while at a high efficiency (84.69%), the initial salt content corresponded to (9.8 g/l). Also, a low wash water rate (23.18 %) indicates a high TVR (731g/cm²), because a high TVR effects on the mixing and settling behavior of wash water than making the desalting less effective.

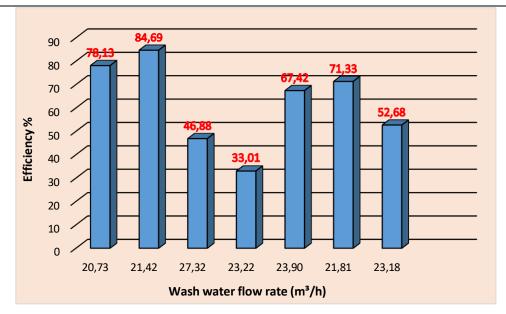


Figure II.5: Distribution of Wash water flow rate (m³/h) data.

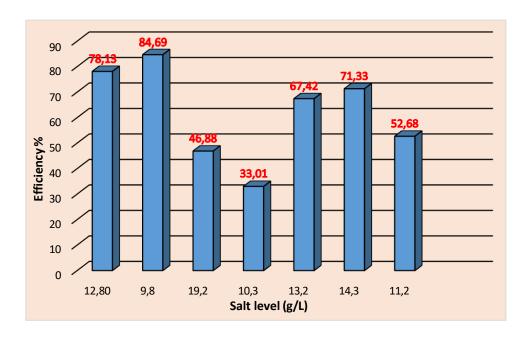


Figure II.6: Distribution of Salt level (g/l) data.

II.2.3. Oil viscosity effect

The resistant force against the approaching move of the water droplets is known as the film thinning force, which mainly depends on the oil viscosity. A well-known fact among the workers in petroleum dewatering and desalting units is that water separation in the summer is more effective than winter.

This refers to the rigorous temperature dependency of oil viscosity, as the oil viscosity is reduced at higher temperatures, the film thinning force declines and water droplets coalesce easier [43].

II.2.4. Mixing effect

Mixing is used in a desalting/dehydration process to promote further dispersion of dilution water and demulsifier/chemical with the emulsion. It is also used to help smaller water droplets coalesce, enhancing the separation/refining efficiency and, in particular, affects the W/O efficiency. High shear actions form emulsions. Similarly, when dilution water (freshwater) is added to an emulsion, one needs to mix them to dissolve the salt crystalline and to aid in coalescing finely distributed droplets. Mixing works in three steps: (1) helps smaller drops to join, mixes chemical/demulsifier with the emulsion, and (3) breaks the free injected volume of wash water into emulsion-sized drops and evenly distributes it [42].

II.2.5. Crude Oil charge (ADU) (m³/h) effect

The flow rate of Algerian crude oil fed to the ADU, which likely includes a desalter unit as a key pretreatment step. High flow rates can sometimes reduce the residence time within the desalter unit, which can affect desalting efficiency if other parameters are not optimized. The crude oil flow rate shows some variability but is generally in the upper range (approximately 560-580 m³/h) for most efficiency levels. The highest efficiency (approximately 84.69%) occurs at a slightly lower flow rate (approximately 450 m³/h). Data suggest that a moderate flow rate may be optimal for achieving high efficiency.

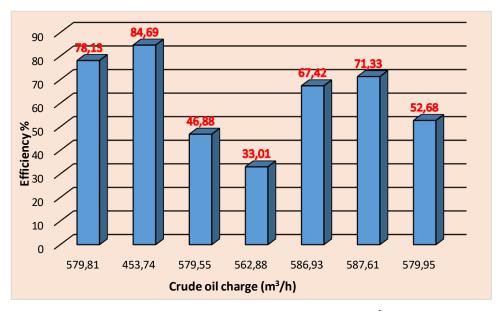


Figure II.7: Distribution of Crude oil charge (m³/h) data.

II.2.6. Pressure drop ΔP (kg/cm².g) effect

Affects the mixing intensity between the crude oil and wash water. Adequate mixing promotes salt dissolution and water droplet aggregation. A pressure drop that is too low may indicate poor mixing, while a pressure drop that is too high may result in a stable emulsion, hindering separation. This is due to the high ratio of BS&W, which leads to blockage and accumulation of solids inside the bowl. The data indicate that the pressure drop fluctuates widely across efficiency levels. The highest efficiency (approximately 84.69%) is associated with a moderate pressure drop (approximately 0.8 kg/cm² g), while at low pressure drops (0.14 kg/cm².g), we observe a decrease in efficiency to (52.68%), and also at low pressure surge (1kg/cm².g) where (46.88%).

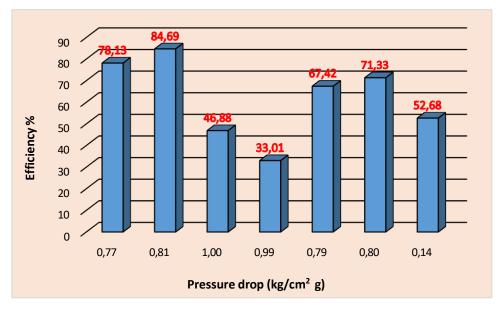


Figure II.8: Distribution of Pressure drop (kg/cm² g) data.

II.2.7. Oil-water interface level (%) effect

This parameter is critical for electrostatic discharge collectors often used in desalter plants. The interface level between the heavier water phase (containing dissolved salts and other impurities) and the lighter oil phase must be carefully controlled to ensure efficient separation under an electric field. Improper interface placement can result in oil-to-water or oil-to-water migration, negatively impacting efficiency and subsequent processing. The highest efficiency (about 84.69%) occurs at an interface level of about (38%). Very low (about 33% at about (33.01%) efficiency) and very high (about (50%) at about (46.88%) interface levels). This change at the interface is caused by the density difference between oil and water and the presence of BS&W.

A larger density difference generally promotes better separation and a more defined interface, while a higher BS&W content can lead to emulsion formation, destabilizing the interface and impeding salt removal, and thus may explain some of the efficiency fluctuations observed.

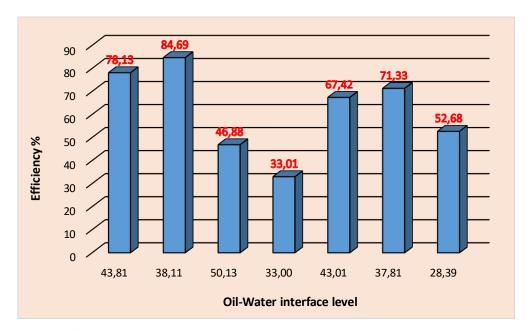


Figure II.9: Distribution of Oil-Water interface level (%) data.

II.3. Modeling and Optimization of Crude Oil Desalting Using JMP 13 and Box-Behnken Design

Crude oil often contains inorganic salts, water, and suspended solids. Before entering the Atmospheric Distillation Unit (ADU), it must undergo desalting, a process designed to reduce these impurities. Desalting involves mixing the crude oil with fresh water, creating an emulsion, and then separating it in an electrostatic separator.

This study was conducted during an industrial internship at the Algiers Refinery (Sidi Rezine) with the goal of modeling and optimizing the desalting unit using statistical experimental design techniques.

The objectives of this work are as follows:

- To identify the main factors affecting desalting efficiency.
- > To develop a reliable predictive model using Response Surface Methodology (RSM).
- > To determine the optimal operating conditions for maximum salt removal.

II.3.1. Variables and response

Independent variables (Factors):

Tabel II.1: Experimental areas of factors.

Code	Variable	Unit	Ranges		
			-1	0	+1
X ₁	Pressure drop across the mixing valve (ΔP)	bar	0.1	0.6	1
X ₂	Oil-water interface level	%	30	38	46
X ₃	Crude oil feed rate to ADU	(m ³ /h)	460	550	600

Dependent Variable (Response):

Y: Desalting Efficiency (% salt removal or salt content in mg/L).

II.3.2. Experimental Design: Box-Behnken Design (BBD)

The Box-Behnken Design (BBD) is a robust and efficient experimental design method within the framework of Response Surface Methodology (RSM), widely used for developing quadratic (second-order) models with a reduced number of experiments.

The table above presents the coded levels of the three independent variables X_1 : pressure drop across the mixing valve, X_2 : oil—water interface level, and X_3 : crude oil feed rate to the Atmospheric Distillation Unit (ADU) used in the Box-Behnken Design, along with the experimental response (Y), representing the crude oil desalting efficiency. Each variable was tested at three levels: -1 (low), 0 (center), and +1 (high).

Fifteen experimental runs were conducted, including three replicates at the center point to estimate experimental error and assess the model's lack of fit. The variation in response values across different experimental combinations reflects the influence of each factor and their interactions on the desalting process. The design ensures an efficient exploration of the response surface while maintaining safe and realistic operating conditions.

Table II.2. Experimental Design Matrix of the Box-Behnken Design.

Run No.	Experimental factor level			Response Y
	X ₁	\mathbf{X}_2	X 3	%
1	1	0	-1	84,69
2	0	1	1	41,50
3	-1	0	1	50,10
4	0	1	-1	78,00
5	-1	0	-1	75,00
6	1	-1	0	78,13
7	-1	1	0	58,58
8	0	0	0	48,82
9	0	0	0	70,26
10	1	0	1	30,50
11	0	0	0	43,62
12	0	-1	-1	88,00
13	1	1	0	51,13
14	-1	-1	0	51,30
15	0	-1	1	38,00

One of the main advantages of the BBD is that it avoids experimental combinations in which all factors are simultaneously at their extreme levels, thereby protecting sensitive refinery equipment from potentially harmful operating conditions. This makes BBD particularly suitable for industrial processes like crude oil desalting, where safety and efficiency are paramount. The structured layout of the BBD also ensures balanced data distribution and efficient use of resources, facilitating the generation of a statistically valid and predictive response surface model.

In this type of experimental design, a second-order polynomial equation (Eq. III.1) is commonly employed in process optimization studies [45]. This model describes the relationship between the response variable and the independent factors as follows:

$$Y_e = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j$$
 (eq. II.1)

Where \hat{Y}_e represents the predicted response, b_0 is the intercept or constant term, b_i are the linear coefficients, b_{ii} are the quadratic coefficients, and b_{ij} are the interaction coefficients between the variables x_i and x_j , which correspond to the coded values of the independent variables.

This equation allows for the modeling of curvature and interaction effects in the response surface. The experimental data obtained from the Box-Behnken Design were analyzed using JMP 13 statistical software. The Analysis of Variance (ANOVA) was used to evaluate the significance of each model term and to provide statistical indicators such as the F-ratio, P-values, and R-squared, which together assess the goodness of fit and reliability of the model. This analysis is crucial in determining whether the model accurately captures the behavior of the system and can be used for reliable prediction and optimization of the desalting process.

II.3.3. Statistical Analysis of the Box-Behnken Design

The model is statistically significant (Table II.3), as indicated by the very low p-value (0.0001) and the high F-ratio (18.63). This confirms that the quadratic model reliably explains the variation in the desalting performance based on the selected factors.

Table II.3: Analysis of Variance (ANOVA) for the Quadratic Model

Term	LogWorth	P-Value	Significance
X ₃	4.630	0.00002	Very High
$X_1 \times X_2$	1.181	0.06584	Marginal
$X_1 \times X_3$	0.963	0.10882	Low

The coefficient of determination ($R^2 = 0.8355$) suggests that 83.55% of the variability in the response is explained by the model (Table II.4). The adjusted R^2 (0.7907) corrects for the number of predictors and still shows good model fit. A relatively low Root Mean Square Error (RMSE) confirms the accuracy of the predictions.

Table II.4: Model Fit Summary

Source	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio	p-Value
Model	3	3935.76	1311.92	18.63	0.0001
Residual	11	774.79	70.44		
Total	14	4710.55			

The crude oil feed rate (X_3) has the most significant influence on the desalting efficiency, as shown by its very low p-value. The interaction between mixing valve pressure drop (X_1) and oil—water interface (X_2) is borderline significant and may influence performance under specific conditions. The $X_1 \times X_3$ interaction is less influential.

Table II.5: Lack of Fit Test

Source	Degrees of Freedom	Sum of Squares	Mean Square	F- Ratio	P- Value
Lack of Fit	9	375.99	41.78	0.21	0.9614
Pure Error	2	398.80	199.40		
Total Residual	11	774.79			

The high p-value (0.9614) indicates that there is no significant lack of fit (Table II.5). This suggests that the model is adequate and that most of the residual variation can be attributed to pure experimental error rather than model misspecification.

II.3.4. Model Predictive Ability: Observed and Predicted Values

The graphical comparison between the observed and predicted response values (Figure II.10) provides a visual validation of the regression model developed through the Box-Behnken Design. Each data point represents an experimental run, with the x-axis showing the predicted desalting efficiency calculated by the model, and the y-axis showing the actual measured values. The alignment of most points along the 45-degree diagonal line indicates a strong correlation between the predicted and experimental results. This close agreement demonstrates that the quadratic model captures the behavior of the process accurately, with minimal deviation or bias. Therefore, the model can be considered reliable for prediction and optimization purposes within the experimental domain. The high R² value (0.8355) further supports the model's robustness in explaining the variability of the response.

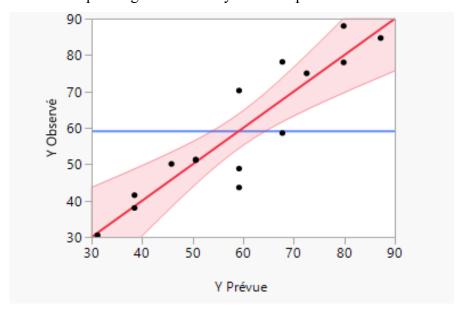


Figure II.10: Observed and predicted values plot.

The final predictive model highlights the strong influence of the crude oil feed rate (X_3) on desalting efficiency, along with notable interaction effects between X_1X_2 and X_1X_3 .

$$Y=58.8087+10,4817*X3+4,9815*X1*X2+4,7932*X1*X3$$
 (eq II.2)

II.3.5. Interpretation of main and interaction effects

The Box-Behnken experimental design and subsequent ANOVA analysis allow us to evaluate how each factor, individually or in combination, influences the desalting efficiency. Below is a detailed interpretation of the main effects and interaction effects based on the statistical output.

II.3.5.1. Main effect of $X_1 - \Delta P$ (Pressure drop across the mixing valve)

Although not statistically highlighted as highly significant in the summary table (since only interactions involving X_1 were emphasized), the main effect of X_1 remains practically important in the process. The pressure drop (ΔP) directly controls the degree of mixing between crude oil and wash water.

- ightharpoonup High ΔP values typically result in stronger mixing, which may increase the formation of small water droplets. While this can improve contact and salt transfer, it might also lead to stable emulsions that are harder to separate.
- \triangleright Low $\triangle P$ values might cause insufficient mixing, reducing desalting efficiency.

In the results, X_1 is more impactful when involved in interactions, suggesting that its influence is context-dependent, it depends on the levels of other factors.

II.3.5.2. Main effect of X₂ – Oil–Water interface position

X₂ affects the settling and separation efficiency inside the desalter.

- ➤ When the interface is too high or too low, this can indicate poor phase distribution or control, which can lead to water in the crude oil stream or oil in the water phase.
- Although X_2 's individual effect does not appear statistically dominant, it becomes more relevant when combined with X_1 (ΔP), as seen in the interaction effect X_1*X_2 .

This suggests that precise control of the interface, especially under specific mixing conditions, is important for achieving optimal separation.

II.3.5.3. Main effect of X₃ – Crude Oil feed rate

- \triangleright As previously discussed, X₃ shows a highly significant effect (p = 0.00002), making it the most influential main factor.
- ➤ It affects residence time, flow dynamics, and throughput of the unit, all of which are critical to desalting performance.

X₃, representing the crude oil feed rate to the atmospheric distillation unit, emerged as the dominant variable in this study and should therefore be a primary focus for process control and optimization. While X₁ (pressure drop across the mixing valve) and X₂ (oil–water interface position) were not individually as significant as X₃, their influence becomes particularly notable through interaction effects, especially X₁X₂ and X₁X₃. This indicates that the desalting performance is not solely governed by isolated factors but rather by the synergistic effects between them. These results underscore the effectiveness of Response Surface Methodology (RSM) in capturing complex interdependencies among process variables, which might otherwise remain undetected with traditional one-factor-at-a-time experimental designs.

II.3.5.4. Analysis and Interpretation of Interaction effects

The **prediction profiler** highlights two notable interaction effects X_1X_2 and X_1X_3 , which are consistent with the outcomes shown in the effects summary table.

❖ Interaction X₁X₂ (Pressure Drop * Interface Level)

This interaction is close to the threshold of statistical significance, with a p-value slightly above the conventional cutoff (typically 0.05). Although not strongly significant, it suggests a potential influence on the predicted response in specific operating ranges. This interaction could become particularly relevant under critical process conditions where small variations in pressure drop or interface level may lead to noticeable changes in desalting performance. Therefore, it would be valuable to investigate this interaction further, especially through response surface plots or local sensitivity analyses.

❖ Interaction X₁X₃ (Pressure Drop * Feed Rate)

While less pronounced statistically, the X_1X_3 interaction may still hold practical importance. From a process-engineering standpoint, the combined effect of pressure drop across the mixing valve (X_1) and crude oil feed rate to the ADU (X_3) can influence the dynamics of emulsion formation. Increased turbulence due to high-pressure drop, when combined with high flow rates, may intensify mixing at the oil—water interface, thereby affecting the coalescence of water droplets and ultimately affecting desalting efficiency. Thus, including this interaction in the model could enhance predictive accuracy in real-world operating scenarios.

In summary, even though these interactions do not meet strict statistical significance criteria, incorporating them into the regression model may improve its robustness and predictive capability across a wider range of process conditions. Their inclusion is further justified by the physical relevance and potential operational impact they may represent in the crude oil desalting process.

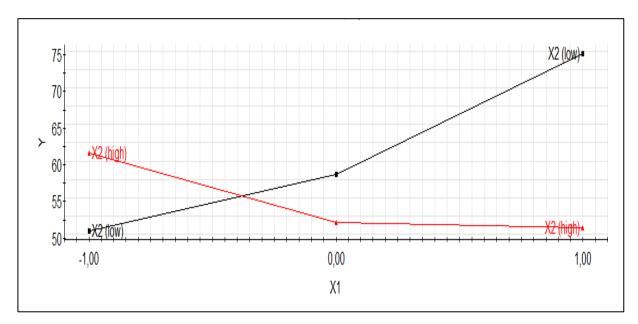


Figure II.11: Interaction X₁X₂ (Pressure Drop * Interface Level).

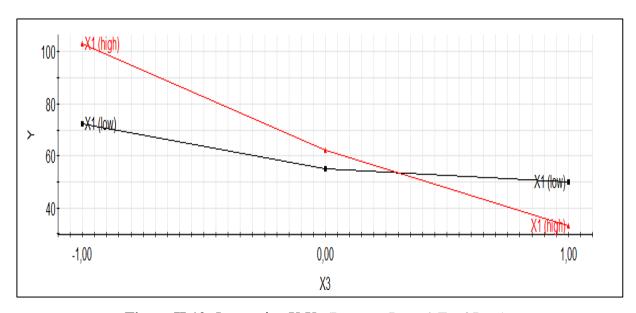


Figure II.12: Interaction X₁X₃ (Pressure Drop * Feed Rate).

II.3.6. Prediction Profiler and Desirability Function Analysis

The Prediction Profiler provides a dynamic visual representation of how each individual factor (X₁: pressure drop across the mixing valve, X₂: oil—water interface position, and X₃: crude oil feed rate) affects the response variable, which in this case is the desalting efficiency. By simultaneously adjusting the levels of the input variables within their experimental range, the profiler shows how the predicted response changes, helping identify optimal operating conditions.

In this study, the profiler reveals that X_3 has the most significant impact, confirming its dominant effect observed in the ANOVA. A higher crude feed rate (X_3) tends to lower the efficiency due to reduced residence time, while proper control of X_1 and X_2 , particularly at their optimal levels—can partially compensate for this effect and improve performance.

The desirability function quantifies how close the predicted response is to the desired target, which is typically maximizing desalting efficiency (. The desirability value ranges from 0 (completely undesirable) to 1 (ideal outcome). In this case, the desirability score at the optimal conditions identified by the profiler is high, indicating that the combination of variable levels proposed by the model leads to near-optimal process performance. This supports the utility of RSM and the Box-Behnken design in achieving practical, data-driven optimization for industrial desalting processes.

Based on the statistical modeling and optimization using the desirability function, it is possible to determine the optimal operating conditions that maximize crude oil desalting efficiency.

The desirability approach, which transforms multiple responses into a single scale ranging from 0 (completely undesirable) to 1 (fully desirable), was employed to identify the settings of the independent variables that yield the best predicted outcome.

In this case, the maximum desirability value tends toward 1, indicating that an optimal solution has been reached. The combination of variable levels that provides the highest predicted desalting efficiency is as follows:

- $ightharpoonup X_1 = 0.1$ bar (Low pressure drop across the mixing valve)
- \succ $X_2 = 46 \%$ (High oil-water interface level)
- $X_3 = 460 \text{ m}^3/\text{h}$ (Low crude oil feed rate to the ADU)

This result suggests that a lower pressure drop and slower feed rate, coupled with a higher interface level, contribute positively to water removal efficiency. From a process standpoint, these conditions may promote better phase separation and reduced emulsion stability, thereby improving overall desalting performance.

Therefore, the use of statistical modeling combined with desirability optimization not only enhances prediction accuracy but also provides a practical basis for adjusting process variables to achieve optimal operational performance.

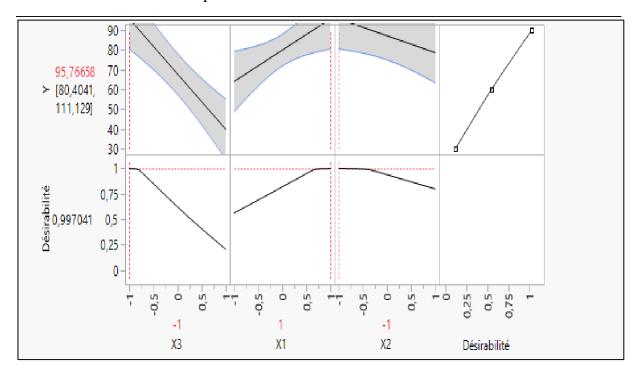


Figure II.13: Prediction Profiler and Desirability Function Analysis.

II.3.7. Interpretation of Response Surface and Identification of Potential Optimization Limits

To better assess the behavior of the process within the range of real operating conditions used in the refinery, two types of graphical representations were generated: response surface plots and contour plots. These tools are useful for visualizing the interaction effects between variables and identifying regions of maximum or minimum response.

In this analysis, the response surface generated for the interaction between X_1 (pressure drop) and X_2 (oil—water interface level), while holding X_3 (crude oil feed rate) constant at -1, did not reveal a distinct optimum within the studied experimental range. Instead, the surface exhibits a saddle-shaped topology, also known as a "saddle point" or "horse saddle" configuration, where no global maximum or minimum is clearly defined. This indicates that the maximum desalting efficiency cannot be achieved within the current boundaries of the experimental design.

Additionally, a contour plot was used to provide a clearer view of the distribution of the response values (desalting efficiency) over the X_1 – X_2 plane. The contour lines further confirm the absence of a well-defined optimal region, as the values tend to plateau or change direction without reaching a distinct peak.

These observations suggest that, while the model is statistically valid and informative, the chosen experimental domain may need to be extended or refined in future studies to fully capture the optimum conditions. It also emphasizes the importance of exploring wider or more focused ranges of key process variables in order to improve the efficiency of the desalting operation.

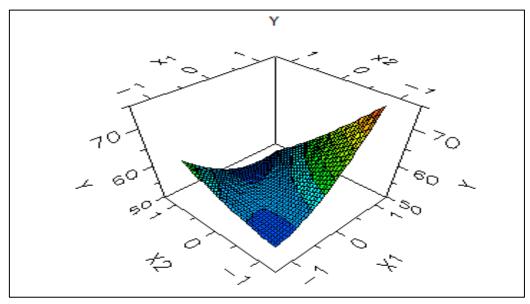


Figure II.14: Response surface of desalting efficiency as a function of pressure drop (X_1) and interface level (X_2) at low feed rate $(X_3 = -1)$.

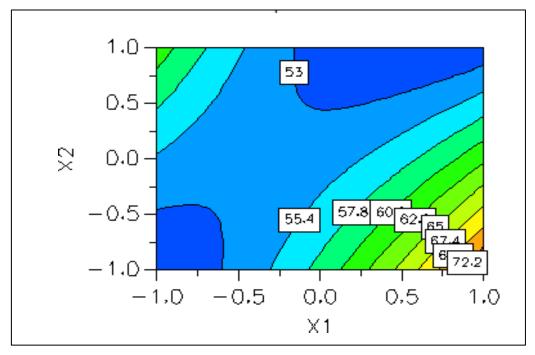


Figure II.15: Contour plot of desalting efficiency for varying X_1 and X_2 at fixed crude oil feed rate $(X_3 = -1)$.

General conclusion	

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Conclusion

The treatment of crude oil by desalination is a crucial stage in the refining process, aimed at eliminating inorganic salts, water and associated impurities that can cause major problems such as corrosion, equipment fouling and catalyst deactivation. This dissertation looks in depth at the operation of the desalting unit at the Algiers refinery (RA1G), with a particular focus on optimizing the parameters influencing the efficiency of the process.

The approach adopted combines an exhaustive review of conventional and modern desalting techniques - including chemical, thermal, electrostatic and multi-stage systems - with rigorous statistical analysis based on Box-Behnken experimental design methodology. This approach identified critical variables such as pressure drop across the mixing valve, oil-water interface level and crude oil feed rate, and assessed their impact, individually and in interaction, on desalting efficiency, due to its direct effect on residence time and hydrodynamic conditions in the unit. Furthermore, the interactions between mixing pressure and interface level, as well as mixing pressure and feed rate, highlight the complexity of water droplet coalescence and separation phenomena. The statistical optimization carried out has led to the recommendation of precise operating conditions: in particular, a low feed rate, a moderate pressure drop and a high interface level, that favor efficient coalescence of the water droplets and a reduction in the residual salt content.

From a practical point of view, this work provides a solid basis for the control and fine-tuning of operating parameters in electrostatic desalting units, making it possible to increase the quality of desalted oil, reduce the risks associated with corrosion and clogging, and optimise water and energy consumption. It also helps to limit environmental impact by minimising salt effluent discharges and chemical product consumption.

To plan the trials, we started by identifying the main statistically significant effects, namely the efficiency of the desalting unit Y (%). Of the six parameters mentioned, and due to lack of data, using the experimental methodology, the Box Behnken design, made it possible to determine the most influential factors on desalination. Which is represented in; X₁: pressure drop across the mixing valve, X₂: oil—water interface level, and X₃: crude oil feed rate to the ADU. The exploitation of experimental results, within the framework of statistical analysis, is carried out by the JMP13 software.

The model is statistically significant, as indicated by the very low p-value (0.0001), among the coefficients, one is most significant, it is the crude oil feed rate (X_3) with the p-value of (0.00002). As for the second-order interactions, only $(X_1 \times X_2)$ and $(X_1 \times X_3)$ are significant with p values of (0.06584); (0.10882) respectively. Indeed, the values of the regression coefficient $(R^2 = 0.8355)$ and the adjusted coefficient $(R^2 = 0.7907)$ are close, so the suggested quadratic model is adequate to predict the response of the experimental data, which confirms the quality of the adjustment.

Finally, this dissertation opens up interesting prospects for future studies, particularly on the integration of real-time control methods based on advanced sensors, the use of new, more environmentally-friendly demulsifying agents, and the adaptation of desalting processes to variations in crude oil quality and the increasingly stringent requirements of environmental and industrial standards.

All of this work confirms that control of operational parameters and a detailed understanding of the physical and chemical mechanisms of desalting are essential to ensure the performance, sustainability and competitiveness of refining units in a modern industrial context.

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