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Synthesis of Water Networks

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Preface

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Abstract

Water is a resource of great relevance for industrial activities. As freshwater will become scarcer and increasing costs are associated with water handling, optimization of its use is of key importance. The issue of water allocation and reuse through mathematical optimization has been addressed in many literature works [1, 2]. However, most of the water networks proposed comprise few contaminants and treatment options, and thus are arguably not fit to manage the complexity of a real industrial case.

In this work, a systematic framework for the formulation and solution of water network problems is proposed, based on the modification of an earlier work [3]. The optimization problem is formulated as a Mixed Integer Linear or Non-Linear Programming (MILP/MINLP), which is solved to identify the best wastewater treatment process among a set of predefined alternatives, according to selected optimum criteria.

The methodology employed is as follows. First, the wastewater sources and the treatment objectives are identified. A superstructure of available technologies for water purification is used in order to identify different process paths; the superstructure is built dividing the treatment operation in tasks to remove the various pollutants and considering different alternatives for each task. Then, the objective function is chosen and the problem is formulated as a MILP or MINLP optimization problem, which is solved in GAMS [4]. A case study of oil refinery wastewater is presented to highlight the features of the tool. A superstructure is built and the optimization problem is formulated and solved for different scenarios and optimality criteria - minimum total annualized cost or maximum water recycle.

The key novelties of the methodology are a comprehensive characterization of the water stream and a functional model of the treatment units, so to obtain information on performance and economics. Furthermore, it allows the evaluation of different scenarios and it can be used for a number of case studies. Thus, it constitutes a useful tool to provide a guideline for the design of wastewater treatment systems for new plants or for retrofitting of existing plants.

Sommario

L'acqua è un'utenza industriale di grande importanza a cui sono spesso associati alti costi di approvvigionamento e di trattamento delle acque reflue, che sono via via crescenti a causa delle sempre più stringenti regolamentazioni ambientali e della limitatezza delle risorse idriche. Per questo, l'ottimizzazione dell'uso delle risorse idriche a livello industriale è di centrale importanza ed è utile disporre di efficaci metodi di progettazione di reti idriche industriali.

Le tecniche di progettazione utilizzate attualmente sono basate principalmente su soluzioni preesistenti, con lo svantaggio di avere un numero di opzioni limitato e spesso non ottimale. Esistono in alternativa metodi di integrazione, basati per esempio sulla pinch technology, che sono però di difficile implementazione nel caso in cui si coinvolgono un numero elevato di correnti e contaminanti, come spesso accade per problemi di dimensione industriale. Recentemente sono stati sviluppati metodi basati sull'ottimizzazione matematica che permettono la gestione di problemi di più grande complessità. Data la versatilità e la completezza offerta da questi metodi, essi sono ritenuti i più adatti per affrontare problemi di scala industriale. Il problema di allocazione e riutilizzo dell'acqua tramite ottimizzazione matematica è stato affrontato in svariati articoli di letteratura [1, 2]. Tuttavia, la maggior parte delle reti idriche proposte comprende un numero limitato di contaminanti e di opzioni processuali per il trattamento, e di conseguenza queste reti non sono adatte alla rappresentazione soddisfacente della complessa realtà di un problema industriale.

In questo lavoro di tesi si è sviluppato un metodo sistematico per la progettazione di reti idriche industriali basato sull'ottimizzazione matematica che risulta completo e flessibile, in modo da avere un livello di dettaglio soddisfacente per essere utilizzato convenientemente nel caso di problemi industriali reali e da poter essere applicato agevolmente a molteplici casi di studio. Il metodo è basato sulla modifica di un lavoro precedente [3], riadattato per soddisfare le peculiari caratteristiche dei processi di trattamento dell'acqua. Il problema di ottimizzazione è formulato come un problema di ottimizzazione lineare o non lineare (Mixed Integer Linear/Non-Linear Programming, MILP/MINLP), che è risolto per identificare il miglior processo di trattamento dell'acqua secondo un criterio di ottimo prescelto tra un insieme di alternative predefinite.

La metodologia utilizzata è la seguente. Innanzitutto, si identificano le correnti di acqua reflua da trattare e gli obiettivi del trattamento. La rete idrica è schematizzata secondo una sovrastruttura a blocchi nella quale le acque da trattare sono connesse agli obiettivi del trattamento attraverso una serie di processi di trattamento. Questi sono organizzati per tipo sulla base del tipo di contaminante da rimuovere o del principio fisico utilizzato, e per ogni tipo di trattamento sono disponibili diverse tecnologie alternative. Le connessioni tra acque reflue da trattare, obiettivi di trattamento e processi di trattamento definiscono la topologia della rete. Ciascun blocco della sovrastruttura è modellato secondo un modello comune. Per i blocchi di

trattamento è stato utilizzato un modello semplice ma descrittivo dei parametri di interesse, così da limitare le difficoltà matematiche del modello e allo stesso tempo mantenere le informazioni processuali significative. Altre equazioni sono utilizzate per assicurare il rispetto dei bilanci materiali, il rispetto dei vincoli imposti dagli obiettivi di trattamento e altre relazioni logiche sussistenti riguardo la scelta delle diverse alternative processuali.

Le equazioni del modello costituiscono i vincoli di uguaglianza e disuguaglianza del problema di ottimizzazione in cui la funzione obiettivo è scelta in relazione all'indice di performance desiderato. Nel caso più generale, il problema di ottimizzazione risultante è un MINLP, in cui le variabili continue sono le portate e le variabili discrete la selezione degli intervalli. Il problema è risolto in GAMS con l'algoritmo DICOPT [4]. Per far fronte alle difficoltà matematiche associate alla risoluzione di un problema non lineare di larga scala, si utilizzano strategie di semplificazione nel caso in cui si incontrino complicazioni nella soluzione diretta del problema - decomposizione del problema in sottoproblemi, selezione di un appropriato punto iniziale. Inoltre, il MINLP è non convesso, perciò il raggiungimento dell'ottimo globale non è garantito.

Nella progettazione è importante considerare la variazione temporale delle portate e della concentrazione di ciascun contaminante delle acque da trattare, poiché essa può influenzare la scelta del treno di trattamento ottimale. Per tenere conto di questo effetto, è possibile formulare un problema di ottimizzazione stocastico in modo da raggiungere una soluzione robusta in grado di soddisfare gli obiettivi di trattamento a fronte della variabilità delle correnti di acqua in ingresso. Ovviamente, questo avviene a spese di una maggiore dimensione del problema matematico e spesso di più alti costi di processo.

Allo scopo di illustrare le caratteristiche del metodo, si è analizzato un caso di studio riguardante il trattamento di acque reflue di impianti di raffineria, che appartengono a uno tra i settori industriali caratterizzati da un maggior consumo di acqua. Sulla base di dati reali, sono stati identificati le principali correnti di acqua reflua da trattare e i principali obiettivi del trattamento, che prevedono sia lo scarico che opzioni di riciclo di acqua semitratata come acqua di processo. Si è costruita una sovrastruttura comprendente un numero significativo di trattamenti più comunemente utilizzati a livello industriale e si è formulato e risolto il problema di ottimizzazione per differenti scenari e criteri di ottimalità - minimo costo totale annualizzato o massimo riutilizzo di acqua.

La soluzione trovata restituisce uno schema completo delle correnti e dell'evoluzione di ciascun contaminante nel treno di trattamento. Inoltre, fornisce informazioni di interesse sull'economia del processo tra cui i costi di investimento e i costi operativi, in particolare in relazione al consumo di utenze esterne e allo scarto, nonché il risparmio legato al riciclo di acqua nel caso in cui tra gli obiettivi di trattamento scelti sia compresa un'opzione di riciclo. Si hanno anche informazioni sul contributo di ciascun trattamento e di ciascun tipo di utenza in relazione al costo totale.

Rispetto alle reti idriche presenti in letteratura, quella sviluppata in questo lavoro di tesi accomoda un'ampia gamma di contaminanti estendibile a seconda delle necessità del caso e utilizza un modello semplice ma funzionale per le unità di trattamento, così da poter ricavare utili informazioni sulle prestazioni e sull'economia del processo a soluzione ottenuta. La funzionalità della metodologia sviluppata può essere potenziata con la possibilità di raggiungere l'ottimo globale utilizzando tecniche di soluzione di MINLP più avanzate, per esempio attraverso una riformulazione convessa del problema di ottimizzazione. La metodologia sviluppata consente di trattare la complessità e le dimensioni di un problema industriale ed è

flessibile rispetto alla valutazione di diversi scenari quali differenti criteri di ottimalità, acque reflue da trattare, regolamentazioni ambientali, livello di contaminanti consentito nel caso in cui l'acqua sia riciclata al processo stesso e differenti prestazioni delle unità di trattamento considerate. Infine, essa può facilmente essere modificata ad hoc per coprire uno svariato numero di casi di studio. Per questi motivi, e in luce della tipologia e della varietà delle informazioni ottenute, la metodologia sviluppata è un valido strumento di predizione da utilizzarsi in sede di decisione sia per la progettazione di nuove reti idriche industriali sia per l'ammodernamento di impianti esistenti.

Chapter 1

Introduction

This chapter gives an overview of the motivation behind this work and of the main issues involved in water management and in wastewater treatment, with special focus on industrial wastewater treatment. It also describes the state of the art of the design of water management systems and how the problem has been addressed in various literature works. Since the focus will be on oil refinery complexes, some general information on the water handling in refineries is provided.

1.1 Motivation

Water is a valuable resource of great relevance for humanity. The total volume of water present on Earth amounts to $1.386 \cdot 10^9$ km³, of which only 2.5% is freshwater and the rest is salty water; of the freshwater, 30% consists of aquifer groundwater and the rest is embodied in glaciers [5]. In 2010, the freshwater ground withdrawal on a global level amounted to around $3.9 \cdot 10^3$ km³/yr, of which 60% is dedicated to agricultural use, 22% to domestic use, and 18% to industrial use; these figures have a huge variability between regions: the water withdrawal is proportional to the size of the country and the major consumers are India (761.0 km³/yr), China (578.9 km³/yr) and the United States (482.2 km³/yr); the breakdown of the water withdrawal ranges from 91%, 7% and 2% for agricultural, domestic and industrial use respectively in South Asia to 8%, 16% and 77% respectively in Western Europe [6, 7]. Of course, part of the water extracted is renewed.

The growing population and the consequent higher demand for food and other goods will lead to an increment in the water consumption, which has increased markedly over the last 50 years and is expected to grow more in the future: water withdrawals are predicted to increase by 50% by 2025 in developing countries, and by 18% in developed countries [8]. Figure 1.1 shows the trend of the cumulative water withdrawal for the agricultural, domestic and industrial sectors.

The water resources are being consumed at a faster rate than they can be replenished, and it is estimated that by 2025, 1,800 million people will be living in countries or regions with absolute water scarcity, and two-thirds of the world population could be under water stress conditions [8]. Continuous withdrawal from surface waters and underground aquifers and factors such as pollution of freshwater resources and inefficient use worsen the situation.

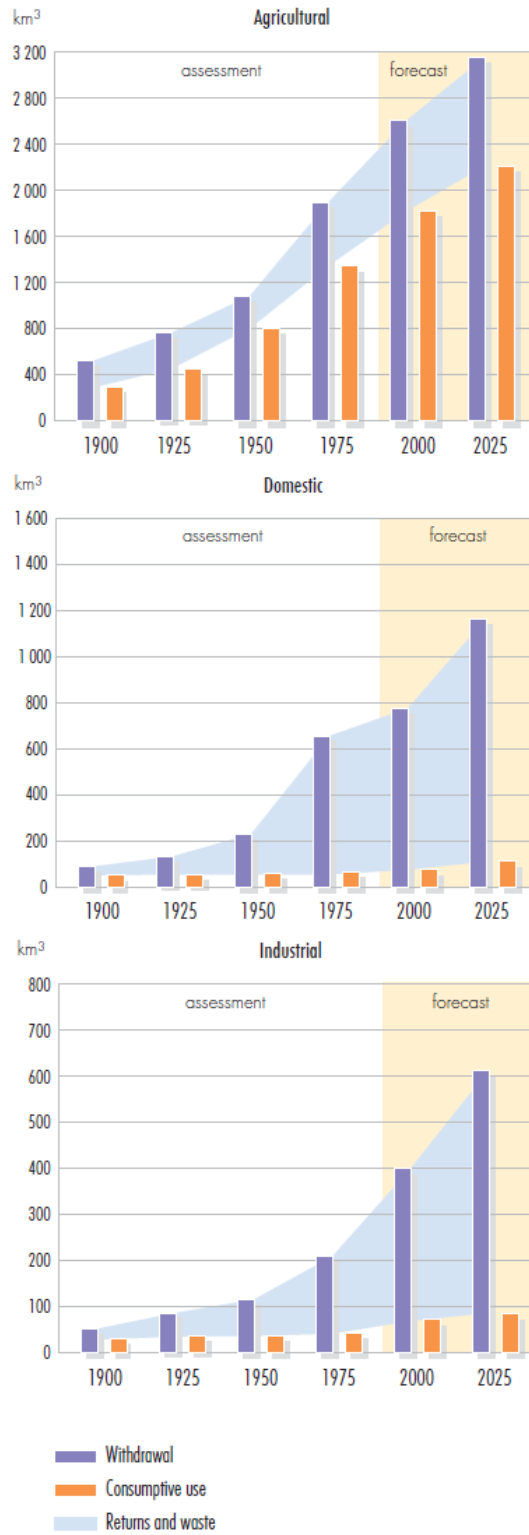


Figure 1.1 – Cumulative global water use by sector [8].

The optimization of water use is of key importance in order to cope with these issues and to employ this resource in the most efficient way. Engineering knowledge can make an important contribution here, especially in the industrial field. In industry, water is used mainly for processing, cooling and washing. The major water using industries include steel, chemicals, and petroleum refinery [9]. If water is not recycled internally in the plant, the water demand of the industrial site needs to be supplied with external water sources, thereby leading to additional expenses. The water effluents generated need to be treated to comply with the environmental limitations in force and the cost associated with this treatment can have a more or less high impact on the operating costs, which are desired to be as low as possible. These reasons, along with the aforementioned shortage of freshwater and its increasing cost, provide a strong motivation for developing approaches and techniques to design more efficient and cost-effective water networks. The increasing importance of these factors in very different industrial sectors motivates the need for systematic design tools for water management systems.

Wastewater treatment is of major relevance for water management systems. The wastewater originating from different process units in an industrial site can be discharged or reused after total or partial treatment, depending on the limitations imposed by discharge receiving locations and water using processes.

In almost all plants, wastewater must be treated before release in order to remove contaminants to comply with environmental regulations. The standard practice is to merge the various contaminated wastewater streams produced in a plant into a single wastewater stream which is then treated in a centralized wastewater treatment plant. The treatment is often divided into three stages: primary, secondary and tertiary treatment. Various methods are used depending on the pollutants to be removed. The treatments can be classified on the basis of the removal principle as physical, chemical, biological or thermal. This is further discussed in section 1.2.

The practice of merging the streams together has the consequence of obtaining streams which are more difficult to treat due to their complex composition, thus causing higher processing costs. In distributed wastewater treatment systems, the streams to be treated are either treated separately or only partially mixed, and this enhances the efficiency of the treatment and reduces the flow rate to be processed, and consequently the investment. This suggests that an efficient design of effluent treatment systems should segregate the streams for treatment and combine them only if it is appropriate.

Another issue related to the wastewater management is the possibility of using part of the wastewater in other process units present in the plant which require water. This can be done without treatment (water recycle) or with partial treatment (water reuse). The advantage of this practice is to reduce the freshwater consumption, thus reducing the cost associated with it that can be high for plants situated in water scarce sites, and leading to a more environmentally friendly process. Furthermore, reusing water can be more cost-effective than disposal if stringent limitations are imposed on the wastes or the discharge. This is the basis of the zero water discharge concept, which has been regarded with interest in the last decades.

Thus, research in the area of wastewater management is needed for a mindful use of water to minimize the costs associated with its handling and to decrease the environmental impact of process plants. The aim of this work is to develop a methodology which can be used for the design of water networks in industrial sites, with special focus on the wastewater treatment aimed at both release and recycle.

1.2 Wastewater treatment: an overview

A review of the literature provides the following observations. A large variety of pollutants can be present in industrial wastewater, ranging from free oil, suspended solids, hydrocarbons, heavy metals, salts, and pathogens. Some characteristics of wastewater are also important to determine its degree of contamination, such as its alkalinity, odor, turbidity etc. The type and the amount of contaminants present in the wastewater is highly dependent on the industry which generates it. A number of laboratory analysis are available to quantify the contamination of a certain water stream, but not all the species present can be traced, especially if their amount is small. Wastewater normally contains a very wide range of different organic compounds and a quantification of the amount of each individual compound would be impossible. Different collective analyses which comprise a greater or minor part of the organics are commonly performed; the most used ones are the biochemical oxygen demand over 5 days (BOD_5^1), the chemical oxygen demand (COD^2), the total organic carbon (TOC^3). Nutrients such as nitrogen and phosphorous can be present in various forms in the wastewater effluents, and the amount discharged must be monitored to avoid eutrophication. Sulfurous compounds are usually associated with unpleasant odors and can be dangerous for the environment. Heavy metals are often toxic and their discharge must be controlled. Also the alkalinity and the temperature at which the wastewater is discharged can alter the natural conditions of the receiving water surface. Oil and grease and suspended solids may be harmful for the environment and are subject to regulations. Other compounds of known toxicity, such as phenols, benzene etc., deserve attention in case they are present. If the water is to be recycled to process units, its hardness must be also monitored in addition to the previous contaminants, so ions like magnesium or carbonate become important.

The goal of the wastewater treatment is to reduce the pollutants contained in the wastewater stream to an acceptable level for discharge in the environment. There are generally three stages of wastewater treatment: a primary treatment, based on physical operations to remove free oil or suspended solids; a secondary treatment for removal of dissolved contaminants through chemical or biological action; and a tertiary treatment for removal of residual contaminants. The following gives a broad overview of the technologies commonly employed in industry. A complete and descriptive overview of technologies and issues related to wastewater treatment operations is found in [10, 9]. In the following, a short summary is given based on the information reported in these same sources.

In the primary treatment, free oil and solids are separated by sedimentation, filtration or grit removal. Equipment which is usually employed in industry includes the American Petroleum Institute (API) separator and/or the corrugated or parallel plates interceptor (CPI/PPI),

¹The biochemical oxygen demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to degrade organic material present in a given water sample at certain temperature over a specific time period. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20 °C (BOD_5). [9]

²The chemical oxygen demand (COD) is the amount of dissolved oxygen needed to oxidize organic material present in a given water sample to CO_2 , NH_3 , H_2O at certain temperature over a specific time period. The COD value is most commonly expressed in milligrams of oxygen consumed per liter. [9]

³The total organic carbon (TOC) measures the CO_2 released from the total oxidation of the organic matter in the wastewater. The TOC is a good measurement of the total amount of carbonaceous species in the waste water, but does not give information on their oxidation state and hence no information on how much oxygen is needed for their oxidation. [9]

where free oil floats on the surface and solids settle to the bottom, where they are skimmed and scraped off, respectively. Other physical or chemical methods are used to separate the remaining emulsified oil from the wastewater, with or without the addition of coagulants: induced air flotation or dissolved air/nitrogen flotation (IAF/DAF/DNF) systems are common physical separation methods. These treatment processes produce a solid and oily sludge which is often hazardous and that must be treated before disposal. Common treating methods for sludge comprise dewatering and incineration.

Secondary treatment often consists of biological operations where dissolved hydrocarbons and other organic components are consumed thanks to the action of microorganisms. These can be distinguished between suspended growth processes, in which the biological sludge is suspended in the wastewater to treat, and attached growth processes, in which the microbial activity takes place on a fixed support. An example of the first type is the activated sludge systems, where the bacterial mass is suspended in the wastewater in a basin, then it is separated through a clarifier and is then recycled back; examples of the second type are the trickling filter or the rotating biological contactor, where a biofilm grows on a fixed bed or on a rotating shaft with disks, respectively. Aerated lagoons or stabilization ponds are also examples of suspended growth processes: they consist of a basin in which wastewater is allowed to rest under the action of biomass; however, these are not so common due to their large ground requirements. The activated sludge process can be enhanced with addition of powdered activated carbon (PACT process); this alternative can be used in substitution to a traditional activated sludge for better performance. Another biological process which is often employed for the treatment of industrial waste is the membrane bioreactor, which is a combination of an activated sludge with a microfiltration membrane. Depending on the operating conditions and on the presence of oxygen, a biological treatment can accomplish also nitrification (conversion of ammonium to nitrite and then to nitrate) and denitrification (conversion of nitrate to nitrogen gas), thus acting also towards the reduction of the nitrogenous species contained in the wastewater. These biological treatment processes produce a biomass sludge that must be dewatered and treated before disposal.

Tertiary treatment is installed where the wastewater needs further treatment in order to meet the discharge limitations or to be recycled for use in the plant. Tertiary treatment comprehends a variety of options which rely on a wide range of techniques, for example stripping with air or steam, adsorption on activated carbon or sand, oxidation with chlorine, hydrogen peroxide, or other oxidants, precipitation of metals or phosphorous, filtration with fine membrane such as microfiltration, nanofiltration, ultrafiltration or reverse osmosis. Disinfection is necessary in case pathogens are present in the wastewater stream.

In a wastewater treatment plant, neutralization and equalization are often needed to dampen variations in wastewater flow rate and pollutant load to reduce the negative impact that shock loads can have on downstream processes.

The choice of one or the other treatment alternative, as well as their specific design, depends on the type and the level of contaminants present in the wastewater. Most of the contaminants and the treatment options mentioned above are common to any type of industrial wastewater treatment plant, however, the structure of the wastewater treatment, the operating parameters and the specifications for each unit must be tailored for the specific site in order to achieve the best performance. Usually, a certain treatment train is used to treat a specific type of industrial wastewater and the choice relies mostly on common practice and previous experience.

1.3 Water in oil refineries

Water management in oil refineries represents an interesting case study not only because refineries are characterized by an intensive use of water, but also because they are often located in countries which are scarce in freshwater. Additionally, refineries are very different from each other in terms of water flow rates involved and level of contaminant present in their wastewaters, as well as in terms of configuration of water users and producers, which depends on the complexity of the specific refinery considered.

The world refinery capacity in 2010 was 88.677 millions of barrels per day, of which 28% is located in Asia and the Pacific, 28% in Europe, 22% in North America and 9% in the Middle East [11]. Petroleum refineries range in size from small plants that process about 150 barrels of crude oil per day to giant complexes with a capacity of more than 600,000 barrels per day [12]. A typical refinery flow diagram is shown in Figure 1.2. The crude is sent first to the crude distillation unit, where light and heavy fractions are separated; the heavy fractions are sent to the cracking operations (coking, visbreaking, catalytic cracking and hydrocracking), which break down large and heavy hydrocarbon molecules into smaller ones through the application of heat or through the use of catalysts. Other refinery operations involve the combination of hydrocarbons, where two or more hydrocarbon molecules are linked together to form a larger molecule (e.g., conversion of gases into liquids). Alkylation and polymerization combine smaller molecules to produce high octane gasoline blending stock. Catalytic reforming and isomerization are commonly used for hydrocarbon rearrangement, which involves the alteration of the original structure of the molecule to produce a new molecule with different characteristics. Other units deal with the processing of petroleum products to remove sulfur, nitrogen, heavy metals, and other impurities. Blending is the last phase of the refining process and is used to obtain the desired final products. In addition, a variety of processes are employed to produce specialty products such as lubricating oils, greases, waxes, and asphalts.

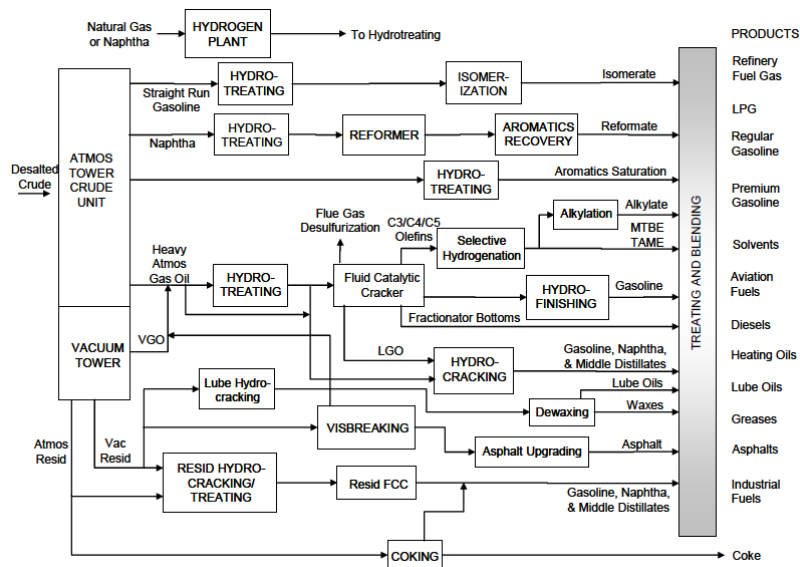


Figure 1.2 – Typical oil refinery flow diagram [13].

The amount of water used by a refinery can vary significantly, depending on process configuration, refinery complexity, capability of recycle, degree of sewer segregation, and local rainfall. In 1992, the average amount of fresh water used in refineries in the United States was estimated between 65 and 90 gallons per barrel of crude oil processed (between 1.55 and 2.14 m³ of water per m³ of crude oil), while the amount discharged via National Pollutant Discharge Elimination System (NPDES) permit or to public water treatment facilities was estimated to be in the range of 20 to 40 gallons per barrel of crude (between 0.48 and 0.95 m³ of water per m³ of crude oil) with once-through cooling water and no coking [13]. Refinery process wastewater flow rates reported in EPA's 1996 Preliminary Data Summary range from 0.4 to 8.1 million gallons per day, which equals to 150 to 3,000 million gallons per year. The median flow rate for a refinery was 1.5 million gallons per day and the average 2.3 million gallons per day. Much of this water is moderately or highly contaminated, requiring primary, secondary and sometimes tertiary treatment.

In refineries, water is used as cooling water, boiler feed water, and for washing operations, as well as in any other chemical processing industry. Additionally, water is heavily employed in the form of steam in many units, such as crude distillation, steam stripping, coking, hydrocracking, visbreaking, sweetening, hydrotreating, alkylation, etc.; water is also used in the desalter to remove solids and salts from the crude prior to sending it to the crude distillation units. Figure 1.3 shows the typical distribution of water consumption in a refinery.

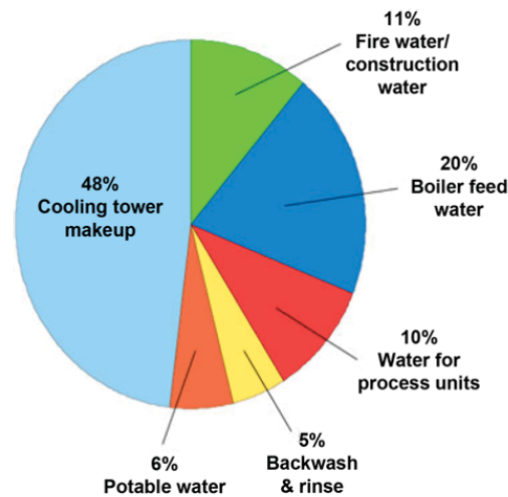


Figure 1.3 – Water use in oil refineries [14].

The wastewater produced by refinery processes is highly variable in flow rate and composition. Wastewater typically contains hydrocarbons, dissolved materials, suspended solids, phenols, ammonia, sulfides, and other compounds. Sources of wastewater include condensed steam, stripping water, spent caustic solutions, cooling tower and boiler blowdown, as well as wash water, alkaline and acid waste neutralization water, and other process-associated water. The amount and composition of wastewater discharged is specific to each refinery and is dependent upon the properties of the crude oil, the type of processing units, the final

product mix, and the method of treatment and disposal [15]. Table 1.1 shows the amount of wastewater produced in the various refinery operations. More detailed information on the production of wastewater from the various processing units can be found in the report Energy and Environmental Profile of the U.S. Petroleum Refining Industry [13] and in the Handbook of Industrial and Hazardous Wastes Treatment [12]. Many refinery operations generate sour wastewaters. Sour wastewaters generally result from water brought into direct contact with a hydrocarbon stream (e.g. when water is used as a washing medium or steam is used as a stripping or mixing medium). Sour wastewaters contain sulfides, ammonia, phenols, and other organic chemical constituents of the crude oil [15]. Another kind of wastewater generated is spent caustic. Spent caustics come from the use of caustics to neutralize acid solutions and to extract acidic materials that may occur naturally in crude oil, acidic reaction products that may be produced by various chemical treating processes, and acidic materials formed during thermal and catalytic cracking such as H_2S , phenolic compounds, and organic acids [12]. Caustics are also added to desalting water to neutralize acids and reduce corrosion, and are employed for washing the isomerization, alkylation and drying and sweetening units. Phenols are expected to exist in high concentration in the spent caustic streams [16].

Wastewater from various refining processes is treated by both primary and secondary processes, and some refineries must also employ polishing to meet discharge limitations. Sour wastewater from distillation units and fractionators contains high level of ammonia and sulfides, so it is commonly treated prior to mixing with the main wastewater stream. This is usually done by stripping it in a tower with air or steam where hydrogen sulfide, other organic sulfur compounds, and ammonia are removed. Then, the wastewater can be discharged to the primary treatment or to the secondary treatment. The stripped water is normally reused in the desalter, since this unit usually does not require water of high grade [17, 18]. A scheme of the wastewater treatment structure usually implemented in refineries is shown in Figure 1.4.

The discharge limits to open surfaces (sea, river, etc.) or to a municipality sewer are highly dependent on the location of the refinery. Also the maximum levels allowed for each contaminant in the water sent to recycle are highly specific with the industrial site. The contaminants which are usually set under regulation for refineries are nitrogen as ammonia, 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total and hexavalent chromium, oil and grease, phenolic compounds, sulfides, total suspended solids, pH and temperature. For example, in the United States, limitations for wastewater effluents for refineries are set by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419 [19] on the daily maximum amount of discharge and on the average over 30 days, accounting for the category of the refinery (topping, cracking, petrochemical, lube, or integrated) and a size factor.

Table 1.1 – Sources of wastewater in oil refinery, adapted from [13].

Process	Largest Sources of Process Wastewater	Flow [gal/bbl]	% of total
Crude Distillation	Oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol).	26.0	44%
Fluid Catalytic Cracking	Sour wastewater from the fractionator/gas concentration units and steam strippers (high levels of oil, hydrogen sulfide, ammonia, suspended solids, phenols, cyanides).	15.0	26%
Catalytic Reforming	Process Sour wastewater (hydrogen sulfide, ammonia, suspended solids, mercaptans, oil).	6.0	10%
Alkylation	Wastewater from water-wash of reactor hydrocarbon products (suspended solids, dissolved solids, hydrogen sulfide). Spent potassium hydroxide stream (hydrofluoric acid).	2.6	4%
Crude Oil Desalting	Hot salty process water (salts, metals, suspended solids, hydrogen sulfide, ammonia, phenol).	2.1	4%
Catalytic Hydrocracking	Sour wastewater from the fractionator and hydrogen separator (hydrogen sulfide, ammonia, suspended solids).	2.0	3%
Thermal Cracking or Visbreaking	Sour wastewater from the fractionator (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids).	2.0	3%
Coking	Coke-laden water from coking operations in delayed cokers. Sour water (hydrogen sulfide, ammonia, suspended solids).	1.0	2%
Isomerization	Sour water (hydrogen sulfide, ammonia) and caustic wash water (calcium chloride and other chloride salts).	1.0	2%
Catalytic Hydrotreating	Sour wastewater from the fractionator and hydrogen separator (hydrogen sulfide, ammonia, suspended solids, phenols).	1.0	2%
Ether manufactures	Pretreatment wash-water (nitrogen contaminants); cooling and alcohol wash water are recycled.	≤1.0	
Sulfur Removal or Claus Process	Sour wastewater (hydrogen sulfide, ammonia).	≤1.0	
Lubricating Oil Manufacture (deasphalting, solvent extraction, dewaxing)	Steam stripping wastewater (oil and solvents) and solvent recovery wastewater (oil and propane).	≤1.0	
Sweetening/ Mercox Process	Little or no wastewater generated.	-	

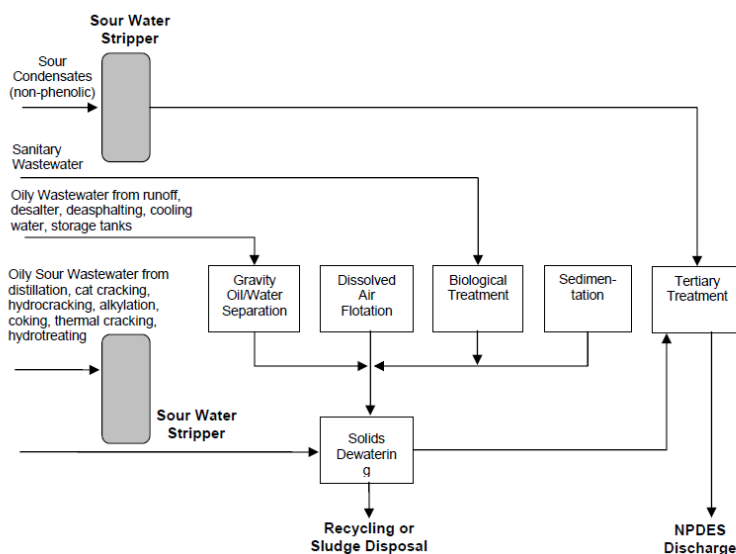


Figure 1.4 – Typical oil refinery wastewater treatment scheme [13].

1.4 Water network synthesis: current state of the art

Two main methodologies have been employed for the synthesis of water networks and water integration: insight-based methodologies and optimization-based methodologies. Also hybrid methods between the two exist, which use the first approach to locate a feasible starting point for an optimization procedure.

The most important technique belonging to the first group is the water pinch technology, which relies on mass exchange networks (MENs) techniques based on a graphical approach similarly to the method employed for the design of heat exchanger networks (HENs). The wastewater that can be integrated allocating it to the different water using processes is found on the basis of the available streams and their level of contamination. A complete review of the achievements obtained with this approach was recently published by Foo [20]. This technique is more immediate, but it is suitable only for simple problems which involve a limited amount of streams and at the most one contaminant.

The second methodology relies on a mathematical formulation of the water network based on a superstructure in which wastewater sources to treat, treatment objectives and water using units and/or treatment units are connected to each other. The problem is formulated as an optimization problem where the objective function is usually minimum freshwater consumption or minimum total cost, and gives as a result the best network configuration using the flow rates as optimization variables. This approach can in principle handle a higher number of streams and contaminants and consequently it has a high potential for application to complex and large problems with more completeness. On the other hand, it often results in the formulation of large and complex optimization problems, whose solution is not trivial, and may require effective approaches to handle numerical difficulties and the availability of reliable solution techniques. Since the attempt of the present work is to face the problem through mathematical optimization, in the following the focus is on this second alternative.

The basics of mathematical optimization are described in [21]. Mathematical optimization is a quantitative tool for decision making. Its goal is to find the values of the variables involved in the process that yield the best value of a certain performance criterion. The optimization problem is defined by an objective function to be optimized and the constraints, which are represented in form of equality or inequality equations; both are function of a certain number of variables and fixed parameters. In the optimization of chemical processes, the objective function is often a cost function and the constraints constitute the model of the process. Most of the problems encountered in chemical engineering involve both continuous and discrete variables; in this case, the optimization problem is called mixed integer programming problem. The optimization problem is linear if the objective function and all the constraints are linear, or non-linear if one or both are non-linear. In the first case, the problem is called Mixed Integer Linear Programming (MILP), or Linear Programming (LP) if it involves only continuous variables; in the second case, the problem is called Mixed Integer Non-Linear Programming (MINLP), or Non-Linear Programming (NLP) if it involves only continuous variables. A feasible solution is a set of variables that satisfies the constraints. The collection of all the feasible solutions is called feasible region. An optimal solution is a feasible solution which provides an optimal value of the objective function. In some cases there is a unique optimal solution, in some other not. The optimal solution can be absolute (or global) or relative (or local). The problem can be convex or non-convex. For convex problems, the global optimum can be reached more easily and it is easier to prove its globality, while for non-convex problems this is not the case. While proven and reliable solution strategies exist for linear problems (LP and MILP), the solution strategies for non-linear and especially non-linear mixed integer problems (NLP and MINLP) are still object of study. The difficulties in solving these problems arise from the non-linear nature of constraints and objective function. The algorithms for solving MINLP problems often involve an iterative procedure and they can be divided into two classes: algorithms that work with NLP tree evaluation (branch and bound methods) and algorithms that decompose the MINLP problem into NLP and MILP subproblems which are solved sequentially (outer approximation methods or other techniques).

The problem of the synthesis of water management systems has been decomposed into the design of two interacting subsystems: one problem is the freshwater and wastewater allocation to the processing units which use water and the other is the wastewater treatment problem. Some of the networks presented in literature deal with the allocation of water and/or wastewater considering both water using processing units and water treatment units, while some others consider only one of the two. The water network can represent the interaction between wastewater producer units and water user units differently. The first option is to solve a total water network, thus having water using processes and water treatment operations combined into a single network with freshwater as inlet stream and water to discharge as outlet stream, like for example in Karuppiah and Grossmann [22]. The second option is to set the water demands of water using processes as treatment objectives (water sinks) and the wastewaters produced by them as sources along with freshwater (water sources), as for example in Khor et al. [23]. A good review on the design of wastewater networks can be found in [24].

Mathematical optimization was initially applied to the study of water networks by Takama et al. in 1980 [25], who solved a water network for a refinery including both water using processes and water treatment processes. This can be considered as the seminal paper in this area. Since then, many researches have focused on the optimization of water networks

by using linear or non-linear programming. Refinery wastewater has been object of a lot of studies due to the fact that refineries are among the chemical plants with the largest water consumption and that they are usually located in freshwater scarce countries. A review article on design procedures for water networks in process plants, with special emphasis on refineries, was published by Bagajewicz in 2000 [26]. Significant contributions in the 90s were given by Doyle and Smith [27], Alva-Argaez et al. [28] and Huang et al. [29].

The wastewater network treatment problem is generally formulated including wastewater sources with known flow rate and composition, treatment processes with their design model and water sinks on which limits on contaminant concentrations and flow rate are imposed. The variables of the models are the total flow rate of water, which is considered constant, and the concentrations of the contaminants, which often amount to a small number. The objective is to design a network which minimize or maximize a certain performance index (usually the total cost or the freshwater consumption) and the optimization variables are the flow rates sent to the various treatment units present in the superstructure. Usually, the models of the treatment units are simplified to a given removal ratio of the contaminants, as for example in Galan and Grossmann [1], or to fixed outlet concentrations, as for example in Ponce-Ortega et al. [2]. The investment cost is based on a function of the nominal flow rate and it can be linear or non-linear, and often also the operating cost is expressed as a function of the total flow rate. The optimization problem is mixed integer if binary variables are associated with the selection of the different treatment units and can be linear or non-linear depending on the mass balance equations and on the cost objective function considered; the most common situation is to have a non-convex mixed integer non-linear problem (MINLP).

The solubility of these MINLP problems is the heart of the challenge, since often the optimization problems originated from water network models are large scale and non-convex, which are not easy to handle numerically and present various local optima. For this reason, many papers have addressed the problem of finding a global optimum for quite simple water networks. A number of papers have been reported to handle the non-convex terms within the models through the use of deterministic optimization techniques and algorithms that employ mathematical decompositions; significant progress has been made in global optimization methods, even if they often require a certain computational effort. Important contributions towards the possibility of reaching global optimality were given by Grossmann and coworkers. The solution of water networks with techniques for global optimization are treated in Grossmann and Galan [30], Lee and Grossmann [31], Karuppiah and Grossmann [22] and others. In their most recent works, Galan and Grossmann [1] proposed a comprehensive superstructure with processing units which are more connected to reality, even if they are modeled as blocks without giving details on them except for cost and waste.

As discussed above, in most of the literature works presented, the wastewater treatment units are represented as blocks in which a certain contaminated flow enters the unit and a certain percentage of contaminant is found at the outlet, thus neglecting the engineering complexity of the treatment unit. Some exceptions exist, such as Khor et al. [23], who consider a detailed model for the reverse osmosis unit - however, in their network only this treatment unit is present, and Dzhygyrey et al. [32], who consider removal ratios which are function of the inlet flow rate and concentrations.

It is evident that the general trend is towards the solution of rather specific case studies with a simple representation of the processes involved. Since limits are posed by the difficulties encountered in the solution of the MINLP problems, often a lot of emphasis is put on

the development of robust optimization techniques and on the research of the global optimum rather than on giving a descriptive model of the water treatment units. For the same reasons, the network developed often involve few treatment alternatives and few contaminants. As a consequence, most studies represent a rather academic illustration with simplified water networks, which accounts for a reduced number of contaminants and process alternatives, that are often represented as black boxes; only a few papers covered case studies of actual industrial size or a more detailed modeling of the treatment units, which may be important in the design or redesign stage of a wastewater management plant. Thus, the field is dealing with a still open problem and there is still need for robust and flexible approaches that are able to handle the complexity and the dimension of an actual industrial problem, and that will find wider application in practice.

1.5 Outline of the work

As highlighted in section 1.4, the literature works which deal with the problem of optimal water treatment and allocation through mathematical methods propose networks with few contaminants and often do not consider issues of key importance for process equipment, such as limiting inlet concentrations and flow rates, utility consumption and other engineering aspects which may be important for wastewater treatment units when taking design decisions. Additionally, the case studies treated deal with small networks which are of academic interest only. Thus, these networks are arguably not fit to manage the complexity of a real industrial case.

The aim of this work is to develop a systematic framework for the formulation and solution of water networks which can give a more realistic representation of a real industrial case. The intent is to tackle the problem through mathematical programming in a way which is more close to reality through a descriptive modeling of the treatment units and a complete characterization of the water stream. The water network is built comprising wastewater sources and available treatment units to reach certain defined treatment objectives, which include both discharge and reuse options. The network is solved though mathematical optimization making use of simplification strategies suggested by engineering insights to reduce the complexity of the problem when necessary. The methodology must be flexible with respect to different types of industrial wastewater, so that it can be applied to a number of case studies without major modifications, and with respect to the evaluation of the effect of different scenarios e.g. different optimum criteria, different possible environmental regulations on water discharge, different contaminant loads on purified water to recycle etc. The methodology proposed can be used effectively for the design of new wastewater treatment plants as well as for retrofit or expansion of existing plants.

In Chapter 2, the methodology employed and the models and the tools underlying it are presented. In Chapter 3, the methodology is applied to a case study of refinery wastewater. The huge water consumption and the high variability of wastewater sources and objectives make the refinery wastewater treatment a problem which is interesting to study and which is of significant industrial interest. Then, Chapter 4 presents the conclusions and some indications for further work.

Chapter 2

Method

This chapter describes how the water network problem is posed and the models and tools underlying the methodology used to solve it. The problem is posed as follows: given a set of wastewater streams, a set of treatment objectives to reach, and a set of treatment technologies organized in a superstructure, identify the configuration of the treatment process which maximizes or minimizes a certain performance parameter. In order to rationalize the problem and allow for the systematic treatment of any case study, a methodology which relies on mathematical optimization is developed. The steps of the methodology and a description of them is presented in section 2.1. The models used for the characterization of the water stream and for the mathematical representation of the water network are exposed in section 2.2. Finally, in section 2.3 it is shown how the optimization problem is formulated and solved.

2.1 Methodology

The methodology employed goes through the following steps:

1. Problem definition

- Scope statement
- Identification of the wastewater sources
- Identification of the treatment objectives

2. Network definition

- Division of the treatment operation in removal tasks
- Identification of process alternatives for each removal task
- Superstructure definition

3. Model development

- Modeling of each treatment alternative according to a common structure
- Mathematical modeling of the network

4. Optimization problem formulation and solution

- Formulation and solution of the MILP/MINLP optimization problem
- Analysis of the uncertainties
- Analysis and discussion of the results

The problem definition involves the definition of the scope that is desired to achieve and the identification of the wastewater sources to treat (in terms of flow rate and concentration of contaminants), which can be in-plant or external, and of the treatment objectives (in terms of the limitations on the maximum flow rate and concentration of contaminants imposed on them), which can be either discharge or recycle options. The two are connected by the treatment operation, which is organized in tasks on the basis of the pollutants removed or of the removal principle, and for each task different alternatives are proposed; this constitutes the superstructure configuration. Each of the treatment units is modeled according to a common framework, and the different treatments differ only in the parameters of performance and cost employed - this is done in the attempt to get a trade-off between the representation of the relevant elements of the treatment units and the simplification needed to model them in a way to originate an optimization problem which is easy to solve. Then, the mathematical model underlying the network is solved as an optimization problem having the desired criterion to optimize as objective function. Once the optimal network with respect to the desired objective has been identified, the same superstructure can be used for the evaluation of different scenarios, e.g. different optimum criteria, contaminant level of the wastewater sources, environmental regulations on discharge, contaminant load on purified water to recycle etc.

The key novelties of the proposed framework are the inclusion of environmental and chemical engineering insights in the water network built, which allow for a comprehensive characterization of the water stream and a more descriptive model of the treatment processes considered. These characteristics make the methodology able to handle the complexity and the dimension of an actual industrial problem and flexible with respect to the needs of evaluation of the user, thus making it suitable for ready application to different case studies. The methodology can be used to face different case studies by tailoring the input data - wastewater sources, treatment objectives, treatment units, superstructure organization, and the various parameters. The methodology could be employed for design of new plants as well as for retrofitting, expansion or simply optimization of existing water treatment systems.

2.2 Models

In this section, the models used for the mathematical description of the water network are exposed. In section 2.2.1, the issue of wastewater characterization is addressed: the generic characteristics of a wastewater stream are illustrated, along with the simplifications used in order to have a compact stream characterization which is as descriptive as possible; then, in section 2.2.2 the network architecture and the equations underlying it are presented.

2.2.1 Water characterization

The wastewater streams produced by a chemical plant contain thousands of different contaminants, which makes practically impossible to measure and track all of them. As it was

highlighted in section 1.4, when modeling water optimization problems the tendency is to use only the major contaminants or to lump them into a few representative ones. However, reducing too much the number of pollutants considered leads to an over-simplified view of the wastewater composition and causes a loss of the complexity of the real system. Additionally, there are properties of wastewater (such as temperature, turbidity, alkalinity etc.) which are important to track because they are of significance for the stream characterization, and often they are also subject to limitations if water is to be discharged or reused. These properties are mostly related to the chemical species present in the wastewater stream (for example, alkalinity) but sometimes they are independent on them (for example, temperature). The degree of contamination of a water stream is determined on the basis of both, thus both must be monitored.

In this work, an attempt is made to find the best trade-off between quality of the results and problem complexity of the wastewater characterization; this is done by using some environmental engineering knowledge while at the same time avoiding a too detailed and onerous characterization of the wastewater. In order to keep track of all the relevant characteristics of the wastewater, the streams are characterized by two classes of elements: the independent mass elements and the properties. The main difference between the two is that an item belonging to the former category stands as independent mass and often owns a defined stoichiometry, while an element belonging to the latter does not. In this way, it is possible to have a satisfactory characterization of the water stream both in terms of chemical species, which might be useful to back calculate other dependent properties - for example, the pH or the conductivity, and in terms of other relevant properties - for example the turbidity or the biodegradability of the contaminants. This characterization has the advantage of allowing the possibility to reduce or extend the elements considered according to the specific needs of each case study. In theory, any chemical species or any property of interest can be included in one or the other category. However, for reasons of simplicity only the most relevant ones are considered depending on the case. On the basis of the various substances involved in the wastewater treatment operations, it is expected that for any kind of wastewater case study the two types of characteristics should include:

1. Independent mass elements

- Water, H_2O
- Gases (O_2 , CO_2 , N_2 , H_2S)
- Carbonaceous species
 - $C_{18}H_{19}O_9N$, representative of non biological organic carbonaceous species
 - $C_5H_7NO_2$, representative of biological organic carbonaceous species
- Ions (among which, most often there are NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-})
- Separate liquid phase - Oil and grease (O&G)
- Separate non-organic solid phase - Inert solids (or fixed suspended solids, FSS)

Since the species representing independent mass are usually present in minor quantity with respect to water, the density of the total flow can be assumed equal to the one of water ($\rho=1000 \text{ kg/m}^3$).

2. Properties

- Total suspended solids (TSS)
- Biochemical oxygen demand (BOD₅)

While the meaning of the first is self-explanatory, the second one is a measure of the biodegradability of the carbonaceous material contained in the water stream. Other relevant properties such as temperature can be included in this category, however, this was not done in this work.

The unit in which the independent mass elements are measured is $[kg]$ or $[kg/s]$, while for the properties it can either be $[kg]$ or $[kg/s]$ - for example in the case of the total suspended solids, or any other meaningful unit - for example $[K]$ in the case of temperature. In the first case, the evolution of the property can also be represented in terms of flow rate, otherwise this is not the case. In this work, only properties of the first type are considered, and the others will be addressed in further studies.

In order to clarify the motivations behind this choice, in the following the various classes of components present in a generic wastewater stream are reviewed, and on the basis of various considerations the choice of the above species as independent mass elements or properties will be drawn.

2.2.1.1 Carbonaceous species

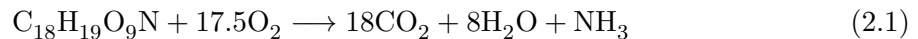
As discussed in section 1.2, the carbonaceous content of the wastewater can be quantified through the COD, BOD₅ and TOC analyses. All of these analyses provide relevant information about the carbonaceous content of the wastewater but none of them is comprehensive enough to characterize exactly the amount and the quality of carbonaceous species present. Here, the COD is chosen as a representative measure of the the carbonaceous species over which the mass balance is made. The COD is also used as a basis for the mass balance in the development of mathematical models for wastewater treatment, for example the activated sludge models (ASM1, ASM2, ASM3) [33].

The carbonaceous species included in the COD account for various kind of organic material, which can be classified as shown in Figure 2.1, similarly to the classification reported in [9]. The total COD is the sum of both biodegradable (bCOD) and non-biodegradable (nbCOD) carbonaceous material. Both the bCOD and nbCOD can be soluble (sbCOD and snbCOD) or colloidal or particulate (pbCOD and pnbCOD). Thus, the COD accounts for both carbonaceous components dissolved and those present in different phases, for example in emulsified liquid or suspended solid form. Furthermore, a correlation exist between the biodegradable part of the COD and the BOD₅ [9], but the relation between the two is usually determined experimentally and is highly dependent on the type of wastewater considered.

The distinction of the four fractions of COD is needed in order to model with sufficient detail the biological treatment units. Some mathematical relationships have been proposed in order to relate the various fraction to other properties, for example the biodegradable fraction of COD is often estimated on the basis of the BOD₅, even if the various COD fractions are better determined through measurements aimed at wastewater characterization. The BOD₅/COD ratio will frequently vary for effluents as compared to untreated wastes; furthermore, there will

be no correlation between COD and BOD₅ if the wastewater contains only slowly biodegradable organic suspended solids or refractory substances [10]. Since it is difficult to track the evolution of the various fractions through mathematical relationships and since the distinction is required only for a comprehensive model of the biological processes, the COD is not differentiated in its fractions. On the other hand, it is of interest to distinguish which part of the organic material is present as solid or as a different liquid phase and which part of it is biodegradable, because some treatment techniques rely on the basis of one or the other property and because their concentration needs to be kept under control in order to comply to effluent limitations. Thus, these characteristics are monitored including them in the model as if they were properties: part of the total suspended solids account for the portion of COD which is present as a different solid phase, and the BOD₅ indicates the biodegradability of the carbonaceous species present in the wastewater. These are included in the model as properties, since no specified stoichiometry is associated to them. However, the total suspended solids can account for both carbonaceous material and non-carbonaceous material, so only part of them overlaps with the COD. Then, it is necessary to introduce another independent mass species which account for the non-carbonaceous material present as solid of unspecified stoichiometry, the inert solids or fixed suspended solids (FSS). This will be discussed in section 2.2.1.6. Organic substances are also present as oil and grease (O&G). However, since it constitutes a well defined separate phase and part of it may not be oxidized in the COD test, it is accounted as a separate independent mass element from the COD even if it constitutes organic material.

The only distinction made on organic matter as COD is between the one that represent biomass and the one that represent substrates. This is done because when biological treatment is considered, the microorganisms contribute to the creation of carbonaceous material, which is of a different kind from the one that is already present in the wastewater: the latter constitutes the substrate thanks to which the former grows and reproduces - for more details, see Appendix B.3. The carbonaceous material which represents biomass (microorganisms) is defined in terms of the species C₅H₇NO₂ [9, 34], while the carbonaceous material which represents the substrates (carbonaceous species) is defined in terms of the pseudo-component C₁₈H₁₉O₉N [34]. In the following, C₅H₇NO₂ is indicated by the subscript M and C₁₈H₁₉O₉N by the subscript C. Assuming that the wastewater source does not contain biomass, the amount of carbonaceous species present in it is computed considering the oxygen demand for its complete oxidation, which is the COD value:



Thus, the content of carbonaceous species as COD is computed as:

$$C_C^0 = \frac{C_{\text{COD}}^0}{17.5} \cdot \frac{MW_C}{MW_{\text{O}_2}} \quad (2.2)$$

being C_{COD}^0 the concentration of COD and C_C^0 the concentration of the pseudo species C, in [mg/L]. This definition allows to consider specific organic compounds separately. If some specific organic compound needs to be monitored (e.g., benzene, phenol), it can be considered as an independent chemical species provided that the associated oxygen demand is subtracted from the total COD.

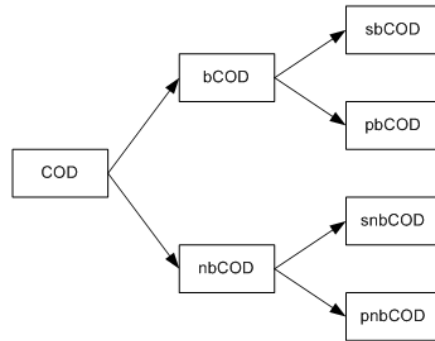


Figure 2.1 – Classification of organic compounds as COD.

2.2.1.2 Nitrogenous species

Nitrogen can be present in different forms and in different oxidation states: organic nitrogen (ON), ammonia and ammonium (NH_3 and NH_4^+ , -III), nitrogen gas (N_2 , 0) nitrite (NO_2^- , +III), and nitrate (NO_3^- , +V), as can be seen in Figure 2.2.

Organic nitrogen consists of a complex mixture of compounds and, like the COD, can be distinguished in biodegradable (bON) and non-biodegradable (nbON), both of which can be soluble or particulate (sbON and snbON; pbON and pnbON). The total Kjeldal nitrogen (TKN) is a measurement often performed on wastewaters and accounts for organic nitrogen and ammonia ($\text{ON} + \text{NH}_3/\text{NH}_4^+$). For simplicity, organic nitrogen is considered as already included in the carbonaceous account of the COD or completely hydrolyzed as ammonia or ammonium, so that $\text{TKN} \cong \text{NH}_3/\text{NH}_4^+$ and it is sufficient to monitor ammonia only.

Ammonia nitrogen can be present as either dissolved ammonia gas or ammonium ion depending on the pH of the solution according to the equilibrium reaction: $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$, $K_a = 5.62 \cdot 10^{-10}$. As a simplification, it is assumed that all the ammonia present or added to the water is fully ionized, so no NH_3 is present in the wastewater stream.

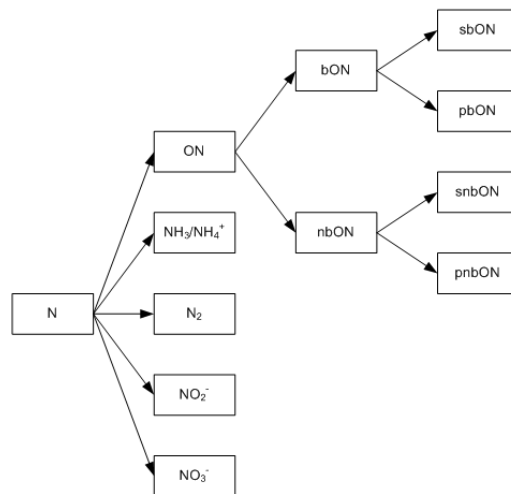


Figure 2.2 – Classification of nitrogen compounds.

2.2.1.3 Phosphorous species

As nitrogen, phosphorous can be present in different forms and in different oxidation states. Organic phosphorous (OP) consists of a complex mixture of compounds; while this is important for municipal wastewaters, it can be considered negligible in most of industrial wastes. The phosphate ion (PO_4^{3-}) can instead be present also in industrial wastewaters [10].

2.2.1.4 Sulfurous species

As nitrogen and phosphorous, sulfurous species can also be present in various forms. Here it is assumed that all the species containing sulfurous are already considered in the other species (ions, solids or organics), and only H_2S is considered as an independent species.

2.2.1.5 Metals and salts

Metal and salts are considered fully dissolved in water when present as contaminants, thus they are represented in terms of ions. Salts are considered as fully dissolved when added to water and as solids when they are removed as waste or added as utility; thus, the solubility equilibrium is neglected, even if the model could accommodate it by differentiation of the species. In theory, any ion can be included in the water characterization. In practice, in order to limit the number of species only the ions associated with the metals and the salts presents in the system will be considered. These are dependent on the specific case study treated, since the contaminants and the utilities used in the treatment units vary with them.

2.2.1.6 Total solids

The classification of the total solids (TS) is presented in Figure 2.3. The total solids (TS) are distinguished between total suspended solids (TSS^1) and total dissolved solids (TDS^2). Both TSS and TDS comprise a volatile fraction (VSS and VDS^3) and a fixed fraction (FSS and FDS^4).

The TDS are already fully accounted for as soluble COD, salts or metals (ions) and are thus no further discussed. A more detailed classification of the TSS is again useful for a comprehensive modeling of the biological treatment. The VSS can be biodegradable (bVSS) or not (nbVSS), and the FSS are considered the inert fraction of the total suspended solids (iTSS). The organic fraction of the solids is often associated with the volatile solids. Consequently, while the volatile fraction of the suspended solid is already accounted for through the COD, the fixed solid part is not. Thus, as anticipated in section 2.2.1.1, the FSS is included among the independent mass element to represent an undefined separate solid phase.

¹The TSS is the fraction of the TS which are retained on a filter with a specific pore size (usually $1.58 \mu\text{m}$) measured after being dried at a specific temperature (150°C). [9]

²The TDS is the fraction of the TS which pass through the filter and are then evaporated and dried at a specific temperature; it should be noted that what is measured as a TDS is comprised of colloidal in the range from 0.001 and 1μ and dissolved solids. [9]

³The VSS and the VDS are those solids that can be volatilized when the TSS and TDS are ignited at $500 \pm 50^\circ\text{C}$, respectively. [9]

⁴The FSS and the FDS are those solids that remain as a residue when the TSS and TDS are ignited at $500 \pm 50^\circ\text{C}$, respectively. [9]

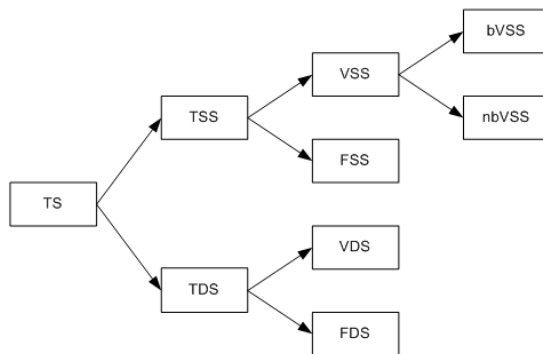


Figure 2.3 – Total solids classification.

2.2.2 Network model

The wastewater streams to be treated (sources) can reach the purified states or treatment objectives (sinks) passing through the treatment train. The configuration of the water network, i.e. the connections between the wastewater sources, treatment processes and treatment objectives, is represented in terms of a superstructure. The treatment operation is represented as a series of removal tasks in which one or more pollutants are removed. Various technological alternatives are proposed for each removal task. Thus, the columns represent a certain removal task and the rows represent different alternatives to perform it. The division in tasks is done on the basis of the type of pollutant to remove - for example, removal of H_2S , or on the principle on which the treatment relies - for example, treatments which rely on biological action belong to the same task. This duplicity arises from the need to address the removal of specific compounds, but because a treatment process often removes more than one pollutant it is difficult to organize the treatment only on this basis, thus the second criterion is introduced. For each removal task, a bypass option is introduced aside to the treatment units in order to allow the possibility of bypassing a certain type of treatment. A schematic representation of the resulting superstructure can be seen in Figure 2.4.

The various elements contained in the water network (water sources, water sinks, treatment units and bypasses) are represented in terms of blocks, or intervals. The model underlying these intervals are described in section 2.2.2.1. These equations are related to the mass balance satisfaction. In order to obtain a complete model of the network, additional equations are necessary. These are presented in section 2.2.2.2, which collects all the equations that constitute the network model: if the network is modeled in an optimization framework, these equations represent the constraints that the network has to satisfy. The objective functions which are considered are described in section 2.2.2.3. In the following, the generic characteristic of the water stream (either independent mass element or property) is denominated as t , the independent mass elements are denominated as i and the properties are denominated as j ; thus, $t = i + j$. When considering a treatment unit, the variation and the transformation of the former are considered in detail, while for the latter only the global variation over the interval is considered - this will be further discussed in section 2.2.2.1. The intervals involved in the superstructure are kk .

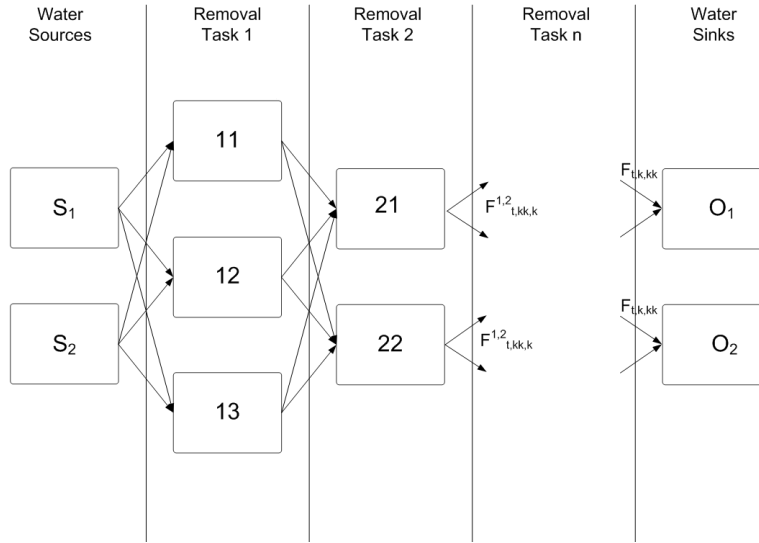


Figure 2.4 – Schematic representation of the superstructure architecture.

2.2.2.1 Models of the superstructure elements

Two kinds of intervals are considered: one representing a process interval and one representing an empty interval. The first is used to model a water treatment unit while the second is used to model a bypass, a source or a sink. The schematic representation of the two types of interval can be seen in Figure 2.5 and 2.6, respectively, and the equations characterizing them are illustrated below.

Process interval

The generic process interval is modeled on the basis of the scheme presented in [3]. It includes use of and mixing with utilities, dissolution of non-aqueous utilities in water (new element introduced with respect to [3]), reaction, waste and product separation and transportation. The cost associated with the transportation operation, which was formulated for enterprise-wide processes, is treated here as piping cost. This structure represents the most generic case according to which a treatment unit can be modeled. If one or more of the available operations is absent from a specific process interval, it could be suppressed along with the relevant variables and equations.

The variables used are the component mass flow rates, and for each interval kk the operations are modeled as follows:

- **Mixing:**

$$F_{i,kk}^M = F_{i,kk}^{in} + \alpha_{i,kk} \cdot R_{i,kk} \quad (2.3)$$

where $F_{i,kk}^M$ is the flow after mixing and $F_{i,kk}^{in}$ is the inlet flow of component i . The parameter $\alpha_{i,kk}$ is the fraction of utility i mixed with the stream out of the total utility flow consumed for the interval, $R_{i,kk}$, which is given by:

$$R_{i,kk} = \sum_t \left(\mu_{i,t,kk} \cdot F_{t,kk}^{in} \right) \quad (2.4)$$

where $\mu_{i,t,kk}$ is the specific consumption of utility i based on the inlet flow rate of element t .

- **Dissolution in water:**

$$F_{i,kk}^{aq} = F_{i,kk}^M + \sum_{rr} \sum_{react} \left(\gamma_{i,rr} \cdot \theta_{aq_{react,kk,rr}} \cdot F_{react,kk}^M \right) \quad (2.5)$$

where $F_{i,kk}^{aq}$ is the flow of component i after dissociation, $\gamma_{i,rr}$ is the reaction mass stoichiometry of component i and $\theta_{aq_{react,kk,rr}}$ is the fraction of the species $react$ which is dissolved in water; the subscripts rr and $react$ refer to a reaction and the corresponding key reactant, respectively (in this case the reaction is a dissociation reaction). As a simplification, the dissolution equilibria are not considered and $\theta_{aq_{react,kk,rr}} = 1$. The dissolution in water is taken into account only for those species introduced as utilities which do so; this is done through the proper selection of $\theta_{aq_{react,kk,rr}}$: $\theta_{aq_{react,kk,rr}} = 0$ if the utility does not dissociate or $\theta_{aq_{react,kk,rr}} = 1$ if the utility dissociates.

- **Reaction:**

$$F_{i,kk}^R = F_{i,kk}^{aq} + \sum_{rr} \sum_{react} \left(\gamma_{i,rr} \cdot \theta_{react,kk,rr} \cdot F_{react,kk}^{aq} \right) \quad (2.6)$$

where $F_{i,kk}^R$ is the flow of component i after reaction, $\gamma_{i,rr}$ is the mass stoichiometry of component i , and $\theta_{react,kk,rr}$ is the fraction of converted key reagent; the subscripts rr and $react$ refer to a reaction and the corresponding key reactant, respectively.

- **Waste separation:**

$$F_{i,kk}^{out} = F_{i,kk}^R \cdot (1 - SW_{i,kk}) \quad (2.7)$$

$$F_{i,kk}^w = F_{i,kk}^R \cdot SW_{i,kk} \quad (2.8)$$

where $F_{i,kk}^{out}$ is the flow after waste separation and $F_{i,kk}^w$ is the wasted flow of component i , and $SW_{i,kk}$ is the fraction of component i thrown away as waste.

- **Product separation:**

$$F_{t,kk}^1 = F_{t,kk}^{out} \cdot \epsilon_{t,kk} \quad (2.9)$$

$$F_{t,kk}^2 = F_{t,kk}^{out} \cdot (1 - \epsilon_{t,kk}) \quad (2.10)$$

where $\epsilon_{t,kk}$ is the split factor for separation and $F_{t,kk}^1$ and $F_{t,kk}^2$ are the two different streams of element t originated from the separation, the primary stream and the secondary stream respectively.

Each of the two product streams of the process interval kk can be sent to another process interval k :

$$F_{t,kk,k}^1 = F_{t,kk}^1 \cdot SP_{kk,k} \cdot SM1_{kk,k} \quad (2.11)$$

$$F_{t,kk,k}^2 = F_{t,kk}^2 \cdot S_{kk,k} \cdot SM2_{kk,k} \quad (2.12)$$

where $SP_{kk,k}$ and $S_{kk,k}$ contain the superstructure information ($SP_{kk,k}, S_{kk,k} = 1$ if the process intervals kk and k are connected by the primary or secondary stream respectively, $SP_{kk,k}, S_{kk,k} = 0$ otherwise). The split factors of the outgoing stream $SM1_{kk,k}$ and

$SM2_{kk,k}$ represent the fraction of the stream $F_{t,kk}^1$ and $F_{t,kk}^2$ that goes to interval k . For consistency, they should sum up to one:

$$\sum_k SM1_{kk,k} = 1 \quad (2.13)$$

$$\sum_k SM2_{kk,k} = 1 \quad (2.14)$$

If both the split factors are considered as variables, the presence of the product between $F_{t,kk}^1$ and $SM1_{kk,k}$ in equation 2.11 and between $F_{t,kk}^2$ and $SM2_{kk,k}$ in equation 2.12 is the source of the non-linearity of the problem. These bilinear terms make the problem non-convex. The model can be made linear if the flow cannot split and $SM1_{kk,k}$ and $SM2_{kk,k}$ are equal to unity, and can be made non-linear if they are allowed to vary between 0 and 1 and are considered as variables to optimize. These issues will be further discussed in section 2.3.

Thus, the incoming flow into an interval is the sum of the flows coming from the primary and secondary outlets of the other intervals:

$$F_{t,kk}^{in} = \sum_k \left(F_{t,k,kk}^2 + F_{t,k,kk}^1 \right) \quad (2.15)$$

- **Product transportation:**

This operation accounts for the cost associated to the transportation and pumping of the flow between two process intervals:

$$TranspC_1 = \sum_k \sum_{kk} \left(F_{H_2O,kk,k}^1 \cdot d_{kk,k} \cdot c_{kk,k} \right) \quad (2.16)$$

$$TranspC_2 = \sum_k \sum_{kk} \left(F_{H_2O,kk,k}^2 \cdot d_{kk,k} \cdot c_{kk,k} \right) \quad (2.17)$$

where $d_{kk,k}$ is the distance between interval kk and interval k and $c_{kk,k}$ is the cost for unit mass and unit length of the piping connecting interval kk and interval k ; for simplicity, the cost is computed on the basis of the water flow rate only.

For the independent mass elements, all the previous equations are valid. As it is evident from equation 2.4, the utilities are treated as independent mass elements since they can be mixed with the water stream and directly alter its composition. For the properties, the inlet, outlet and separation equations remain valid (2.9, 2.10, 2.11, 2.12, and 2.15 - i.e. the equations with subscript t), but the mixing, dissolution, reaction and waste are not considered (2.3, 2.4, 2.5, 2.6, 2.7, and 2.8). The outlet flow rate of these species is instead computed as:

$$F_{j,kk}^{out} = F_{j,kk}^{in} \cdot (1 - RM_{j,kk}) \quad (2.18)$$

where the coefficient $RM_{j,kk}$ expresses the global variation of property j over the interval.

In conclusion, the way in which all the treatment units are modeled is the same, and the different process alternatives differ only in the parameters assigned - $\alpha_{i,kk}$, $\mu_{i,t,kk}$, $\theta aq_{react,kk,rr}$, $\theta_{react,kk,rr}$, $SW_{i,kk}$, $\epsilon_{t,kk}$, and $RM_{j,kk}$.

Empty interval

If the process interval represents a bypass, no operation is considered because the outlet is equal to the inlet, and there will be only one outlet stream of the same composition as the inlet. Thus:

$$F_{t,kk}^{out} = F_{t,kk}^{in} \tag{2.19}$$

and equations 2.15, 2.11 and 2.13 remain valid, but in equation 2.11 $F_{t,k,kk}^1$ is computed from $F_{t,kk}^{out}$ instead of $F_{t,kk}^1$.

Since for sources and sinks only the outlet or inlet flow rate matters, respectively, they are modeled with the same structure of the empty interval. The outlet flow rate of a source is assigned to the known composition of the wastewater source $f_{t,kk}^0$ as:

$$F_{t,kk}^{out} = f_{t,kk}^0 \cdot y_{kk} \tag{2.20}$$

with kk indicating an interval representing a wastewater source. If the source is not selected, $y_{kk} = 0$ and its outlet flow is set to zero.

The inlet flow rate of a sink, $F_{t,kk}^{in}$, is assigned as for any other process interval or bypass according to equation 2.15.

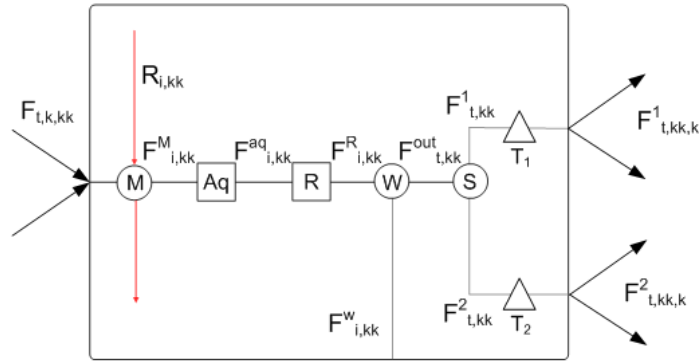


Figure 2.5 – Schematic representation of the process interval.



Figure 2.6 – Schematic representation of the empty interval.

2.2.2.2 Constraints

For the global modeling of the network, the following constraints are enforced:

1. Mass balance constraints

All the equations described in section 2.2.2 represent constraints associated with the mass balance satisfaction. Equations 2.11 and 2.12 determine if the model is linear or non-linear: if the split factors ($SM1_{kk,k}$ and $SM2_{kk,k}$) are set to 1 and are not included among the variables, then the model is linear; if the split factors are allowed to vary between 0 and 1 and are included among the continuous variables, then the model is non-linear. This will be further discussed in section 2.3.

2. Sink limitations constraints

Constraints are set on the maximum flow rate ($F_{O_o}^{max}$) and the maximum composition of pollutant t (C_{t,O_o}^{max}) of the streams to be sent to the generic water sinks O_o as:

$$F_{H_2O,O_o}^{in} \leq F_{O_o}^{max} \quad (2.21)$$

$$F_{t,O_o}^{in} \leq C_{t,O_o}^{max} \cdot F_{H_2O,O_o}^{in} \quad (2.22)$$

The constraint on the concentration is expressed in terms of flow rates and not directly in terms of concentrations as $C_{t,O_o} \leq C_{t,O_o}^{max}$ in order to reduce the non-linearities of the model, since the concentrations C_{t,O_o} would have to be back computed from the flow rate values. For the computation of the maximum flow rate of pollutant t sent to the sink (right hand side of equation 2.22), only the flow rate of water is considered since for the water sinks the flow rates of the other contaminants can be considered negligible.

3. Activation constraints (big-M constraints)

Constraints are added so that if an interval is not selected the incoming and outgoing flow rates are set to zero, as well as the internal flow rates. These constraints are introduced similarly to the big-M reformulation as a MINLP of general disjunctive programming - described in [21]. The activation of the continuous variables (flow rates) which are relevant for a specific interval kk is given as:

$$0 \leq f_{t,kk} \leq y_{kk} \cdot M \quad (2.23)$$

where M is a big enough number and $f_{t,kk}$ is the generic flow rate variable. These constraints are enforced for $y_{kk} = 1$ but become redundant for $y_{kk} = 0$. The activation constraint is given for $F_{t,kk}^{in}$, $F_{t,kk}^{out}$, $F_{t,kk,k}^1$, $F_{t,kk,k}^2$, and $R_{i,kk}$, so that if the process interval kk is not selected it has no inputs and outputs, and consequently its internal flow rates are also set to zero and the interval is completely isolated from the others. Instead, if the process interval kk is selected, those flow rates can vary between 0 and a very big number, thus they can assume the value determined by the other constraints. For example, if interval kk is not selected, equation 2.23 becomes $0 \leq f_{t,kk} \leq 0$, which is $f_{t,kk} = 0$, and if the flow rates specified above are set to zero all the internal flow rates will be set to zero according to equations 2.3-2.20, thus isolating the interval; instead, if interval kk is selected, equation 2.23 becomes $0 \leq f_{t,kk} \leq M$, which allows the flow rate $f_{t,kk}$ to assume any value lower than M which is determined by equations 2.3-2.20.

4. Flow rate limitation constraints

A lower limit is set on the flow rate which can be sent to a certain interval kk . This is done because it is worth selecting a certain interval or increasing the network complexity only if a reasonably high amount of flow rate is involved. For a specific interval kk , the constraint is given as:

$$\sum_i F_{i,kk}^{out} \geq a \cdot y_{kk} \quad (2.24)$$

where a is a coefficient which is chosen depending on the magnitude of the flow rates involved in the problem. In this way, the minimum flow rate that is sent to an interval is reasonably high to consider the selection of the interval itself. The summation is done on i to account only for the independent mass.

5. Logical constraints

Logical constraints are added to enforce logical relationships between the binary decisions.

The first type of logical constraints is used in order to avoid the selection of elements of the equipment downstream unless they are preceded by some elements of the equipment upstream - e.g. a biological treatment cannot be chosen if no primary treatment is chosen, or a tertiary treatment cannot be chosen if no biological treatment is chosen. This is done as an alternative to set constraints on the maximum inlet concentrations of some contaminants, in order to relax them e.g. a wastewater containing too much oil and grease cannot be fed to the biological treatment unit because it would upset it, etc. These constraints are of the type:

$$\sum_{kk} a_{kk} \cdot y_{kk} \geq 0 \quad (2.25)$$

where the coefficients a_{kk} assume the value of 1 or 0 and are determined by the network structure. These constraints are specific for the network studied, thus they will be discussed for the specific case study treated.

The second type of logical constraints are in the form of 2.26 in case the stream is not allowed to split or of 2.27 in case the stream is allowed to split:

$$\sum_{kk} y_{kk} \leq 1 \quad (2.26)$$

$$\sum_{kk} y_{kk} \leq 2 \quad (2.27)$$

for the kk belonging to the same removal task. Constraint 2.26 forbids the streams to split while passing from a removal task to the following, because it imposes the selection of only one treatment alternative per removal task. Constraint 2.27 allows the selection of two alternatives per removal task at the most; this makes sense in first instance since in case more than one element per column is selected the interest would be in the selection of a treatment option and the bypass, which allows to save some cost and to avoid overtreating the stream. This may exclude some feasible configurations which have a better value of the objective function, but allowing for an excessive complexity of the network is judged not reasonable.

2.2.2.3 Objective function

The objective functions considered are:

1. Minimum annualized total cost

The annualized total cost is computed as:

$$Z_1 = \frac{Capex}{A} + Opex - Savings \quad (2.28)$$

where $Capex$ is the total capital cost, which is annualized on a plant lifetime A of 15 years, $Opex$ is the total operating cost, and $Savings$ is the saving associated with the water recycle, if present. The annual operating hours are assumed to be 7,500. The piping cost can be easily included considering the distance between two selected blocks and the cost of piping per unit distance. However, this is neglected in the current model. The total capital cost is:

$$Capex = \sum_{kk} Inv_{kk} \quad (2.29)$$

where Inv_{kk} is the capital cost for process interval kk , which is usually expressed as:

$$Inv_{kk} = Ac_{kk} \cdot F_{H_2O,kk}^{Bc_{kk}} \quad (2.30)$$

where Ac_{kk} and Bc_{kk} are coefficients determined by the cost function. In order to keep the objective function linear, equation 2.30 is linearized around the flow rate treated as:

$$Inv_{kk} = Ac'_{kk} \cdot y_{kk} + Bc'_{kk} \cdot F_{H_2O,kk} \quad (2.31)$$

The coefficients Ac'_{kk} and Bc'_{kk} are obtained by regression of the data in the neighborhood of the flow rate treated as described in Appendix C.3.

The total operating cost is:

$$Opex = \sum_{kk} (UtilC_{kk} + WasteC_{kk}) \quad (2.32)$$

whith $UtilC_{kk}$ is the cost of utilities and $WasteC_{kk}$ is the cost of waste for each process interval kk :

$$UtilC_{kk} = C_i \cdot R_{i,kk} \quad (2.33)$$

$$WasteC_{kk} = CW_w \cdot (b_{i,w} \cdot F_{i,kk}^w) \quad (2.34)$$

where C_i is the specific cost of utility i , CW_w is the specific cost of waste of type w and $b_{i,w}$ is a coefficient which accounts for the specific terms i to be considered in the waste cost of type w . More details about how these are computed and on the input data used can be found in Appendix C.1 and C.2.

The savings are quantified as:

$$Savings = \sum_{O_o \neq O_x} (C_{O_o} \cdot F_{H_2O,O_o}^{in}) \quad (2.35)$$

where O_x represents the sink which stands for water discharge to an open surface - which is free, and C_{O_o} is the cost that would be payed if the water user associated to the sink

received raw or treated freshwater. The cost assigned to each of the sinks is reported in Appendix C.4. No saving or penalty is associated to the water sources, since they are produced in the plant. The possibility of acquiring water to treat from an external source assigning it a revenue could be included, but it is not considered here.

2. Maximum water recycle

The amount of water recycled is quantified by the flow rate:

$$Z_2 = \sum_{O_o \neq O_x} (F_{H_2O, O_o}^{in}) \quad (2.36)$$

where again O_x represents the sink which stands for water discharge to an open surface and the remaining O_o represent recycle options.

While the constraints remain the same for any given network, different objective functions originate different optimization problems.

2.3 Optimization problem formulation and solution

In this section, it is shown how the optimization problem for the solution of the water network is formulated (section 2.3.1) and solved (section 2.3.2).

2.3.1 Formulation

First, the general formulation of a deterministic and a stochastic optimization problem and how this can be applied to the water network modeled in section 2.2.2 is discussed - in sections 2.3.1.3 and 2.3.1.2 respectively. Then, the specific types of optimization problems generated and solved for the water network modeled are presented in section 2.3.1.3.

2.3.1.1 Deterministic formulation

The objective function and all the operational and logical constraints can be formulated in terms of the generic form of a Mixed Integer Non-Linear Programming (MINLP) problem:

$$\min Z = f(\bar{x}, \bar{y}, \bar{p}) \quad (2.37a)$$

$$\text{s.t. } \bar{g}(\bar{x}, \bar{y}, \bar{p}) \geq 0 \quad (2.37b)$$

$$\bar{h}(\bar{x}, \bar{y}, \bar{p}) = 0 \quad (2.37c)$$

$$\bar{x} \in X^n \quad (2.37d)$$

$$\bar{y} \in \{0, 1\}^m \quad (2.37e)$$

$$\bar{p} \in P^l \quad (2.37f)$$

where $f(\bar{x}, \bar{y}, \bar{p})$ is the objective function and $\bar{g}(\bar{x}, \bar{y}, \bar{p})$ and $\bar{h}(\bar{x}, \bar{y}, \bar{p})$ are the vectors of inequality and equality constraints, respectively; \bar{x} represents the vector of the continuous variables which has dimension n , \bar{y} represents the vector of the binary variables which has dimension m , and \bar{p} represents the vector of the parameters which has dimension l ; X^n is a continuous feasible region of the continuous variables and P^l is a region in which the parameters can lie, both are defined by the lower and upper bounds of variables and parameters, respectively.

The formulation is valid both if the objective function is to be minimized or maximized. In the adopted mathematical formulation of the network exposed in section 2.2.2, the continuous variables \bar{x} correspond to flow rates and split factors while the discrete variables \bar{y} correspond to the selection of the various intervals - wastewater source, water sink, process interval or bypass, while the parameters \bar{p} correspond to any input data which is different from those. If a certain interval kk is selected $y_{kk} = 1$, otherwise $y_{kk} = 0$. The nature of the constraints $\bar{g}(\bar{x}, \bar{y}, \bar{p})$ and $\bar{h}(\bar{x}, \bar{y}, \bar{p})$ and the objective function $Z = f(\bar{x}, \bar{y}, \bar{p})$ were presented in sections 2.2.2.2 and 2.2.2.3, respectively. The model is linear if both the objective function and the equality or inequality constraints are all linear, otherwise it is non-linear. Independently of the linearity of the objective function, the problem presents non-linearities in the constraints (equations 2.11 and 2.12) in the general case in which the stream is allowed to split and the split factors are defined as optimization variables. So, the model is a MINLP and the optimization variables are the binary variables, the component flow rates and the split factors.

2.3.1.2 Stochastic formulation

The uncertainty in the parameters has a large effect on the results of the synthesis problem and needs to be properly considered. The wastewater sources can vary in flow rate as well as in contamination level, and the treatment available must still be able to comply with the restrictions imposed on the water sinks in order to avoid harm to the environment and assure correct operation of the water user units. Additionally, the removal of the pollutants or the extent of reaction in the various treatments varies with the conditions of the inlet wastewater, since it often depends on its composition and on the presence of inhibiting components. An important factor which needs to be taken into account is the robustness of the network, meaning its ability to operate within specification under different scenarios of wastewater flow rate, level of contamination and treatment efficiency. This justifies the use of stochastic programming to take meaningful and robust design decisions. In stochastic programming, the scope is to minimize or maximize the expected value of the objective function while ensuring feasibility over all the uncertainty range. Details on how to perform optimization under uncertainty can be found in [35], and many papers deal with this issue.

In the optimization problem formulation presented in section 2.3.1.1, the parameters \bar{p} have a certain defined value - thus the problem is deterministic. The set of parameters subject to uncertainty due to the reasons just discussed is denominated as $\bar{\rho}$. The parameters $\bar{\rho}$ can assume different values between the minimum \bar{p}^{min} and maximum \bar{p}^{max} values; any set of parameters corresponds to a possible future scenario under which the network could operate. The problem is thus reformulated in terms of stochastic programming as:

$$\min E [Z = f(\bar{x}, \bar{y}, \bar{\rho})] \quad (2.38a)$$

$$\text{s.t. } \bar{g}(\bar{x}, \bar{y}, \bar{\rho}) \geq 0 \quad (2.38b)$$

$$\bar{h}(\bar{x}, \bar{y}, \bar{\rho}) = 0 \quad (2.38c)$$

$$\bar{x} \in X^n \quad (2.38d)$$

$$\bar{y} \in \{0, 1\}^m \quad (2.38e)$$

$$\bar{\rho} \in P^l \quad (2.38f)$$

where the symbols used have the same meaning as in 2.3.1.1, except for $\bar{\rho}$, which represents a stochastic parameter, and $E [Z = f(\bar{x}, \bar{y}, \bar{\rho})]$, which is the expected value of the objective func-

tion. The formulation is valid both if the objective function is to be minimized or maximized. The expected value of the objective function is rigorously obtained from multidimensional integration of the probability distribution function of $Z = f(\bar{x}, \bar{y}, \bar{\rho})$, which can be obtained with the use of statistical tools.

In the problem treated, the multidimensional integral is approximated using a Monte Carlo based discretization. Different sets of parameters are extracted from the space P^l in order to approximate the distribution of the uncertain parameters; the sampling technique used is latin hypercube sampling (LHS) as it provides uniform coverage of the sampling space [36]. Then, the expected value of the objective function is computed through sample average approximation. The nature of the constraints and the objective function for the stochastic problem 2.38 are the same as for the deterministic problem 2.37; however, in the case of stochastic programming, the capital cost is obtained from equation 2.31 dimensioning the equipment for the highest water flow rate and the utility and the waste costs are obtained from equations 2.33 and 2.34 respectively as an average of the values computed for each sample.

The number of samples should be high enough to be representative of the population investigated. In order to make sure that the number of samples chosen is high enough, the same stochastic problem can be solved for different sets of samples having the same number of elements: if the results do not differ significantly, then the number of samples chosen is high enough to represent the characteristics of the population from which it is extracted.

The design obtained with this technique is able to accommodate different scenarios (which can be with respect to the wastewater sources pollutant levels, treatment performance etc.) still complying to the limitations imposed on the effluents, and thus represents a robust solution. However, the main drawback of this technique is that the size and the complexity of the problem grow: in the way in which the problem is formulated, every constraint must hold true for any scenario generated, thus the number of constraints grows with the number of scenarios considered. This may lead to two problems. First, it is possible that among the samples generated some prove infeasible due to the fact that the limitations imposed on the water sinks cannot be met. This is due to the assumption of constant removal and conversion and to the network topology. If such samples are present, the whole stochastic problem would be infeasible because the constraints must hold true for all the possible scenarios, i.e. for all the possible samples. Thus, in order to make the problem soluble, these must be removed. Second, the size of the problem may grow so big that it would not be possible to solve the optimization problem with the given computation capacity.

In order to face these problems, the network is solved first as a deterministic optimization problem for each of the generated scenarios. The results will indicate which of the samples generated are infeasible; these can be then eliminated from the set used to solve the stochastic problem. In addition, it is obtained a distribution of optimal processing networks under different realization of the uncertain parameters. The problem size could be reduced excluding the intervals which prove to be never optimal under the different realization of the uncertain parameters, i.e. if a certain interval is never selected for any of the samples tested, the variables and equations associated with it are removed. Then, the resulting reduced stochastic problem is solved. This does not guarantee that the solution found with the employment of stochastic programming represent a situation of global optimality, but at least makes the problem possible to solve. This is similar to what was done by Quaglia et al. [36]. Thus, the analysis performed by solving the network as a deterministic optimization problem for each of the generated samples prior to the solution of the stochastic problem is useful in order to

remove possible infeasibilities and to reduce the size of the problem in case this is needed.

The difference between the solution of the deterministic problem 2.37 and the stochastic problem 2.38 will give an indication of the measure in which the uncertainties in the parameters affect the solution.

2.3.1.3 Problems formulated

The Mixed Integer Non-Linear Programming (MINLP) originating from problems 2.37 and 2.38 can be reduced to:

1. **Mixed Integer Linear Programming (MILP):**

The MILP can be obtained from the general formulation of the problems as MINLP if the split factors $SM1_{kk,k}$ and $SM2_{kk,k}$ in equations 2.11 and 2.12 are set to 1 and are not included among the optimization variables. In this way, both constraints and objective function are linear. Thus, the optimization variables are the binary variables and the component flow rates.

2. **Non-Linear Programming (NLP):**

The NLP can be obtained from the general formulation of the problems as MINLP if a fixed binary configuration is specified, since in this case the binary variables \bar{y} are treated as parameters and not as optimization variables. Thus, the optimization variables are continuous only - flow rates and split factors.

Both types of problems are easier to solve than the general MINLP because of their reduced mathematical complexity. The solution of the two problems can prove useful for the solution of the general MINLP. The MILP can provide a good initial estimate to initialize the solution algorithm of the MINLP. The NLP can be used to challenge the global optimality of the solution found with the MINLP by solving different NLPs corresponding to different fixed binary configurations, and checking if the value of the objective function found in each case is worse than the one obtained from the solution of the MINLP. This will be further discussed in section 2.3.2.

In summary, the following problems can be formulated to face a synthesis problem:

1. **Multi-stream treatment problem**

This is the most general form of problems 2.37 and 2.38. In this case, the split factors $SM1_{kk,k}$ and $SM2_{kk,k}$ in equations 2.11 and 2.12 are allowed to vary between 0 and 1 and are included among the continuous variables. Constraints 2.3-2.27 are enforced, except 2.26. The objective function can be either 2.28 or 2.36, and the supporting equations of both are included. As discussed above, the optimization problem originated is a MINLP. The multi-stream treatment problem represents a situation in which the wastewater sources can be sent to different parts of the treatment and the stream treated can split when passing from one removal task to the next, so that it can be sent to different units belonging to the same removal task. This situation is close to a distributed wastewater treatment system.

2. **Single-stream treatment problem**

This problem is derived as a specific case of the multi-stream treatment problem. In this case, the split factors $SM1_{kk,k}$ and $SM2_{kk,k}$ in equations 2.11 and 2.12 are set to 1 and

are not included among the variables. Constraints 2.3-2.27 are enforced, except 2.27. The objective function can be either 2.28 or 2.36, and the supporting equations of both are included. As discussed above, the optimization problem originated is a MILP. The single-stream treatment problem represents a situation in which the different wastewater sources are all mixed and then treated as a unique stream, which is not allowed to split when passing from one removal task to the following, so that it can be sent to only one unit belonging to a certain removal task. This situation corresponds to a centralized wastewater treatment. These results can be used for the design of a treatment process in case it is desired to have one stream only. In addition to representing a possible solution by itself, the solution of this problem is used as a benchmark for the eventual improvements introduced by a distributed wastewater treatment system and provides a good initial estimate for the multi-stream treatment problem, as it will be clarified later in section 2.3.2.

For all the types of problems described above, the objective function can be either 2.28 or 2.36, even if for the single-stream treatment problem, since the stream is not allowed to split, this second objective function makes sense only if the limitation on the total flow rate imposed on any of the sinks associated with a recycle option is higher than the total flow rate treated. Once the desired problem is solved, the values of the binary and continuous variables which maximize or minimize the objective are obtained, and these indicate the structure of the optimal network.

The formulation of the problem as a non-linear optimization problem (NLP) is not useful for synthesis purpose, since the treatment configuration is already set by fixing binary variables. In fact, this case corresponds to a situation in which a certain set of treatment operations, bypasses, sources and sinks are fixed, and the solver optimizes the distribution of the flow among them. However, the solution of this problem may prove useful to check the global optimality of the multi-stream treatment problem, as it will be discussed in section 2.3.2. For the single-stream treatment problem, fixing the binary variables does not make much sense, because if an interval is selected all the stream is treated in it since it cannot split, so the stream distribution is already known once the binary variables are assigned.

The size of the problem depends on the number of intervals considered, N_{kk} (which are differentiated in treatment units N_{kkp} , bypasses N_{kkb} , sources N_{source} and sinks N_{sink}) and of independent mass elements and properties considered, N_i and N_j respectively. The number of variables and equations involved in the single-stream and multi-stream treatment for both the deterministic and stochastic optimization problem is reported in Table 2.1 and in Table 2.2, respectively - other than the symbols already specified, N_{task} is the number of treatment tasks and N are the logical constraints associated with the treatment order. The number of equations and variables for the stochastic problem can be obtained simply multiplying the variables and the equations associated with the flow rates by the number of samples N_s , while the number of variables and equations associated with the objective function remains unvaried (specifically, variables $TranspC_1$, $TranspC_2$, $UtilC$, $WasteC$, $Opex$, Inv_{kk} , $Capex$, $Savings$, Z_1 , Z_2 , and y_{kk} ; and equations 2.25, 2.26 or 2.27, 2.31, 2.29, 2.33, 2.34, 2.32, 2.35, 2.28, and 2.36). The two objective functions Z_1 and Z_2 and the associated variables and equations are included in the total number of variables and equations both when the optimization problem is solved with respect to one or the other because it is interesting to know their value no matter the objective with respect to which the optimization problem is solved. However, in

each case only one of the two is optimized.

CHAPTER 2. METHOD

Table 2.1 – Variable number - SS stands for single-stream and MS stands for multi-stream.

Variable Breakdown		
Item	Deterministic	Stochastic
$F_{t,kk}^{in}$	$N_t \cdot N_{kk}$	$N_t \cdot N_{kk} \cdot N_s$
$R_{i,kk}$	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
$F_{i,kk}^M$	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
$F_{i,kk}^{aq}$	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
$F_{i,kk}^R$	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
$F_{t,kk}^{out}$	$N_t \cdot N_{kk}$	$N_t \cdot N_{kk} \cdot N_s$
$F_{i,kk}^w$	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
$F_{t,kk}^1$	$N_t \cdot N_{kkp}$	$N_t \cdot N_{kkp} \cdot N_s$
$F_{t,kk}^2$	$N_t \cdot N_{kkp}$	$N_t \cdot N_{kkp} \cdot N_s$
$F_{t,kk,k}^1$	$N_t \cdot N_{kk}^2$	$N_t \cdot N_{kk}^2 \cdot N_s$
$F_{t,kk,k}^2$	$N_t \cdot N_{kkp} \cdot N_{kk}$	$N_t \cdot N_{kkp} \cdot N_{kk} \cdot N_s$
$TranspC_1$	1	1
$TranspC_2$	1	1
$UtilC$	N_{kkp}	N_{kkp}
$WasteC$	N_{kkp}	N_{kkp}
$Opex$	1	1
Inv_{kk}	N_{kkp}	N_{kkp}
$Capex$	1	1
$Savings$	1	1
Z_1	1	1
Z_2	1	1
y_{kk}	N_{kk}	N_{kk}
Tot SS	$2N_t \cdot N_{kk} + 5N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} +$ $+N_t \cdot N_{kk}^2 + N_t \cdot N_{kkp} \cdot N_{kk} +$ $+3N_{kkp} + N_{kk} + 7$	$(2N_t \cdot N_{kk} + 5N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} +$ $+N_t \cdot N_{kk}^2 + N_t \cdot N_{kkp} \cdot N_{kk}) \cdot N_s +$ $+3N_{kkp} + N_{kk} + 7$
$SM1_{k,kk}$	N_{kk}^2	$N_{kk}^2 \cdot N_s$
$SM2_{k,kk}$	N_{kk}^2	$N_{kk}^2 \cdot N_s$
Tot MS	$2N_t \cdot N_{kk} + 5N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} +$ $+N_t \cdot N_{kk}^2 + N_t \cdot N_{kkp} \cdot N_{kk} +$ $+3N_{kkp} + N_{kk} + 2N_{kk}^2 + 7$	$(2N_t \cdot N_{kk} + 5N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} +$ $+N_t \cdot N_{kk}^2 + N_t \cdot N_{kkp} \cdot N_{kk} + 2N_{kk}^2) \cdot N_s +$ $+3N_{kkp} + N_{kk} + 2N_{kk}^2 + 7$

Table 2.2 – Equation number - SS stands for single-stream and MS stands for multi-stream.

Equation Breakdown		
Item	Deterministic	Stochastic
Eq. 2.3	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.4	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.5	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.6	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.7	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.8	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.9	$N_t \cdot N_{kkp}$	$N_t \cdot N_{kkp} \cdot N_s$
Eq. 2.10	$N_t \cdot N_{kkp}$	$N_t \cdot N_{kkp} \cdot N_s$
Eq. 2.11	$N_t \cdot N_{kk}^2$	$N_t \cdot N_{kk}^2 \cdot N_s$
Eq. 2.12	$N_t \cdot N_{kkp} \cdot N_{kk}$	$N_t \cdot N_{kkp} \cdot N_{kk} \cdot N_s$
Eq. 2.15	$N_t \cdot N_{kk}$	$N_t \cdot N_{kk} \cdot N_s$
Eq. 2.18	$N_j \cdot N_{kkp}$	$N_j \cdot N_{kkp} \cdot N_s$
Eq. 2.19	$N_t \cdot (N_{kk} - N_{kkp})$	$N_t \cdot (N_{kk} - N_{kkp}) \cdot N_s$
Eq. 2.20	$N_t \cdot N_{source}$	$N_t \cdot N_{source} \cdot N_s$
Eq. 2.21	N_{sink}	$N_{sink} \cdot N_s$
Eq. 2.22	$N_t \cdot N_{sink}$	$N_t \cdot N_{sink} \cdot N_s$
Eq. 2.23 for $F_{t,kk}^{out}$	$N_t \cdot N_{kk}$	$N_t \cdot N_{kk} \cdot N_s$
Eq. 2.23 for $F_{t,kk}^{in}$	$N_t \cdot N_{kk}$	$N_t \cdot N_{kk} \cdot N_s$
Eq. 2.23 for $R_{i,kk}$	$N_i \cdot N_{kkp}$	$N_i \cdot N_{kkp} \cdot N_s$
Eq. 2.23 for $F_{t,kk,k}^1$	$N_t \cdot N_{kk}^2$	$N_t \cdot N_{kk}^2 \cdot N_s$
Eq. 2.23 for $F_{t,kk,k}^2$	$N_t \cdot N_{kkp} \cdot N_{kk}$	$N_t \cdot N_{kkp} \cdot N_{kk} \cdot N_s$
Eq. 2.24	N_{kk}	$N_{kk} \cdot N_s$
Eq. 2.25	N	N
Eq. 2.26 or Eq. 2.27	N_{task}	N_{task}
Eq. 2.31	N_{kkp}	N_{kkp}
Eq. 2.29	1	1
Eq. 2.33	N_{kkp}	N_{kkp}
Eq. 2.34	N_{kkp}	N_{kkp}
Eq. 2.32	1	1
Eq. 2.35	1	1
Eq. 2.28	1	1
Eq. 2.36	1	1
Tot SS	$7N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} + 2N_t \cdot N_{kk}^2 +$ $+N_t \cdot (N_{kk} - N_{kkp}) + 2N_t \cdot N_{kkp} \cdot N_{kk} +$ $+3N_t \cdot N_{kk} + N_j \cdot N_{kkp} + N_t \cdot N_{source} +$ $+N_{sink} \cdot (1 + N_t) + N + N_{task} +$ $+3N_{kkp} + N_{kk} + 5$	$(7N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} + 2N_t \cdot N_{kk}^2 +$ $+N_t \cdot (N_{kk} - N_{kkp}) + 2N_t \cdot N_{kkp} \cdot N_{kk} +$ $+3N_t \cdot N_{kk} + N_j \cdot N_{kkp} + N_t \cdot N_{source} +$ $+N_{sink} \cdot (1 + N_t) + N_{kk}) \cdot N_s +$ $+N + N_{task} + 3N_{kkp} + 5$
Eq. 2.13	N_{kk}	$N_{kk} \cdot N_s$
Eq. 2.14	N_{kk}	$N_{kk} \cdot N_s$
Tot MS	$7N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} + 2N_t \cdot N_{kk}^2 +$ $+N_t \cdot (N_{kk} - N_{kkp}) + 2N_t \cdot N_{kkp} \cdot N_{kk} +$ $+3N_t \cdot N_{kk} + N_j \cdot N_{kkp} + N_t \cdot N_{source} +$ $+N_{sink} \cdot (1 + N_t) + N + N_{task} +$ $+3N_{kkp} + 3N_{kk} + 5$	$(7N_i \cdot N_{kkp} + 2N_t \cdot N_{kkp} + 2N_t \cdot N_{kk}^2 +$ $+N_t \cdot (N_{kk} - N_{kkp}) + 2N_t \cdot N_{kkp} \cdot N_{kk} +$ $+3N_t \cdot N_{kk} + N_j \cdot N_{kkp} + N_t \cdot N_{source} +$ $+N_{sink} \cdot (1 + N_t) + 3N_{kk}) \cdot N_s +$ $+N + N_{task} + 3N_{kkp} + 5$

2.3.2 Solution

The framework is implemented in a software infrastructure based on Excel as GUI for data input and GAMS 23.7.3 for the solution of the MILP or the MINLP problem formulated. The computing platform used is Windows 7 with Intel Core i5 processor at 2.40 GHz and 3.68 GB of RAM. Due to the different mathematical nature of the problems, the solution strategy is distinguished between the one for the single-stream problem and the one for the multi-stream problem, independently on the fact that they are deterministic or stochastic.

2.3.2.1 Single-stream treatment problem

In the single-stream treatment problem, the optimization problem originated by 2.37 or 2.38 is a mixed integer linear problem (MILP). The solver CPLEX is used to solve the MILP. Since the model is linear, the convergence to a global optimum is guaranteed [37]. Thus, no significant difficulties except the ones related to the problem size are expected.

2.3.2.2 Multi-stream treatment problem

In the multi-stream treatment problem, the optimization problem originated by 2.37 or 2.38 is a mixed integer non-linear problem (MINLP). The solver DICOPT is used to solve the MINLP problem. The algorithm inside DICOPT is based on the concept of outer approximation, which involves an iterative procedure of alternately solving a Non-Linear Programming (NLP) and a Mixed Integer Programming (MILP) subproblems [4]. The algorithm underlying DICOPT starts by solving a NLP in which the binary variables are relaxed (Relaxed Non-Linear Programming, RNLP), which means that they can assume any value between 0 and 1. If the solution to this problem yields an integer solution for which the optimality conditions are satisfied the search stops. Otherwise, it continues with an alternating sequence of MILP master problems and NLP subproblems. The NLP subproblems are solved for fixed integer variables (0 or 1) that are predicted by the MILP master problem at each major iteration. Thus, the algorithm goes through the following steps:

1. Solution of the RNLP. The relaxation of the binary variables can be skipped in case a reasonable integer configuration is known and used as a starting point. In this case, the NLP solved has the same characteristics of the NLP subproblems solved in step 3, thus the algorithm starts from that step.
2. Solution of a MILP master problem. The MILP master problem is obtained by generating linearizations which follow from the relaxation of the equality constraints: these are converted from equality constraint into inequality constraints. At each iteration linearizations are generated and accumulated. In the MILP master problems integer cuts are added to the model to exclude previously determined integer combinations, so that each binary combination is not considered twice.
3. Solution of a NLP subproblem in which the binary variables are fixed to 0 or 1 as predicted by the MILP master problem at each major iteration.
4. Repetition of steps 2 and 3 until one of the stopping criteria is met. A stopping criterion that tends to work very well in practice for non-convex problems, and which can be successfully applied as well to convex problems, is based on the heuristic: stop as soon as

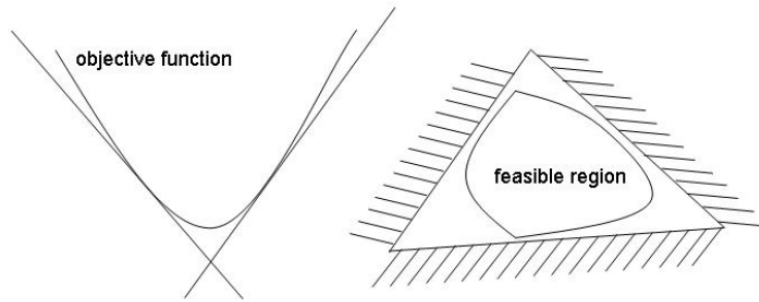


Figure 2.7 – Underestimation of the objective function due to linear approximations and overestimation of the feasible space [38].

the NLP subproblems start worsening (i.e. the current NLP subproblem has an optimal objective function that is worse than the previous NLP subproblem). Additional stopping criteria are imposed on the solver: the search is always stopped when the solver hits the iteration limit or when the MILP master problem becomes infeasible.

The algorithm is guaranteed to reach the global optimum for convex problems [4]. For a convex problem, this technique provides successively improved linear approximations of non-linear functions that underestimate the objective function and overestimate the feasible region, and the master problem provides a lower bound on the objective function (this is valid in the case of minimization, while for the case of maximization the linearizations would lead to an overestimation of the objective function and the master problem would provide an upper bound). The concept of how linear approximations can provide a lower bound for the objective function and how the feasible space is overestimated are better understood looking at Figure 2.7, which reports an example in 1- and 2-dimensions, respectively. The lower bound provided by the MILP increases monotonically as iterations proceed due to the accumulation of linear approximations. This approach relies on the fact that the surface described by a convex function lies above the tangent plane at any interior point of the surface (in 1-dimension, the analogous geometrical result is that the tangent to a convex function at an interior point lies below the curve, as can be seen in Figure 2.7).

These considerations may not be true for a non-convex problem. Although the algorithm has provisions to handle non-convexities, it does not necessarily obtain the global optimum.

The NLP or MILP subproblems can be solved using any solution algorithm available for these types of problems; in this work, CPLEX is used for the MILP subproblems and MINOS and CONOPT are used for the NLP subproblems - MINOS was observed to perform well for the solution of the RMINLP while CONOPT was observed to perform better for the rest of the NLP subproblems.

In the case of the problem treated, the non-linearities arise from the presence of the bilinear terms $F_{t,kk}^1 \cdot SM1_{kk,k}$ in equation 2.11 and $F_{t,kk}^2 \cdot SM2_{kk,k}$ in equation 2.12. This kind of non-linear problem is non-convex and it is known to be affected by problems in the solution, often causing convergence failures in NLP algorithms or leading to suboptimal local solutions [30]. Thus, the possibility of easily reaching a global optimal solution without reformulating the problem is excluded. Still, some considerations are of key importance to reduce the burden

that the solver has to handle [4]:

1. **Scaling:**

Problems based on models that are poorly scaled may cause numerical failure in the NLP solvers, which may not be able find an optimal or even a feasible solution; thus, variables and equations should be scaled so that the order of magnitude of their terms is as contained as possible.

2. **Variable bounds:**

Tight bounds on the variables, suggested by their physical nature, allow to reduce the search space, accelerating the convergence of the algorithm.

3. **Initial estimate:**

If a poor starting point is used, the NLP solver may not be able to find an optimal or even feasible solution, thus a good starting point must be provided; furthermore, for non-convex problems the solution found can vary with a different selection of the starting point.

4. **Size of the problem:**

Smaller problems are more easily solved than large problems due to the lower number of constraints to satisfy, and thus the complexity of the search space.

The size of the problem is determined mainly by the number of pollutants and treatments considered. The water characterization suggested is able to cover a great number of compounds, but only some of them may be present in the wastewater sources or introduced in the treatment units. The exact number of variables and equations depends on the specific problem selected. Thus, the analysis of the model size is reserved for when a case study is defined. Also the scaling and the variable bounds need to be tailored on the basis of the actual numerical data treated. Thus, these issues will be addressed for a defined case study.

In any case, a large scale non-convex problem is expected. Thus, it is likely that this kind of problem will lead to failure of the solution algorithm. In order to minimize the possibility of incurring in problems of convergence, the optimization algorithm is initialized with the selection of a good starting point. For this scope, the solution of the single-stream treatment problem proves useful. In addition to this, different reasonable starting points can be tried to see if the algorithm converges to different solutions, and the global optimality of the solution can be tested solving different NLPs corresponding to different binary variable combinations. Thus, the strategy to solve the MINLP is the following:

1. Solution of the MILP
2. Solution of the MINLP using the solution of the MILP as a starting point
3. Verification of the global optimality of the solution obtained with the MINLP:
 - (a) Using different starting points
 - (b) Solving a number of NLPs for different binary configurations

This can be applied to both the deterministic and stochastic problem.

Chapter 3

Case study: Oil Refinery Wastewater

A case study dealing with oil refinery wastewater is presented. As discussed in section 1.3 in Chapter 1, refineries are water intensive plants whose wastewaters vary in amount and contamination depending on refinery size, configuration and feedstock. Thus, this represents a sector in which tools for a systematic design of the water network is useful.

Section 3.1 gives an overall problem definition, in which the scope is stated. Section 3.2 presents the elements needed to model the water network - the wastewater sources, the treatment objectives, the treatment operation and the resulting superstructure. In section 3.3 the formulation of the optimization problem is discussed. Finally, sections 3.4 and 3.5 present the results obtained, which are then discussed in section 3.6.

3.1 Problem definition

The scope of the present study is to find the configuration of the wastewater treatment process which maximizes or minimizes a certain performance parameter given a set of wastewater sources, treatment objectives, and treatment technologies relative to oil refinery wastewater.

In order to achieve this objective, the steps of the methodology outlined in section 2.1 of Chapter 2 are declined for the case study selected. First, the wastewater sources and the treatment objectives are identified considering the characteristics of wastewater producing processes and water using processes in a refinery. Then, a superstructure is built including water treatment units currently used in the industry, which are connected to water sources and water sinks. The network is modeled mathematically and each of the treatment processes is modeled according to the generic process interval structure with the selection of proper parameters. Finally, the optimization problem is formulated and solved with respect to different objective functions - minimum total annualized cost and maximum water recycle. First, the problem is solved as a single-stream treatment problem for the first objective in order to provide an initial estimate and a benchmark for the solution of the multi-stream treatment problem. Then, the problem is solved as a multi-stream treatment problem for the two objectives, and a trade-off between the two is also investigated. The effect of the uncertainties in the wastewater sources on the network originated will be evaluated if the global optimality is reached.

Steps 1, 2 and 3 of the methodology are condensed into section 3.2, while step 4 is treated in sections 3.3, 3.4, 3.5 and 3.6; this is done to emphasise the results which can be obtained for a single given case study.

3.2 Network definition and model development

In this section, the wastewater sources, the water sinks and the treatment units that concur to define the water network are identified. Since no industrial data is available, the data are retrieved from literature.

Prior to the identification of wastewater sources and treatment objectives, the major pollutants to be considered are chosen on the basis of the ones expected to be present in the wastewaters. The total number of species involved in the system is given by the number of major pollutants summed to the number of species introduced due to the use of specific utilities or to the verification of specific reactions in the treatment units. Thus, the complete set of species involved is determined once also the treatments are defined. The choice of the pollutants to consider is done in section 3.2.1.

Any wastewater originated from any process could theoretically be included as a wastewater source. However, identifying all the sources requires a significant amount of time and endeavor for data collection, and this is also part of the reason why the wastewater streams are most commonly mixed into bigger streams. Furthermore, considering all the streams will lead to an increased complexity of the optimization problem without much benefit from the solution, since small water streams will not have a significant impact on the objective function. For this reason, here the focus is on major key wastewater streams. If needed, the model developed accommodates any number of wastewater sources, of course at the expense of a higher numerical complexity.

Similarly, it is not meaningful to include as treatment objectives all the minor water users but it is better to target the most important ones, which will have the highest impact on the objective function. Additionally, the option of discharge to an open surface is included in case the water sinks cannot accept the total of the flow rate treated - for discharge, no limitation is imposed on the flow rate, while for the recycle options a maximum amount of water can be sent to each unit depending on its needs. The freshwater saved will be the amount supplied to the sinks which represent recycling options.

Wastewater sources and treatment objectives are identified in sections 3.2.2 and 3.2.3.

The treatment units considered are chosen among the ones usually employed in a conventional wastewater treatment plant, as briefly outlined in section 1.2 in Chapter 1. All of the units mentioned there can be employed for the treatment of oil refinery wastewaters. The choice of the treatment units is done in section 3.2.4.

Finally, the superstructure is developed considering the scheme usually employed in the treatment of refinery effluents, as discussed in 1.3 in Chapter 1. In order to facilitate the organization of the superstructure, a sequential number is associated to the wastewater sources (1-9), the treatment objectives (91-99) and the various removal tasks (10-19, 20-29, etc.). A sequential number from 1 to 9 is associated to each alternative belonging to the same task, so that each interval different than sources and sinks is identified by three digits: the first two indicate the task and the third indicates the alternative. The arrangement of the superstructure is discussed in section 3.2.5.

3.2.1 Major pollutants

As discussed in section 1.3 of Chapter 1, the main pollutants in oil refinery wastewater include COD, BOD₅, oil and grease (i.e. petroleum oil), and total suspended solids; furthermore, ammonia, hydrogen sulfide, mercaptans, cyanides, phenols, and dissolved solids are present, as well as chlorides, chromates, and phosphates. Table 3.1 presents the number of contaminants which are considered for the case study - species i are the ones that are classified as independent mass elements while species j are the ones that are classified as properties. The COD will be accounted for as carbonaceous species, as described in section 2.2.1.1; thus, its concentration will be converted from COD to the pseudo species C according to equation 2.2. The only metal considered is Cr⁶⁺, which is the most abundant metal in refinery wastewater. Hydrocarbons of relevant importance for refineries are benzene and phenols; these can be considered as independent species provided that their oxygen demand is subtracted from the total COD, as explained in section 2.2.1. However, these are not considered here.

Table 3.1 – Major pollutants in oil refinery wastewater.

i	j
C	BOD ₅
NH ₄ ⁺	TSS
H ₂ S	
PO ₄ ³⁻	
Cr ₆ ⁺	
CN ⁻	
O&G	
FSS	

3.2.2 Wastewater sources

On the basis of the information presented in 1.3 in Chapter 1, three main sources of wastewater to treat are identified - the number in parenthesis indicates the corresponding numeration in the superstructure:

1. **Caustic wastewater (1):** representative of spent caustic from isomerization, alkylation and drying and sweetening.
2. **Sour wastewater (2):** representative of all sour wastewater sources (distillation, cracking etc.).
3. **Oily wastewater (3):** representative of oily wastewater sources (not sour and not caustic).

This choice represents a trade-off between the complete segregation of the streams and their complete mixing, since it can be considered that the wastewater streams containing similar contaminant in terms of type and level are lumped.

The wastewaters are characterized by the flow rate and the concentration of the contaminants. The characterization of the three wastewater sources can be seen in Table 3.2. The contaminant levels were obtained as an average of the values reported in literature for similar

type of refinery wastewaters while the flow rates are estimated on the basis of a real industrial case reported by Khor et al. [23] and on the proportions between the three as reported by [10] - see Appendix A. These data are used for the computation of the parameters $f_{t,kk}^0$ to use in equation 2.20. Sour wastewater contains high levels of H_2S and NH_4^+ with moderate COD and BOD_5 , while caustic wastewater contains high levels of COD, H_2S and NH_4^+ ; both waters have low level of oil and grease and suspended solids. Oily wastewater contains moderate amount of BOD_5 , COD and suspended solids, with a quite significant amount of oil and grease.

On the basis of the data collected, the level of the contaminants in each type of stream is highly variable. Ammonia, sulphides and organics (COD and BOD_5) have a wide range of variation for all the three types of wastewater sources; in addition, the oily wastewater exhibits high variability in oil and grease, total suspended solid and metals; and also the sour wastewater presents a wide excursion with respect to oil and grease. This is because the contaminant content of the wastewaters produced is highly dependent on the crude processed, which can vary also within the same refinery if different feedstocks are used. Given the wide variability of the contamination level, a sensitivity analysis with respect to this is judged necessary to estimate the impact of the uncertainty of the wastewater contamination.

Table 3.2 – Wastewater sources characterization - flow rate and pollutant concentrations.

	UOM	1	2	3
F	[ton/h]	0.2	100.0	558.8
C	[mg/L]	80,491.4	869.0	1,333.4
NH_4^+	[mg/L]	551.4	1,362.9	79.4
H_2S	[mg/L]	14,512.9	1,553.0	55.2
Cr^{6+}	[mg/L]	5.8	0.0	28.0
O&G	[mg/L]	5.0	281.4	1,475.8
FSS	[mg/L]	0.0	0.0	470.0
BOD_5	[mg/L]	2,176.5	660.0	712.7
TSS	[mg/L]	0.0	0.0	940.1

3.2.3 Treatment objectives

As discussed in the beginning of section 3.2, only the most important water sinks are targeted. Figure 1.3 in section 1.3 of Chapter 1 shows that a big part of water consumption is related to the cooling system and the boiler feed water systems, then to the process units. Among the process units in a refinery, the desalter is one of the most water consuming units [17]. A discharge option is included because the water sinks cannot accept the total of the flow rate treated. Thus, four water sinks (treatment objectives) are identified - the number in parenthesis indicates the corresponding numeration in the superstructure:

1. **Discharge on open surface (91)**
2. **Recycle as boiler feed water (92)**
3. **Recycle as cooling water (93)**

4. Recycle to desalter (94)

The discharge of untreated or partially treated wastewater to a public owned wastewater treatment facility could be another option to evaluate. In this work, this is not considered since the limit concentrations and the cost associated with this option are highly variable with the location of the plant, and thus it is difficult to assign meaningful values to this sink. The limiting compositions and flow rates for the water sinks considered are reported in Table 3.3 - limiting concentrations exist not only on the pollutants considered, but also on all the other species that are considered for the stream characterization, which for the specific case study are reported in Table 3.5 in section 3.2.4. The limit on the maximum flow rate is imposed on the basis of the data reported in Khor et al. [23]. These data define the values of $F_{O_o}^{max}$ and C_{t,O_o}^{max} in equations 2.21 and 2.22.

Table 3.3 – Treatment objectives characterization - limitations on the maximum flow rate and pollutant concentrations.

	UOM	91	92	93	94	Reference
F	[ton/h]	-	198.5	104.6	50.00	[23]
C	[mg/L]	105.3	3.5	52.6	-	[39], [9]
NH ₄ ⁺	[mg/L]	4.9	0.1	-	50	[40], [9], [18]
H ₂ S	[mg/L]	1.1	-	-	10	[39], [18]
PO ₄ ³⁻	[mg/L]	-	-	-	-	
Cr ⁶⁺	[mg/L]	0.1	-	-	-	[39]
Cr ³⁺	[mg/L]	0.4	-	-	-	[39]
Ca ²⁺	[mg/L]	-	0.4	50.0	-	[9]
SO ₄ ²⁻	[mg/L]	-	-	200.0	-	[9]
Fe ²⁺	[mg/L]	-	0.3	0.5	-	[9]
Fe ³⁺	[mg/L]	-	0.3	0.5	-	[9]
Cl ⁻	[mg/L]	-	-	500.0	-	[9]
CO ₃ ²⁻	[mg/L]	-	120.0	24.0	-	[9]
O&G	[mg/L]	10.0	25.0	25.0	-	[39], [23]
FSS	[mg/L]	15.0	5.0	100.0	-	[39], [9]
BOD ₅	[mg/L]	30.0	3.5	52.6	-	[39]
TSS	[mg/L]	30.0	5.0	100.0	-	[39], [9]

3.2.4 Treatment operation

The treatment units considered are chosen on the basis of the pollutants to remove indicated in Table 3.1. A list of the treatment units considered can be seen in Table 3.4. The treatment units are modeled according to the generic process interval architecture presented in section 2.2.2.1 of Chapter 2 - Figure 2.5. The specific utility consumption, the capital cost and the removal performance of each unit are needed for their modeling - $\alpha_{i,kk}$, $\mu_{i,t,kk}$, $\theta aq_{react,kk,rr}$, $\theta_{react,kk,rr}$, $SW_{i,kk}$, $\epsilon_{t,kk}$, $RM_{j,kk}$, AC_{kk} and BC_{kk} . These are obtained from known performance reported in literature or by considering a simple model of the process unit from which this values were extracted. Details on this can be found in Appendix B. All the process intervals include use of utility and waste production, some include utility mixing and dissolution and reaction but none includes separation.

The units considered cover primary treatment (tasks 10 and 11), secondary treatment (tasks 12 and 13) and tertiary treatment (tasks 14, 15, 16, 17, 18, 19a, 19b, 20, 21, 22). The division into tasks is done on the basis of the pollutants removed or of the principle on which the treatment relies.

The various treatments included in the network consume different types of utilities. Electricity is needed for pumping and for running mechanical parts. Steam and cooling water are needed for temperature regulation and for steam stripping processes. Air is accounted for as N_2 and O_2 and it is needed in the flotation units and in biological processes as oxygen supply. Ammonia and phosphoric acid serve as nutrients in biological processes. Sulphuric acid and sodium hydroxide are useful for pH regulation or for washing. Other utilities are used depending on the specific process unit - for example, lime and $FeSO_4$ are used in the precipitations of phosphorous and metals and alum is used as a coagulant in the flotation units. Table 3.5 reports the full set of independent mass elements considered, classified as contaminants, utilities and other species produced as a consequence of the mixing of utilities with the wastewater stream or of reaction. The importance of each utility for each specific unit is discussed in Appendix B.

Table 3.4 – Summary of the wastewater treatment units included in the network.

Principle	Description	ID	No.
Oxidation	Wet Air Oxidation	WAO	201
	Chlorine Oxidation	ChOx	151
Stripping	Sour Water Stripper	SWS	211
	H_2S Stripper	SS	212
	NH_3 Stripper	NS	221
	Air Stripper	AirS	222
Gravity separation	API Separator	API	101
	CPI/PPI Separator	CPI/PPI	102
Floatation	Dissolved Air Flotation	DAF	111
	Induced Air Flotation	IAF	112
Biological treatment	Trickling Filter	TF	121
	Rotating Biological Contactor	RBC	131
	Activated Sludge	AS	132
	Powdered Activated Carbon Treatment	PACT	133
	Membrane Biological Reactor	MBR	134
Adsorption	Adsorption on Granular Activated Carbon	GAC	141
Precipitation	Phosphorous Precipitation	PhPrec	161
	Metal Precipitation	MePrec	171
	Chromium Precipitation	CrPrec	172
Electrostatic separation	Ion Exchange	IE	181
	Electrodialysis	ED	182
Tertiary Filtration	Microfiltration/Ultrafiltration	MF/NF	191a
	Nanofiltration/Reverse Osmosis	NF/RO	191b

Table 3.5 – Complete list of independent mass elements i considered in the case study.

Contaminants	Utilities	Species generated
H ₂ O	EL	O ₂ MO CaCO ₃
C	LPS	N ₂ H ⁺ Ca ₁₀ (PO ₄) ₆ (OH) ₂
NH ₄ ⁺	CW	CO ₂ OH ⁻ Cr(OH) ₃
H ₂ S	NG	NH ₃ Ca ₂ ⁺ Fe(OH) ₃
PO ₄ ³⁻	GAC	H ₃ PO ₄ CO ₃ ²⁻
Cr ₆ ⁺		H ₂ SO ₄ Cl ⁻
CN ⁻		NaOH OCl ⁻
FSS		CaO Fe ₂ ⁺
O&G		FeSO ₄ Fe ₃ ⁺
		Cl ₂ SO ₄ ²⁻
		NaOCl Cr ₃ ⁺
		C ₆ H ₈ O ₇
		Alum

3.2.5 Water network

A representation of the network built including the water sources, the water sinks and the other intervals is shown in Figure 3.1. Also the refinery system with the freshwater feed (FW) and the eventual water recycles are indicated. The tasks are numbered sequentially with 00 corresponding to the water sources and 90 corresponding to the water sinks.

The three sources of wastewater are connected to three blocks: task 20, tasks 21 and 22, and tasks 102 onwards. The first block is designed for treating streams with high COD content, the second for streams with high levels of H₂S or NH₄⁺ and the third for a generic stream containing oil, solids, organics and ions. The sources are connected separately to each block so that a stream with low level of COD can bypass the first and a stream with low levels of H₂S or NH₄⁺ can bypass the second without being mixed with other streams. The sink associated with the recycle to the desalter is connected to the outlet of the H₂S and NH₄⁺ removal block, according to the common practice in refineries - see section 1.3 in Chapter 1.

As explained in section 2.2.2.2, constraints are imposed so that elements downstream are not chosen unless they are preceded by certain elements upstream; this is done in the form of equation 2.25. For the case study presented, the equation is declined as:

$$y_{101} + y_{102} \geq y_{111} + y_{112} \quad (3.1)$$

$$y_{111} + y_{112} \geq y_{121} \quad (3.2)$$

$$y_{111} + y_{112} \geq y_{131} + y_{132} + y_{133} + y_{134} \quad (3.3)$$

$$y_{131} + y_{132} + y_{133} + y_{134} \geq y_{141} \quad (3.4)$$

$$y_{131} + y_{132} + y_{133} + y_{134} \geq y_{181} + y_{182} \quad (3.5)$$

$$y_{131} + y_{132} + y_{133} + y_{134} \geq y_{191a} \quad (3.6)$$

$$y_{131} + y_{132} + y_{133} + y_{134} \geq y_{191b} \quad (3.7)$$

The meaning of these constraints is better understood referring to Figure 3.1.

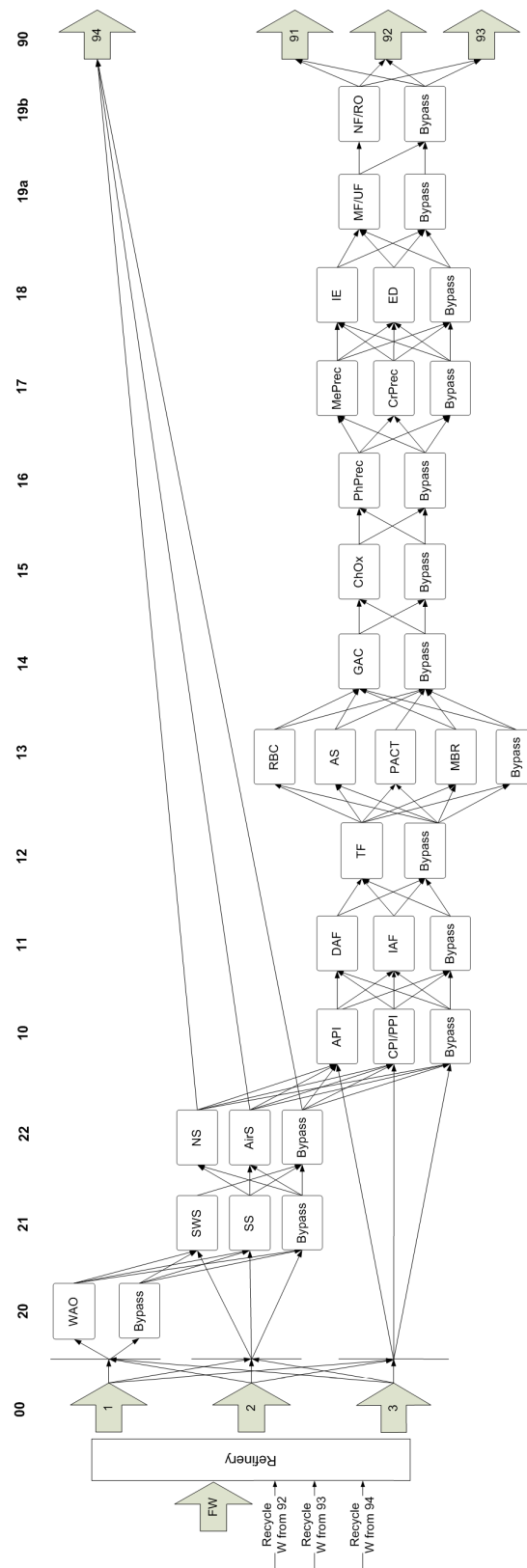


Figure 3.1 – Oil refinery water network.

3.3 Optimization problem formulation

The water network represented in Figure 3.1 can be solved with respect to the desired objective through mathematical optimization.

The mathematical model of the network consists of equations 2.3-2.36 exposed in section 2.2.2 of Chapter 2; given the dimensions of the specific case study treated, the parameters M and a in equations 2.23 and 2.24 are set to 10^6 and 10, respectively.

The optimization problem is formulated as discussed in section 2.3 of Chapter 2; for the same network, four problems are originated: a single-stream treatment problem and a multi-stream treatment problem, which can both be formulated as deterministic (form 2.37) and stochastic (form 2.38). The application of stochastic optimization techniques allows for making robust decisions considering the uncertainties on the input parameters - in the case treated, the different level of contamination of the wastewater sources, at the cost of an increased computational burden of the solver. The single-stream treatment problem is a MILP and the multi-stream treatment problem is a MINLP. The solution of the former corresponds to complete segregation of the wastewater streams and of the treated effluent, while the solution of the latter can be considered close to a distributed water treatment system. While the first one is easy to solve being linear, the second one may lead to convergence problems being non-linear. The solution of the single-stream treatment problem provides a good starting point to use for the solution of the multi-stream treatment problem, and it represents a possible solution by itself. Furthermore, the solution of the single-stream treatment problem is used as a benchmark for the improvements introduced by a distributed wastewater treatment system, which corresponds to the solution of the multi-stream treatment problem. However, the final goal is to solve the multi-stream treatment problem, which represents the most general case. In summary, the solution strategy exposed in section 2.3.2 of Chapter 2 is employed:

1. Solution of the single-stream treatment problem (MILP)
2. Solution of the multi-stream treatment problem (MINLP) using the solution of the single-stream treatment problem (MILP) as a starting point
3. Verification of the global optimality of the solution obtained with the multi-stream treatment problem (MINLP):
 - (a) Using different starting points
 - (b) Solving a number of NLPs for different binary configurations

Thus, the following optimization problems will be solved:

1. Single-stream treatment problem (MILP) - section 3.4
 - (a) Deterministic
 - (b) Stochastic
2. Multi-stream treatment problem (MINLP) - section 3.5
 - (a) Deterministic
 - (b) Stochastic

For the single-stream treatment problem, the only objective function analyzed is the minimum total annual cost (Z_1), while for the multi-stream treatment problem both the objectives of minimum total annual cost (Z_1) and maximum water recycle (Z_2) are investigated, for the reasons exposed in section 2.3.1.3 of Chapter 2.

The stochastic programming will be used to assess the effect of the uncertainties only if the global optimum is obtained. While this is guaranteed for a MILP, it is not in the case of a MINLP - see section 2.3.2. Thus, the stochastic problem will be solved for the single-stream treatment case, and will be solved for the multi-stream treatment case if global optimality for this problem is reached, otherwise this is not considered meaningful because the solution will not give univocal information on the effect of the uncertainties. In order to ascertain that the solution found is the global optimum, the MINLP will be solved using different starting points and for different fixed binary configurations as a NLP: if the solution found proves to be the global optimum, the corresponding stochastic problem will be solved.

As discussed in section 2.3 in Chapter 2, no particular problems are expected in the solution of the single-stream treatment problem since it is linear, but when the multi-stream treatment problem is addressed the problem becomes non-linear and the solver may encounter convergence difficulties. In order to reduce them, the following is done:

1. **Scaling:**

The water flow rate is in ton/h rather than in kg/h, which is the unit of measure for all the other species. In this way, the maximum order of magnitude of the inlet and outlet flow rates of an interval is 10^3 for all the species. The utilities are in suitable units to avoid $R_{i,kk}$ higher than 10^5 (for example MJ/ton for electricity and GJ/ton for steam). Other actions of scaling are not taken, since the flow rates are expected to be highly variable between upstream and downstream even for the same component.

2. **Variable bounds:**

The variables are bounded considering the range in which they can vary physically, and consequently the search space is reduced. The bounds set on the variables can be seen in Table 3.6. The lower bound of all the optimization variables is set to zero. The upper bound for the utilities is set to 10^3 except for electricity, steam, natural gas, and oxygen and nitrogen (air), for which the upper bound is set to 10^5 . This value represents also the upper bound for the internal flow rates of those intervals in which these utilities are mixed with the stream, otherwise their upper bound is set to 10^3 as for all the external flows. If certain utilities are used only in one or two intervals, the upper bound of the utilities in all the other intervals is set to zero. The split factors have upper bound 1. The variables associated with the objective function are left unbounded.

3. **Initial estimate:**

The search of the solution of the multi-stream treatment problem starts from the results obtained from the single-stream treatment problem, as discussed above. In case the solution obtained with this starting point is not satisfactory, a different feasible starting point which is believed to be closer to a better solution is employed.

4. **Size of the problem:**

The model developed can accommodate any number of species or characteristic of water; however, only the ones which are actually present in the wastewater sources or introduced in the treatment units are considered.

Table 3.6 – Variable bounds.

Variable	Min	Max
$F_{t,kk}^{in}$, $F_{t,kk}^{out}$, $F_{t,kk,k}^1$, and $F_{t,kk,k}$	0	10^3
$F_{i,kk}^M$, $F_{i,kk}^{aq}$, $F_{i,kk}^R$, $F_{i,kk}^w$ with $i \neq O_2, N_2$	0	10^3
$F_{i,kk}^M$, $F_{i,kk}^{aq}$, $F_{i,kk}^R$, $F_{i,kk}^w$ with $i = O_2, N_2$ and $\alpha_{O_2/N_2,kk} \geq 0$	0	10^5
$R_{i,kk}$ with $i = O_2, N_2, EL, LPS, CW, NG$	0	10^5
$R_{i,kk}$ with $i \neq O_2, N_2, EL, LPS, CW, NG$	0	10^3
$SM1_{kk,k}$	0	1

As shown in Figure 3.1, the network has and 44 intervals, of which 23 treatment units, 14 bypasses, 3 sources and 4 sinks (thus, $N_{kk} = 44$, $N_{kkp} = 23$, $N_{kkb} = 14$, $N_{source} = 3$, and $N_{sink} = 4$); 42 independent mass elements and 2 properties are considered (thus, $N_i = 42$ and $N_j = 2$). The number of equations of type 2.25 is 7 (equations from 3.1 to 3.7, $N = 7$), and in Figure 3.1 it can be seen the number of tasks is 16 including wastewater sources and water sinks assignment (tasks from 00 to 9, $N_{task} = 16$). The number of variables and equations involved in the problem is computed with the formulas presented in Table 2.2 and Table 2.1, respectively, subtracting the relevant variables and equations relative to the separation task, which is involved in none of the units - namely, variables $F_{t,kk}^1$, $F_{t,kk}^2$, $F_{t,kk,k}^2$ and $SM2_{kk,k}$, and equations 2.9, 2.10, 2.12, and 2.14. The variables $F_{t,kk,k}^1$, which are computed from $F_{t,kk}^1$, can be computed from $F_{t,kk}^{out}$ to keep the connectivity. Table 3.7 shows the number of the total and non-linear equations, the total and binary variables and the possible binary combinations for the different types of optimization problems that have been defined in section 2.3 - single-stream or multi-stream deterministic or stochastic. Only part of these binary combinations is feasible. If intervals kk and k are not connected, the split factor $SM1_{kk,k}$ is fixed to zero, thus these variables are not counted. The number of samples used is $N_s = 150$. Due to the fact that many parameters are specified as zero, the dimension of the problem that the solver has to face is smaller than the one estimated.

Table 3.7 – Problem dimension: single-stream vs. multi-stream treatment, deterministic and stochastic problem.

Problem	EQS	NL-EQS	VAR	BIN-VAR	BIN COMBOS
Single-stream (MILP)					
<i>Deterministic</i>	218,666	0	96,030	44	$1.40 \cdot 10^6$
<i>Stochastic</i>	34,318,897	0	14,086,470	44	$1.40 \cdot 10^6$
Multi-stream (MINLP)					
<i>Deterministic</i>	218,710	129,712	96,155	44	$1.20 \cdot 10^{11}$
<i>Stochastic</i>	34,325,497	19,456,800	14,105,220	44	$1.20 \cdot 10^{11}$

3.4 Single-stream treatment problem

The network is solved for the minimum total annualized cost; in this case, the objective function is represented by equation 2.28. The optimal network is shown in Figure 3.2. The following units are chosen: sour water stripper (211), CPI/PPI separator (102), IAF unit (112), activated sludge (132), microfiltration/ultrafiltration (191a) and nanofiltration/reverse osmosis (191b). The flow is sent to discharge, being this the only sink without limitations on the maximum flow - the total flow rate is too big for any of the recycle options. The choice of the different units can be related to the contaminants present and their level. The sour water stripper unit is selected due to the presence of H_2S . In order to comply to the limit of discharge of NH_4^+ , the trickling filter (121) and the ion exchange (181) would be selected in absence of Cr^{6+} , since these represent the cheapest alternative for ammonia removal. If also Cr^{6+} is present, MF/UF and NF/RO are chosen and the trickling filter and the ion exchange are not selected anymore due to the fact that NH_4^+ is effectively removed by the membrane processes. The reduction of Cr^{6+} could be also accomplished with the employment of precipitation coupled with ion exchange. However, the selection of these units plus the the trickling filter is more expensive than the selection of the filtration units, which are able to treat NH_4^+ and Cr^{6+} together. Thus, the results seem to be in line with the expectations of the equipment which leads to the minimum total cost for the whole system, and this can be considered a qualitative validation of the solution obtained. The global optimality of the solution is guaranteed since the problem is linear.

The concentrations at the outlet of each interval are reported in Table 3.8, where also the limits imposed on the discharge are reported: it can be seen that the limitations are respected. A summary of the performance metrics associated with the treatment is reported in Table 3.9; the total annualized cost and its breakdown in utility and waste cost is shown, along with the total capital cost and the specific values; also the fraction of the total amount of water treated which is saved, discharged or wasted ($W_{s/d/w}/W_t$) are reported. The utility cost has the major impact on the objective function, contributing to 63.3% of it, and a quite high fraction of the water treated is wasted as a consequence of the selection of the tertiary filtration units, which produce a retentate stream to dispose of. The contribution of each unit to the total costs is illustrated in Figure 3.3. The sour water stripper is the unit which affects the objective function the most, and this is due to its high utility consumption, whose cost breakdown is 71.3% for steam, 25.5% for electricity, and 3.2% for cooling water. A significant portion of the capital and the utility cost is associated with the filtration units, while the units which have the greatest impact on the waste cost are the primary and secondary treatments.

These results represent a situation in which the different wastewater streams are all mixed and then fed to a single treatment train. As discussed in section 1.1, this leads to streams which are more difficult and more expensive to treat. From the outlet concentrations obtained, it can be seen that the stream discharged is overtreated with respect to organics (COD and BOD_5), sulfides (H_2S) and oil and solids (O&G, FSS and TSS). Part of the flow could bypass the sour water stripper, the activated sludge and the tertiary filtration, thus decreasing the cost associated with them. Furthermore, if the contaminant concentrations of the stream are below the maximum allowed for discharge, they are also low enough to allow for the recycle of part of the stream as cooling water, consequently reducing the freshwater consumption and saving money. Thus, it is worth to investigate the possibility of stream splitting. However, first the effect that different contamination levels have on the solution is investigated.

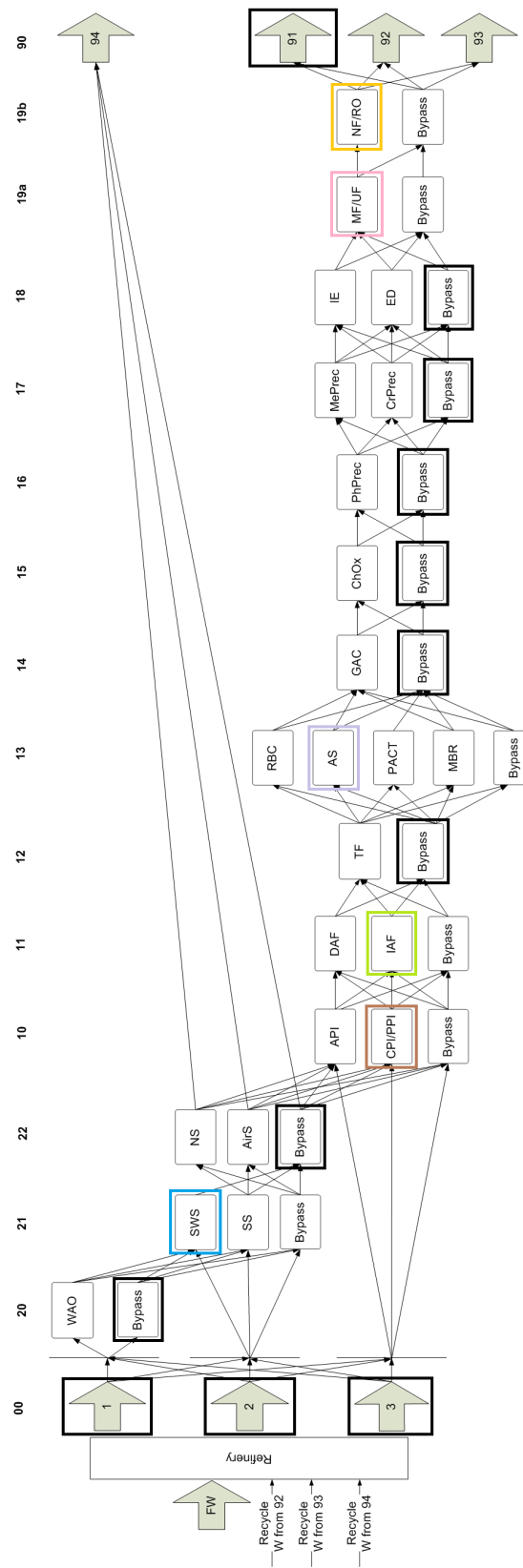


Figure 3.2 – Network corresponding to the single-stream treatment solution: objective is minimum total annualized cost (Z_1).

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Table 3.8 – Effluent concentrations for minimum total annualized cost (Z_1), single-stream treatment solution - UOM: [mg/L].

	202	211	223	102	112	122	132	142
C	1,289.88	1,289.88	1,289.88	748.13	486.29	486.29	133.72	133.72
H ⁺							0.66	0.66
Cr ⁶⁺	23.76	23.76	23.76	23.76	23.76	23.76	23.75	23.75
H ₂ S	287.49	0.11	0.11	0.11	0.11	0.11	0.11	0.11
NH ₄ ⁺	274.92	49.49	49.49	49.49	49.49	49.49	37.55	37.55
O&G	1,297.05	1,297.05	1,297.05	129.70	9.08	9.08	0.95	0.95
FSS	399.49	399.49	399.49	159.79	27.96	27.96	7.69	7.69
BOD ₅	706.78	706.78	706.78	409.93	225.46	225.46	23.67	23.67
TSS	798.97	798.97	798.97	319.59	55.93	55.93	15.38	15.38
	152	162	173	183	191a	191b	91	$C_{t,91}^{max}$
C	133.72	133.72	133.72	133.72	35.20	24.21	24.21	105.3
H ⁺	0.66	0.66	0.66	0.66	0.78	0.97	0.97	-
Cr ⁶⁺	23.75	23.75	23.75	23.75	2.50	0.08	0.08	0.1
H ₂ S	0.11	0.11	0.11	0.11	0.13	0.17	0.17	1.1
NH ₄ ⁺	37.55	37.55	37.55	37.55	39.54	1.24	1.24	4.9
O&G	0.95	0.95	0.95	0.95				10.0
FSS	7.69	7.69	7.69	7.69	0.31	0.01	0.01	15.0
BOD ₅	23.67	23.67	23.67	23.67	4.85	3.33	3.33	30.0
TSS	15.38	15.38	15.38	15.38	0.63	0.02	0.02	30.0

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Table 3.9 – Summary of results for minimum total annualized cost (Z_1), single-stream treatment solution.

	UOM	Value	Specific Value [\$/ton] or [ton/ton]	$W_s/d/w/W_t$
Z_1	[M\$/yr]	17.454	3.540	
Capex	[M\$]	22.800	4.623	
Opex	[M\$/yr]	15.934	3.231	
Utility Cost	[M\$/yr]	11.049	2.241	
Waste Cost	[M\$/yr]	4.886	0.991	
Savings	[M\$/yr]	-	-	
Water Saved	[ton/h]	-		-
Water Discharged	[ton/h]	449.53		68.4%
Water Wasted	[ton/h]	208.02		31.6%

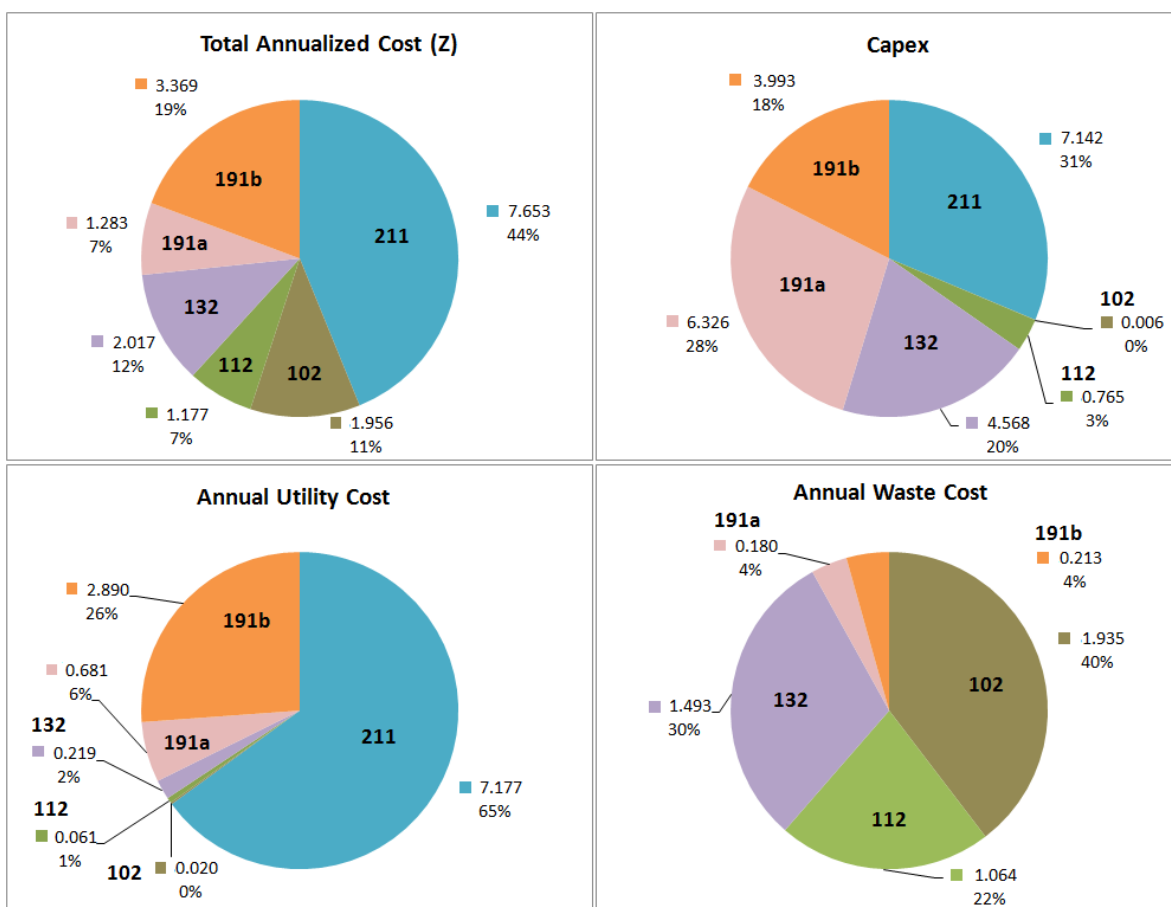


Figure 3.3 – Breakdown of total annualized cost (Z_1) [M\$/yr], capital cost [M\$], utility cost [M\$/yr] and waste cost [M\$/yr].

3.4.1 Sensitivity analysis

In the following, a sensitivity analysis with respect to the contamination level of the wastewater sources is performed. As anticipated in section 3.2.2, a high variability is observed in the contaminant concentrations in the different wastewater sources. Table 3.10 reports the range of variation of the contaminants on the basis of the data collected in literature. The average value reported is the one used in the deterministic problem previously solved. A set of 150 samples is extracted from this space to represent possible future scenarios under which the network could operate, as described in section 2.3. In order to assure that the number of samples is high enough to represent the population from which they are extracted, three different sets are produced and the same analysis is done for all the three sets of samples: if the results obtained do not differ significantly, then the number of samples chosen is high enough and the results are acceptable, otherwise a higher number of sample must be selected. The pollutants sampled include H_2S , NH_4^+ , Cr^{6+} , oil and grease, COD, and TSS. The FSS are assumed to be half of the TSS and, in order to have meaningful values of BOD_5 and COD, the BOD_5 is not sampled but it is estimated on the basis of the COD with the relationship between BOD_5 and COD reported experimentally for refinery wastewaters - see Figure 3.4.

Table 3.10 – Range of variation of the major contaminants in oil refinery wastewater, in [mg/L].

Source	1			2			3		
Contaminant	Average	Min	Max	Average	Min	Max	Average	Min	Max
H_2S	14,512.9	0.2	48,500.0	1,553.0	19.0	4,320.0	55.2	1.5	121.6
NH_4^+	551.4	2.8	1,100.0	1,362.9	36.1	3,342.5	79.4	2.9	205.9
COD	114,695.1	302.0	364,100.0	1,238.3	935.0	1,530.0	1,900.7	450.0	4,774.0
O&G	0.0	0.0	0.0	281.4	12.7	550.0	1,475.8	22.6	9,357.5
Cr_6^+	0.0	0.0	0.0	0.0	0.0	0.0	28.0	0.3	121.6
TSS	0.0	0.0	0.0	0.0	0.0	0.0	940.1	200.5	4,781.5

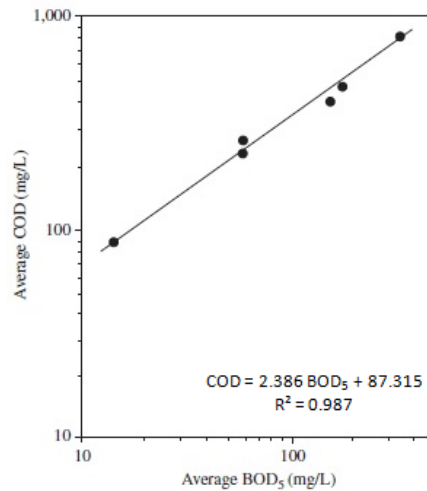


Figure 3.4 – Relation of COD and BOD_5 in oil refinery wastewaters [10].

If the samples extracted are tested with respect to the network selected in the deterministic case - shown in Figure 3.2, 70.7% of them turns infeasible. This is due to the fact that the concentration of Cr^{6+} at the discharge (91) exceeds the limit, while the limits for all the other pollutants are respected. Figure 3.5 reports the empirical cumulative distribution function of the discharge concentration of Cr^{6+} : the limit (0.1 mg/L) is respected only in 29.3% of the cases. The EU Directive 91/271/EEC [41] regulates the number of samples measured which are allowed to exceed the limits posed on the effluent concentration for domestic wastewater treatment plants: for a yearly number of samples between 141 and 155 the maximum number of samples which is permitted to fail to conform to the limits is set at 12, which is around 8.1%. If this is extended to industrial wastewater, the percentage in which the limits are exceeded is not acceptable and this justifies the research of a solution which is able to comply with the law in force.

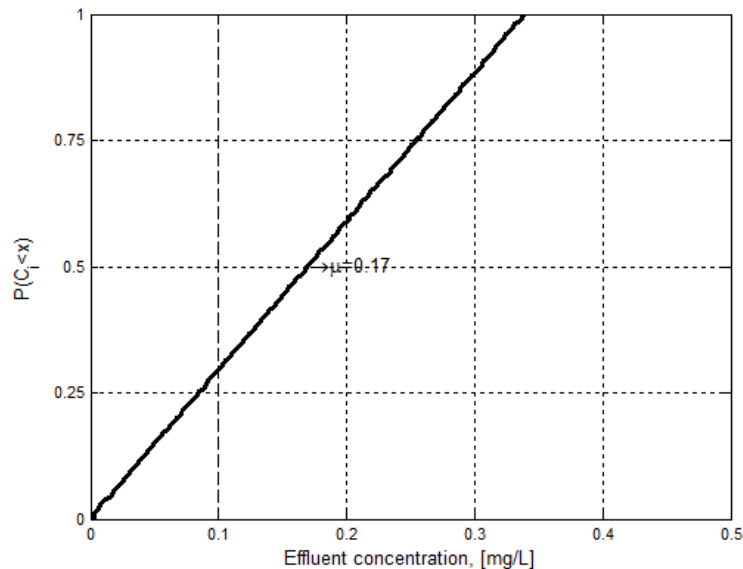


Figure 3.5 – Empirical cumulative distribution function of the concentration of Cr^{6+} at the discharge (91) for the network shown in Figure 3.2.

The sensitivity analysis study is done on the track of what explained in section 2.3.1.2 in Chapter 2.

First, it is investigated if different networks would be selected for different inlet contaminant concentrations and these networks are ranked (part 3.4.1.1). This is done solving the network as a single-stream treatment deterministic optimization problem for each of the generated scenarios. The result is a distribution of optimal processing networks and of objective function values obtained under different realization of the uncertain parameters. The frequency of occurrence of a certain network is an indication of how good the network is to stand uncertainties in the inlet contaminant level. However, it does not tell how bad it is when it is not selected.

Then, the optimization problem is formulated as a stochastic problem, which enables to identify an optimal solution that ensures feasibility over the entire uncertain space (part 3.4.1.2). If compared to the solution found for the deterministic problem, this represents a robust

solution because it gives a network which is able to handle the expected variability of the contamination level in the wastewater sources still complying with the limitations imposed on the water sinks. However, the drawback is that the size and the complexity of the problem grow. Every constraint must hold true for any future scenario, thus the number of constraints grows with the number of scenarios considered. The analysis done with the network ranking is useful in order to determine the possible existence of infeasible samples among the ones generated: some samples may prove infeasible due to the assumption of constant removal and conversion and to the network topology, i.e. the contamination level associated with them is so high that no network exist which is able to treat them. If such samples are present, the problem would be infeasible because the constraints must hold true for all the possible scenarios. Thus, in order to make the problem soluble, these must be removed. Furthermore, this analysis can help to reduce the problem size excluding the intervals which prove to be never optimal.

3.4.1.1 Network ranking

The network is solved as a deterministic optimization problem for each sample. Figure 3.6 shows the distribution frequency of the optimal networks and Figure 3.7 reports the dispersion of the total annualized cost for each network. The optimal network found solving the problem in original deterministic form ranks third. With respect to this network - shown in Figure 3.2, the one ranked in first position includes the ion exchange unit (181 instead of 183), while the one that ranks second allows for the complete bypass of the UF/RO unit (192b instead of 191b). Table 3.11 reports the networks obtained - the sources (1, 2, 3) and the sink (91) are not shown as they are selected for each network. Of the 44 intervals, 7 are always optimal (202, 112, 142, 152, 162, 173, 91) while 17 are never selected (201, 103, 111, 113, 131, 133, 134, 135, 141, 151, 161, 171, 172, 182, 94, 92, 93).

On the basis of the values obtained for the objective function, an empirical cumulative distribution is derived and plotted in Figure 3.8, where also its mean value (23.0 M\$/yr) is indicated. This plot is useful to infer which is the probability associated to the realization of a total annualized cost equal or below a certain value accounting for the variability of the contamination level in the wastewater sources. The value found with the deterministic solution is 17.454 M\$/yr, which is around 75.8% of the mean. Thus, the solution of the network in a deterministic form leads to an underestimation of the costs associated with the treatment.

Table 3.11 – Ranking of selected networks - single-stream treatment problem; the intervals which are different from the ones selected in the deterministic case are highlighted in bold.

1	202	211	223	102	112	122	132	142	152	162	173	181	191a	191b
2	202	211	223	102	112	122	132	142	152	162	173	181	191a	192b
3	202	211	223	102	112	122	132	142	152	162	173	183	191a	191b
4	202	211	223	101	112	122	132	142	152	162	173	181	191a	191b
5	202	211	223	101	112	122	132	142	152	162	173	181	191a	192b
6	202	211	223	102	112	121	132	142	152	162	173	181	192a	192b
7	202	211	223	101	112	122	132	142	152	162	173	183	191a	191b
8	202	211	223	101	112	121	132	142	152	162	173	181	191a	192b
9	202	212	223	102	112	122	132	142	152	162	173	181	191a	191b
10	202	213	222	102	112	122	132	142	152	162	173	181	191a	192b

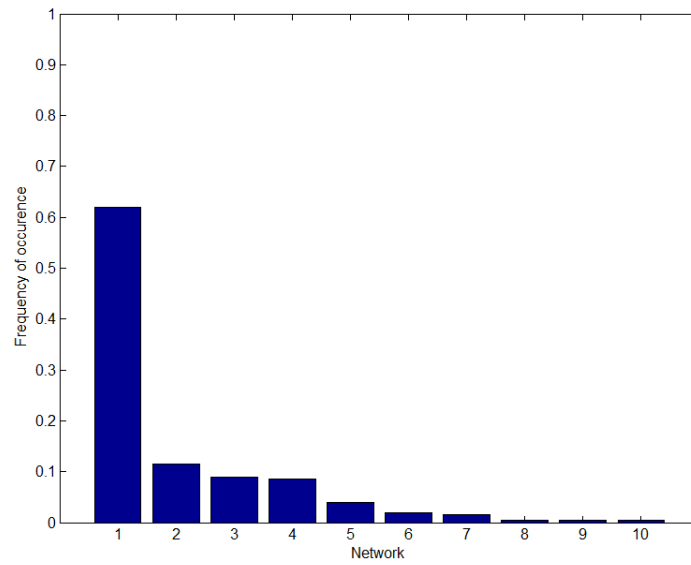


Figure 3.6 – Frequency of occurrence of network type as a consequence of the uncertainty in the contaminant level in the wastewater sources for the single-stream treatment problem.

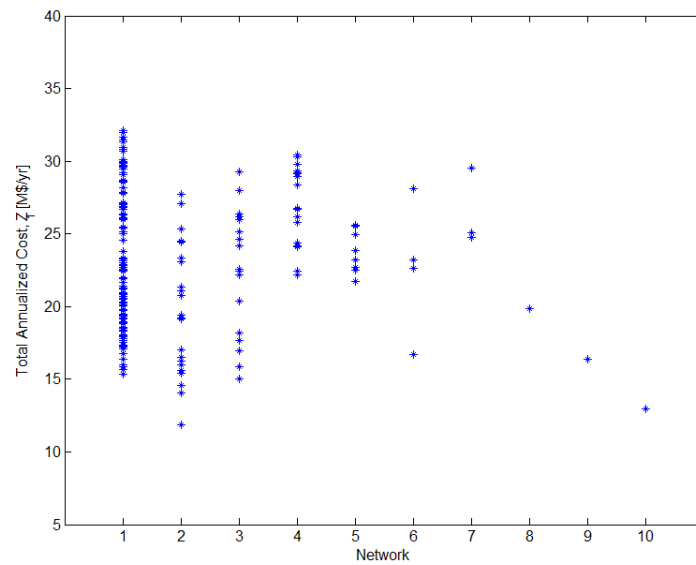


Figure 3.7 – Distribution of the values of the objective function Z_1 for each network type in Figure 3.6.

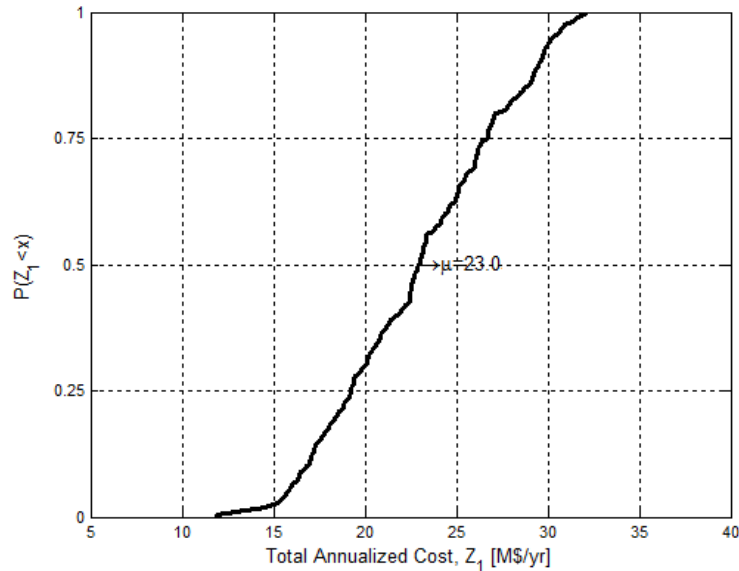


Figure 3.8 – Empirical cumulative distribution function of the objective function Z_1 .

3.4.1.2 Stochastic programming

A different problem is the selection of a network which is able to handle all the possible future scenarios while assuring the satisfaction of the limits imposed. In order to investigate this possibility, the problem is reformulated in terms of stochastic programming as described in section 2.3.

The analysis done in section 3.4.1.1 is useful in order to exclude the possible infeasible samples among the ones generated, which would make the problem infeasible. However, no sample generated was infeasible and consequently all the samples can in principle be used. A comparison between the dimension of the deterministic and the stochastic models was presented in Table 3.7. The solution of the stochastic model for the complete superstructure and the complete set of samples is not possible with the available system capacity due to limits in memory allocation (see section 2.3.2 in Chapter 2). Thus, the results of the network ranking described in section 3.4.1.1 are used in order to reduce the size of the problem, by eliminating the intervals that are never selected. After this reduction, if a removal task contains only a bypass this is removed and the previous removal task is connected to the following; furthermore, if any utility or species is not present anymore in the remaining process intervals, it is removed. This gives the possibility to solve the network up to 150 samples. This number of samples is considered satisfactory to obtain a meaningful solution because if the same analysis is repeated with different sets of 150 samples the result differ of 0.01% at the most. The number of variables and equations involved in the stochastic optimization problem before and after the reduction can be seen in Table 3.12.

The only difference in the interval selected between the deterministic and the stochastic solution is that in the latter also the ion exchange (181) is selected; this is not surprising, since when testing the deterministic network with respect to the different samples it was seen that the only source of infeasibility was the high chromium concentration at the discharge, and the

selection of this unit allows for an extra removal of chromium. The performance parameters of the deterministic solution and the robust solution are compared in Table 3.13. It can be seen that the expected value of the total annualized cost found with the stochastic solution is 36.1% higher than the one found with the deterministic solution, and this is to be attributed not only to the selection of an extra treatment unit (the ion exchange contributes in a measure of 0.659 M\$/yr to the total annualized cost, which is less than 3%) but mainly to the waste cost, that increases by 115.9% due to the higher amount of oil and grease, suspended solids and COD which can be present in the wastewater: in fact, the annual cost of the units which produce this kind of waste (102, 112, and 132) grows of 165.0% for the producers of oily waste (102 and 112) and of 47.5% for the producer of biological waste (132).

The solution found by stochastic programming is by definition completely robust with respect to the uncertainty, thus no sample among the ones generated is infeasible and the discharge limits are always met. However, as mentioned in section 3.4.1, the legislation allows some violation of the limits, and this solution would be most likely associated to a lower cost since it is allowed for a relaxation of the constraints represented by equation 2.22. However, since in the problem formulation for single-stream treatment the flow cannot split, there would be no difference in the solution because the same intervals would be selected anyways, and the investigation of this possibility requires a different model formulation.

Table 3.12 – Problem dimension: single-stream complete vs. reduced stochastic problem for $N_s=150$.

			EQS	NLEQS	VAR	BINVAR	Status
Stochastic	$N_s=150$	Complete	34,318,897	0	14,086,470	44	Not solved
		Reduced	4,446,064	0	1,722,214	22	Solved

Table 3.13 – Summary of results for minimum total annualized cost (Z_1), single-stream treatment solution: deterministic vs. stochastic solution obtained with 150 samples.

Item	UOM	Deterministic	Stochastic	Relative Variation
Z_1	[M\$/yr]	17.454	23.762	36.1%
Capex	[M\$]	22.800	25.217	10.6%
Opex	[M\$/yr]	15.934	22.081	38.6%
Utility Cost	[M\$/yr]	11.049	11.535	4.4%
Waste Cost	[M\$/yr]	4.886	10.546	115.9%
Savings	[M\$/yr]	-	-	-
Water Saved	[ton/h]	-	-	-
Water Discharged	[ton/h]	449.53	448.96	-0.1%
Water Wasted	[ton/h]	208.02	207.76	-0.1%

3.5 Multi-stream treatment problem

In the multi-stream treatment problem it is possible to allocate the water stream to different units in the same removal task, select different water sinks and split the flow so that the outlet concentrations are met without treating a higher amount of water than required. The problem is solved with respect to two objective functions: the minimum total annualized cost (Z_1) and the maximum water recycle (Z_2). This second objective was not considered in the single-stream treatment problem because in the superstructure built the stream cannot be recycled unless it is split, since no water sink associated to a recycle option can accommodate the whole flow rate treated due to the imposed limitations on the maximum flow rate. A trade-off between the two objectives is also investigated.

3.5.1 Minimum total annualized cost

In this case, the objective function is represented by equation 2.28. If the multi-stream treatment optimization problem is solved using the single-stream treatment solution obtained in section 3.4 as a starting point (SP1), the optimal network found looks like the one in Figure 3.10, where also the split factors are indicated - if different than 1. With respect to the single-stream treatment solution, part of the flow is sent to the ion exchange (98.8%), part bypasses the activated sludge unit (18.8%) and part bypasses the NF/RO unit (67.0%). Some oily wastewater (1.3%) is sent to the downstream treatment (to 102) without passing through the H_2S and NH_4^+ removal units (tasks 21 and 22), thus decreasing the cost associated with the sour water stripper, which represented the highest contribution to the objective function - see Figure 3.3. However, the contribution of the sour water stripper to the objective function is decreased of only 1.1%. This is because the amount of water that can bypass the H_2S removal units is limited by the strict limitation at the discharge; with this limited bypass the limits on H_2S at the discharge are already very tight - see Table 3.15, where the concentrations of the sinks are compared with their limitations. The maximum amount of water that can be recycled to the desalter (7.7% of the total flow out of interval 223) is sent to the corresponding sink; this has the duplice effect of obtaining savings for the recycle and of decreasing the flow rate treated in the downstream processes, and correspondingly their cost.

The concentrations at the outlet of each interval are reported in Table 3.15, where also the limits imposed on the discharge concentration are reported. It can be seen that the limits on H_2S and Cr^{6+} for the discharge (sink 91) are very tight; also the limit for the COD for the recycle as cooling water (sink 93) is very tight, and for NH_4^+ for the recycle to the desalter (sink 94). At the discharge, the organics and the solids are still undertreated, as well as ammonia.

The total annualized cost, along with its breakdown in utility and waste cost and the total capital cost, is shown in Table 3.14, where it is compared with the solution previously obtained for the single-stream treatment problem for the same objective function. The total annualized cost decreases of 15.5%, and this is due to a decrease of the same entity of the utility and waste cost; the capital cost decreases of 6.9% only. This solution also allows for recycle of 23.5% of the treated water to the desalter (7.6%) and the cooling water make-up (15.9%). Correspondingly, the water discharged decreases from 68.4% to 57.8%. Due to the bypass of the tertiary filtration units, also the water wasted decreases from 31.6% to 18.6%. Thus, the multi-stream treatment proves advantageous with respect to the single-stream treatment not

only from economical point of view, but also from an environmental perspective. Figure 3.9 compares the solutions of the single-stream and the multi-stream treatment with respect to the contributions of the different treatment units to the objective function. The main contribution is still represented by the sour water stripper, but as it was discussed in the previous paragraph, this cannot be significantly reduced due to the strict limitations of H₂S at the discharge. The bypass of the activated sludge concurs to reduce its cost of 24.3% and the bypass of the NF/RO unit leads to a decrease of 68.6% of the associated costs. The contribution of units 102, 122 and 191a is reduced of around 7%.

For the multi-stream treatment solution found, pie charts illustrating the contribution of each treatment unit to the capital cost and the annual utility and waste cost can be obtained similarly to the ones shown in Figure 3.3 for the single-stream treatment solution.

Table 3.14 – Summary of results for minimum total annualized cost (Z_1), single-stream vs. multi-stream treatment solution.

	UOM	Single-stream	Multi-stream	Relative variation	$W_{s/d/w}/W_t$
Z_1	[M\$/yr]	17.454	14.749	-15.5%	
Capex	[M\$]	22.800	21.227	-6.9%	
Opex	[M\$/yr]	15.934	13.365	-16.1%	
Utility Cost	[M\$/yr]	11.049	9.240	-16.4%	
Waste Cost	[M\$/yr]	4.886	4.125	-15.6%	
Savings	[M\$/yr]	-	0.031	-	
Water Saved	[ton/h]	-	154.6	-	23.5%
Water Discharged	[ton/h]	449.53	380.35	-15.4%	57.8%
Water Wasted	[ton/h]	208.02	122.59	-41.1%	18.6%

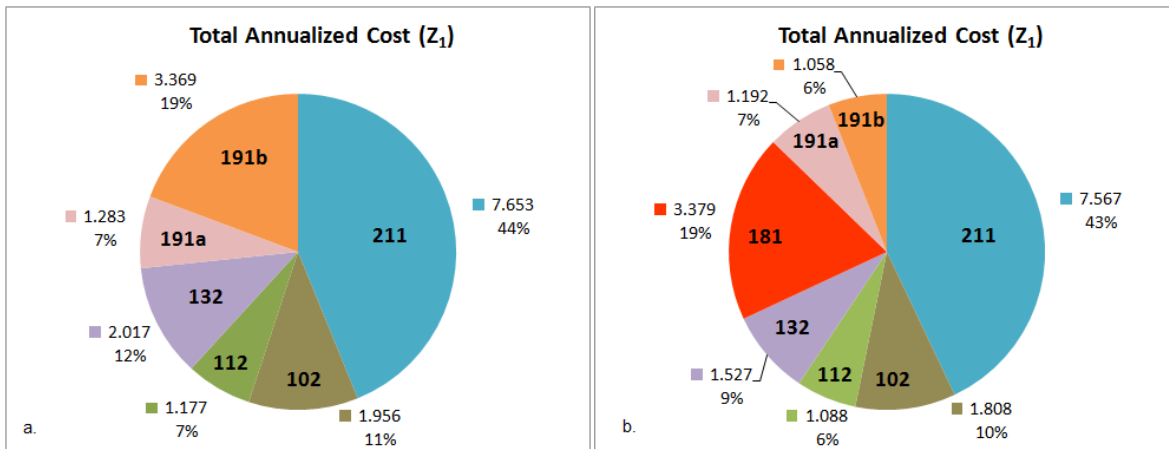


Figure 3.9 – Contribution of the different treatment units to the objective function (Z_1): single-stream treatment solution (a) vs. multi-stream treatment solution (b).

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Table 3.15 – Effluent concentrations for minimum total annualized cost (Z_1), multi-stream treatment solution - UOM: [mg/L].

	211	223	102	112	122	132	135	142
C	1,289.35	1,289.35	748.16	486.30	486.30	133.72	486.30	199.96
H ⁺						0.66		0.54
OH ⁻						0.09		0.07
Cr ⁶⁺	23.71	23.71	23.76	23.76	23.76	23.76	23.76	23.76
H ₂ S	0.12	0.12	0.80	0.80	0.80	0.80	0.80	0.80
NH ₄ ⁺	49.89	49.89	50.26	50.26	50.26	38.41	50.26	40.64
O&G	1294.95	1294.95	129.72	9.08	9.08	0.95	9.08	2.48
FSS	398.66	398.66	159.82	27.97	27.97	7.69	27.97	11.50
BOD ₅	706.69	706.69	409.93	225.46	225.46	23.67	225.46	61.58
TSS	797.32	797.32	319.64	55.94	55.94	15.38	55.94	23.00
	152	162	173	181	183	191a	191b	192b
C	199.96	199.96	199.96	199.96	199.96	52.63	36.20	52.60
H ⁺	0.54	0.54	0.54	0.54	0.54	0.63	0.79	0.63
OH ⁻	0.07	0.07	0.07	0.07	0.07	0.08	0.10	0.08
Cr ⁶⁺	23.76	23.76	23.76	1.19	23.76	0.15	0.00	0.15
H ₂ S	0.80	0.80	0.80	0.80	0.80	0.93	1.17	0.93
NH ₄ ⁺	40.64	40.64	40.64	2.03	40.64	2.63	0.08	2.63
O&G	2.48	2.48	2.48	2.48	2.48			
FSS	11.50	11.50	11.50	11.50	11.50	0.47	0.01	0.47
BOD ₅	61.58	61.58	61.58	61.58	61.58	16.21	11.15	16.21
TSS	23.00	23.00	23.00	23.00	23.00	0.94	0.03	0.94
	91	93	94	C_{91}^{max}	C_{93}^{max}	C_{94}^{max}		
C	46.70	52.60	1,289.35	105.3	52.6	-		
H ⁺	0.69	0.63		-	-	-		
OH ⁻	0.09	0.08		-	-	-		
Cr ⁶⁺	0.10	0.15	23.71	0.1	-	-		
H ₂ S	1.02	0.93	0.12	1.1	-	10		
NH ₄ ⁺	1.71	2.63	49.89	4.9	-	50		
O&G			1294.95	25	-	-		
FSS	0.31	0.47	398.66	15	100	-		
BOD ₅	14.38	16.21	706.69	30	52.6	-		
TSS	0.61	0.94	797.32	30	100	-		

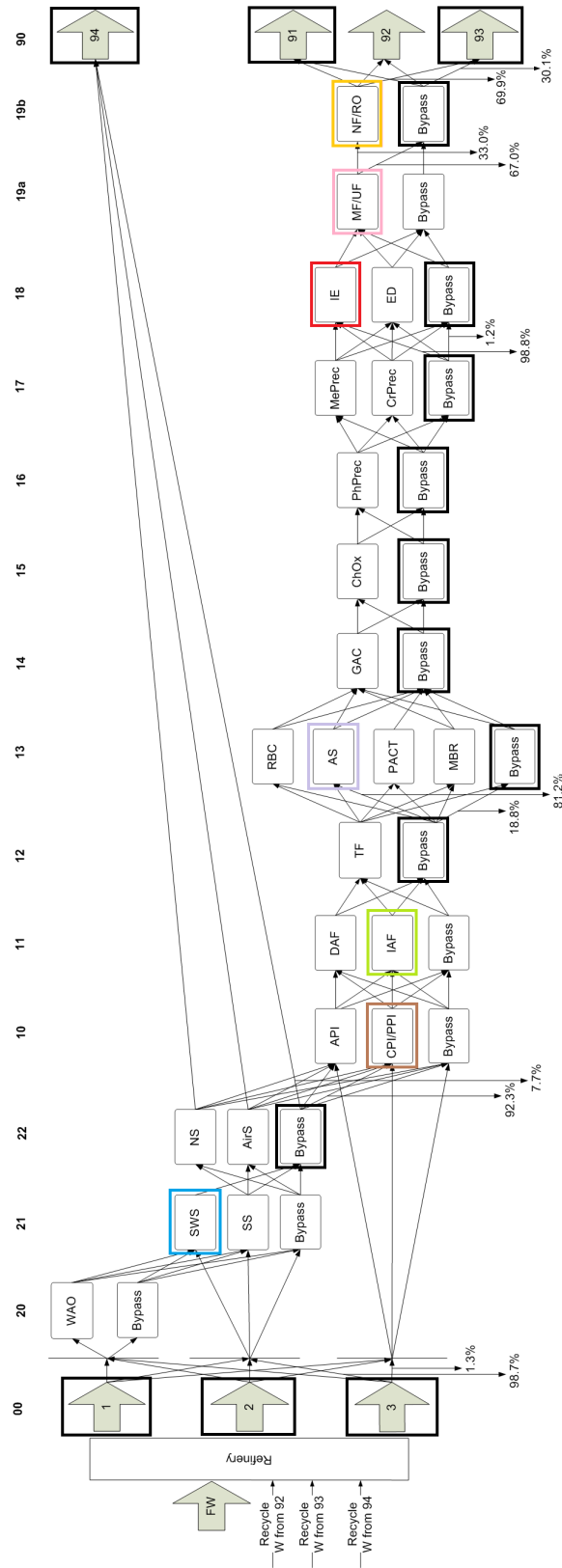


Figure 3.10 – Network corresponding to the multi-stream treatment solution: objective is minimum total annualized cost (Z_1).

The solution found is indicated as non-optimal by the solver. This suggests that it may be a local optimum. The optimization problem is solved using a different starting point to investigate if the solution is sensitive to it. A new starting point (SP2) is chosen varying the solution obtained for the single-stream treatment problem on the basis of the overtreatment identified in section 3.4: with respect to the configuration shown in Figure 3.2, some flow is sent to the desalter after the sour water stripper (7.5% of the outlet flow from 223 goes to 94, and the rest to 102), some flow bypasses the activated sludge (10% of the outlet flow from 122 goes to 135, and the rest to 132) and some water is sent to sink 93 (25% of the outlet flow from 191b goes to 93, and the rest to 91). With this different starting point, a different solution is found: the objective function has the value of 15.289 M\$/yr and different intervals are selected (212, 213, 222, 223, 102, 103, 112, 113, 122, 131, 135, 142, 152, 162, 173, 183, 191a, 191b, 192b, 91, 93, 94). This indicates that the solution is sensitive to the selection of the starting point and may not be the global optimum.

In order to verify if the solution found is or not the global optimum, different binary configurations are fixed and the optimization problem is solved as NLP. The binary configurations are chosen so that a decrease in the objective function is expected taking the solution of the single-stream treatment problem as a reference (i.e. if a process alternative is selected, part of the flow can bypass it, so also the bypass is selected). The flow rates and the split factors are optimized by the solver. The binary combinations considered are reported in Table 3.16 and a graphical representations of the solutions obtained for each of them is displayed in Figure 3.11. The solution corresponding to the MINLP solved as just discussed is indicated as network no. 0. Other 20 binary configurations were tested. The first 15 involve the selection of only one treatment unit or one treatment unit and the bypass per removal task. It can be seen that the solution found is not the global optimum: a lot of different binary combinations presents a better value of the objective function. Nevertheless, the solution of the multi-stream treatment problem as MINLP obtained using the solution of the single-stream treatment problem as a starting point led to a decrease of the objective function of 15.3%, which still represents a good gain. Significant improvements in the objective function can be achieved by selecting different intervals in the removal tasks related to the H₂S removal (tasks 21 and 22); this is not surprising, since it was shown that unit 211 has the biggest impact on the total annualized cost. The best solution found corresponds to network no. 12 and is 12.442 M\$/yr, which represents an improvement of 28.7% with respect to the single-stream treatment solution and of 15.8% with respect to the original multi-stream treatment solution found. Other 5 binary configurations were tested in which the constraint on the selection of maximum two intervals per task (equation 2.27) is removed; in this way, more than two alternatives can be selected for each removal task. The advantage associated with this is significant for the objective function, but the improvement gained by expanding the search space is comparable with the one obtained in some of the binary configurations tested previously, so this option is considered not worth.

Since the solution found for the multi-stream treatment problem is not the global optimum, which was instead the case for the single-stream treatment problem solved in section 3.4, the type of analysis done in section 3.4.1 to investigate the effect of different level of contamination in the wastewater sources is not performed here since the solution would be not meaningful.

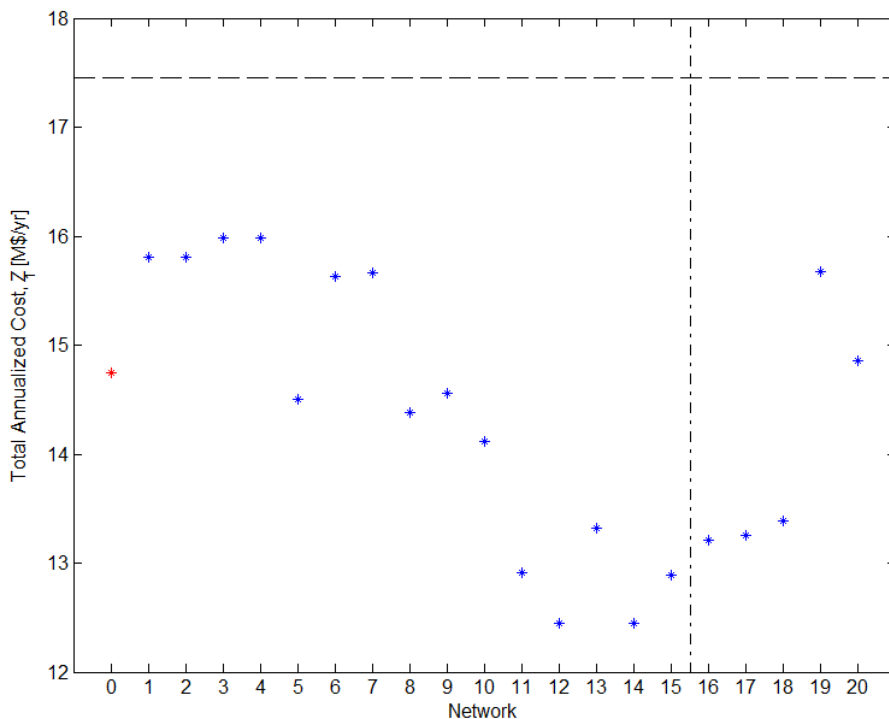


Figure 3.11 – Solutions of the multi-stream treatment problem formulated as NLPs for different fixed binary combinations: the solution of the MINLP solved using the single-stream treatment solution as a starting point is marked in red, the solutions of the NLPs solved for different binary sets are marked in blue and the dashed line indicates the solution of the single-stream treatment problem - networks in Table 3.16.

Table 3.16 – Binary combinations for which the NLP was solved with minimum total annualized cost as objective function - results in Figure 3.11.

No.	211, 212	223	102, 112	122	132, 135	142	152	162	173	181, 183	191a	191b, 192b	91, 93, 94
0	211, 212	223	102, 112	122	132, 135	142	152	162	173	181, 183	191a	191b, 192b	91, 93, 94
1	211	223	102, 112	122	132, 135	142	152	162	173	183	191a, 192a	191b, 192b	91, 93, 94
2	211	223	102, 112	122	132, 135	142	152	162	173	183	191a	191b	91, 93, 94
3	211	223	102, 112	122	132	142	152	162	173	183	191a	191b, 192b	91, 93, 94
4	211	223	102, 103, 112	122	132	142	152	162	173	183	191a	191b, 192b	91, 93, 94
5	211	223	102, 112	122	132, 135	142	152	162	173	181	191a, 192a	191b, 192b	91, 93, 94
6	211, 213	223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
7	211, 213	221, 223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
8	211, 213	222, 223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
9	211, 213	222, 223	102, 112	122	132, 135	142	152	162	173	183	191a, 192a	191b, 192b	91, 93, 94
10	211, 213	222, 223	102, 112	122	132, 135	142	152	162	173	183	191a	191b	91, 94
11	211, 213	222, 223	102, 112	122	132, 135	142	152	162	173	181, 183	191a	191b, 192b	91, 94
12	211, 213	222, 223	102, 112	122	132, 135	142	152	162	173	181	191a	191b, 192b	91, 94
13	211, 213	222, 223	102, 103, 112	122	132	142	152	162	173	181	191a	191b, 192b	91, 94
14	211, 213	222, 223	102, 103, 112	122	132, 135	142	152	162	173	181	191a	191b, 192b	91, 94
15	211, 213	222, 223	102, 112	122	132, 135	142	152	162	173	181	191a, 192a	191b, 192b	91, 94
16	211, 212, 213	222, 223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
17	211, 212, 213	221, 222, 223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
18	211, 212, 213	221, 223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
19	211, 212, 213	223	102, 112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
20	211, 213	222, 223	102, 112	121, 122	133	142	152	162	173	181	191a	191b, 192b	91, 92, 93, 94

3.5.2 Maximum water recycle

In this case, the objective function is represented by equation 2.36. If the solution obtained for the single-stream treatment problem is given as a starting point (SP1), the solution found allows for recycle to 91 and 93 only, which clearly does not correspond to a solution in which the water recycled is maximum. A different starting point (SP3) is given. This starting point allows part of the stream to go to the desalter after the sour water stripper (7.7% of the flow out of 223 goes to 94, and the remaining to 102; in order to have a low enough concentration of ammonia, 1.2% of source 3 must be sent to 102 without passing through tasks 20, 21 and 22) and the stream is treated down to the stricter composition of the sinks (boiler feed water, 92) without splitting before the end, where 25% of the outlet flow from 191b is sent to sinks 92 and 93 while the rest goes to 91. The binary configuration that allows purification of water down to the stricter composition is found solving the network as a single-stream treatment problem with the minimum annualized cost as objective function and forcing the stream to choose sink 92 removing the limitation imposed on the maximum flow rate. In order to reach the strict composition imposed on the boiler feed water, with respect to the units selected in the single-stream treatment solution (shown in Figure 3.2), also the trickling filter (121) and the ion exchange (181) are necessary and the powdered activated carbon treatment is selected instead of the activated sludge (133 instead of 132). With this new starting point, a solution is obtained in which all the water sinks are selected and receive the maximum flow rate allowed, which clearly corresponds to the maximum water recycle possible. Figure 3.12 shows the network obtained, where also the split factors are reported - if different than 1. The results in terms of total annualized capital cost, its breakdown and the water saved, discharged and wasted can be seen in Table 3.17, where they are compared with the best solution found for the total annualized cost. It can be seen that 53.7% of the water treated is recycled, even if the savings are still not a significant contribution to the objective function. The total annualized cost associated to this treatment is higher: for the solution found, it is 18.229 M\$/yr, which is higher than all the solutions found in section 3.5.1. However, this value is not representative in the sense that various configurations exist which allow for the maximum water recycle at different costs; the solution found here is the closest solution to the starting point given. For this reason, next section deals with the research of a trade-off solution between the maximum water recycle and the minimum total annualized cost.

Table 3.17 – Summary of results for best found multi-stream treatment solution for Z_1 vs. found multi-stream treatment solution for Z_2 .

	UOM	Best Multi-Stream (for Z_1)	Best Multi-Stream (for Z_2)	Relative variation	$W_{s/d/w}/W_t$
Z_1	[M\$/yr]	12.442	18.229	46.5%	
Capex	[M\$]	18.232	27.637	51.6%	
Opex	[M\$/yr]	11.237	17.238	53.4%	
Utility Cost	[M\$/yr]	7.585	12.239	61.4%	
Waste Cost	[M\$/yr]	3.652	4.999	36.9%	
Savings	[M\$/yr]	0.010	0.851	8,491.9%	
Water Saved (Z_2)	[ton/h]	50.00	353.10	606.2%	53.7%
Water Discharged	[ton/h]	495.19	145.39	-67.7%	22.1%
Water Wasted	[ton/h]	112.34	192.23	7.6%	29.2%

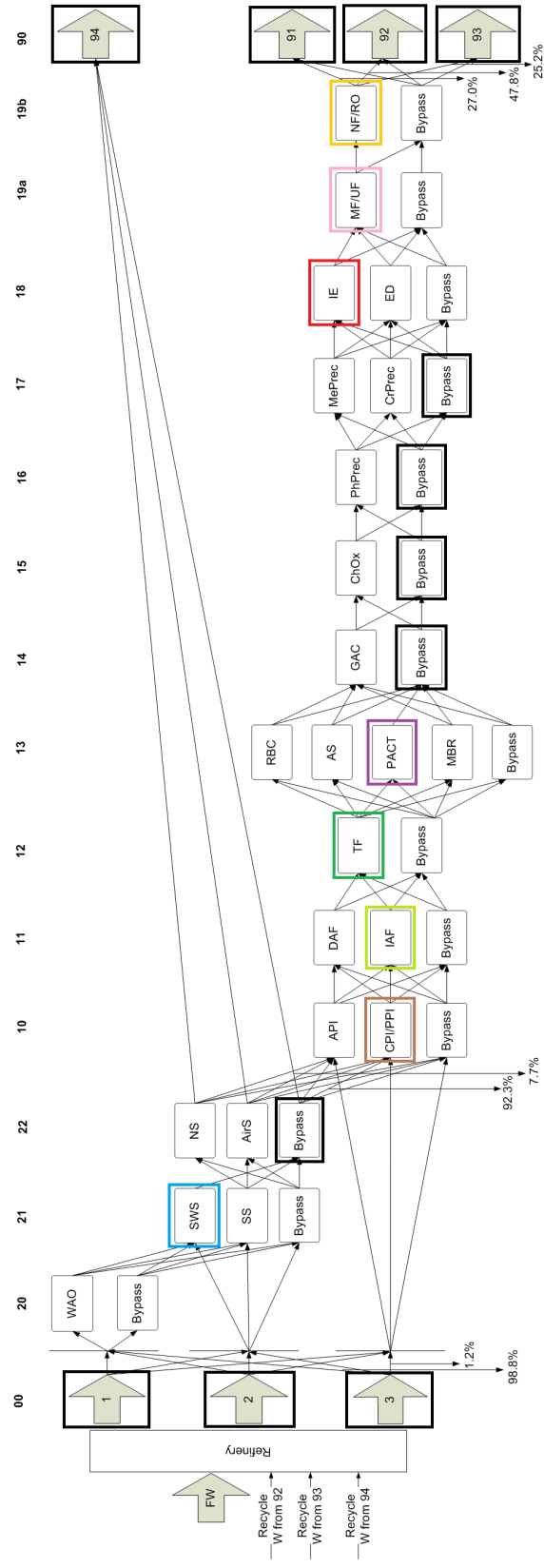


Figure 3.12 – Network corresponding to the multi-stream treatment solution: objective is maximum water recycle (Z_2).

3.5.3 Minimum total annualized cost vs. maximum water recycle

As seen in section 3.5.2, a higher water recycle involves a higher treatment cost because the treatment must be able to comply with the strictest composition limits of the water sinks. However, the situation in which the maximum amount of water is recycled does not correspond to a unique value of the total annualized cost, because different possible configurations exist in which the water recycle is maximum and the treatment cost have different values.

It would be interesting to find the network which allows for the maximum water recycle at the minimum cost. If the optimization problem is solved for the minimum total annualized cost as in section 3.5.1 with the additional constraint of maximum water discharge ($F_{\text{H}_2\text{O},\text{O}_o}^{\text{in}} = F_{\text{O}_o}^{\text{max}}$, with $\text{O}_o \neq \text{O}_x$) using the single-stream treatment solution as a starting point (SP1), the total annualized cost is 16.022 M\$/yr. However, the solution suffers of the same inconveniences encountered in section 3.5.1: different initializations lead to different solutions close to the starting point and the solution found is not a global optimum. Thus, it is tried to find the cheapest solution for the maximum water recycle considering the trade-off between the two objectives.

The trade-off between the total annualized cost and the amount of water recycled can be highlighted by investigating different feasible integer variable combinations associated with a certain level of discharge and solving the NLP with respect to the minimum total annualized cost. The values of the total annualized cost (Z_1) and of the water recycled (Z_2) can be plotted one against each other (the so called Pareto diagram) and the best solution can be identified depending on the optimum criterium desired - minimum total annualized cost or maximum water recycle. Since Z_1 is to be minimized and Z_2 is to be maximized, if Z_1 lies on the vertical axis and Z_2 on the horizontal axis an utopic solution would lie in the bottom-right corner. If different integer variable configurations are considered which allow for the purification of the flow down to the lowest limits of composition of the sinks, this method could help to find the network which gives the maximum water recycle at the lowest cost. The different binary combinations tested are listed in Table 3.18 and Figure 3.13 shows the Pareto plot obtained. The minimum cost associated to the selection of all the recycle option (sinks 92, 93, 94, with $Z_2 = 353.10$ ton/h) is found to be 15.424 M\$/yr and corresponds to network no. 3; there is no guarantee that this is the global optimum, since other better binary configurations may exist which were not tried. Networks no. 1, 2 and 8 allow for reaching the stricter composition of the sinks, but only part of the flow is sent there to keep the costs lower. As was seen in section 3.5.1, the network which is associated to the minimum cost, here indicated as network no. 11, corresponds to the selection of sink 94 only with a recycle of $Z_2 = 50.00$ ton/h. A recycle of $Z_2 = 154.60$ ton/h can be obtained at intermediate cost (networks 9 and 10).

Figure 3.14 and Figure 3.15 report the water discharged and wasted for the same binary configurations considered. The network with the lowest cost have the highest water discharge, and vice versa. The water wasted increases with the increase of the water recycled because the units which produce water waste (the tertiary filtration units, 191a and 191b) are used more intensely when the purity to reach is higher - which is required for satisfying the constraints on the composition of sink 92. The excursion of the waste is contained though, because these units are necessary even if the stream is sent only to discharge, as was seen in section 3.4. The amount of the water wasted ranges between 29.2% and 16.6% of the total treated, which is a quite high percentage. It would be good to consider if to treat the retentate in the same treatment train recycling it back as a source or to the same filtration units.

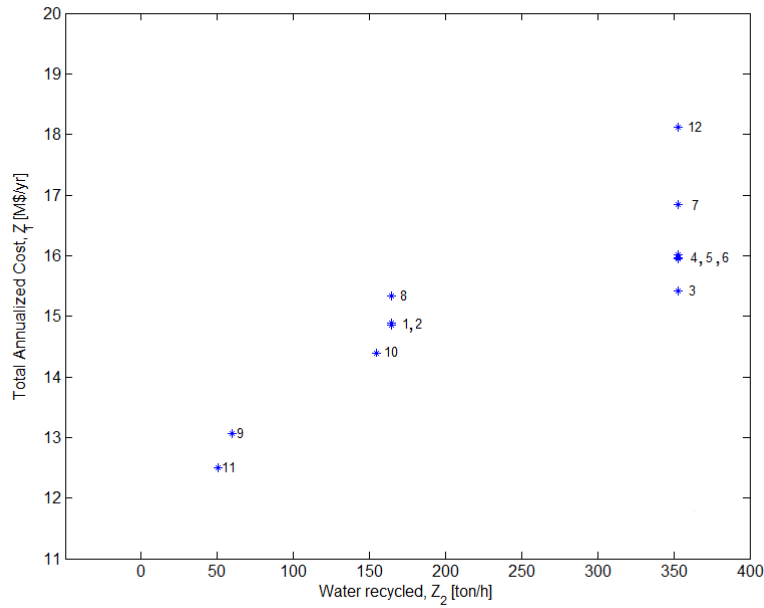


Figure 3.13 – Pareto plot for Z_1 - total annualized cost, in [M\$/yr] vs. Z_2 - water recycled, in [ton/h].

Table 3.18 – Binary combinations for which the NLP was solved with minimum total annualized cost as objective function - results in Figure 3.13.

No.														
1	211, 213	222, 223	102	112	121, 122	133	142	152	162	173	181	191a	191b, 192b	91, 92, 93, 94
2	211, 213	222, 223	102	112	121, 122	133, 135	142	152	162	173	181	191a	191b, 192b	91, 92, 93, 94
3	211, 213	222, 223	102	112	121, 122	133, 135	142	152	162	173	181, 183	191a	191b, 192b	91, 92, 93, 94
4	211, 213	222, 223	102	112	121, 122	133	142	152	162	173	181, 183	191a, 192a	191b, 192b	91, 92, 93, 94
5	211, 213	222, 223	102	112	121, 122	133, 135	142	152	162	173	181, 183	191a, 192a	191b, 192b	91, 92, 93, 94
6	211, 213	222, 223	102	112	121	133, 135	142	152	162	173	181, 183	191a, 192a	191b, 192b	91, 92, 93, 94
7	211, 213	222, 223	102	112	121	133	142	152	162	173	181, 183	191a	191b	91, 92, 93, 94
8	211, 213	222, 223	102	112	121, 122	133, 135	142	152	162	173	181	191a, 192a	191b, 192b	91, 92, 93, 94
9	211, 213	222, 223	102	112	122	132, 135	142	152	162	173	181	191a, 192a	191b, 192b	91, 93, 94
10	211, 213	222, 223	102	112	122	132, 135	142	152	162	173	183	191a	191b, 192b	91, 93, 94
11	211, 213	222, 223	102	112	122	132, 135	142	152	162	173	181	191a	191b, 192b	91, 94
12	211	223	102	112	121	133	142	152	162	173	181	191a	191b	91, 92, 93, 94

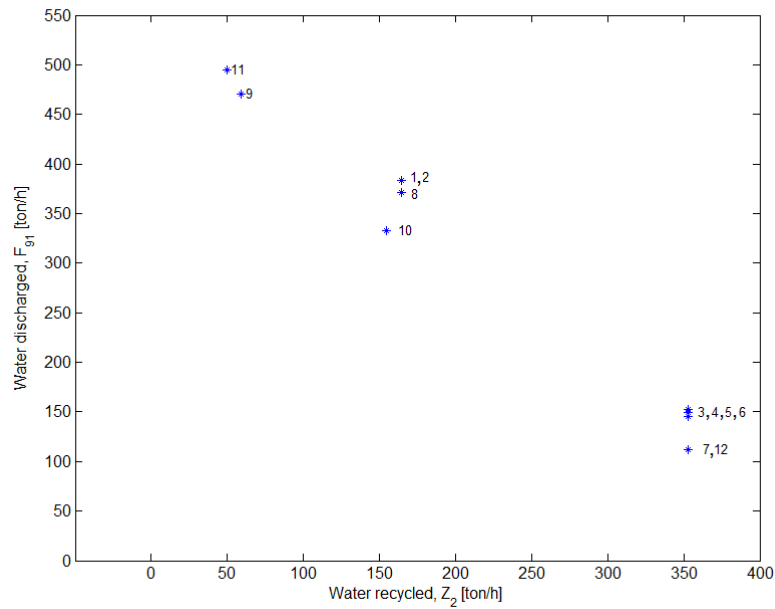


Figure 3.14 – Pareto plot for $F_{\text{H}_2\text{O},91}^{in}$ - water discharged, in [ton/h] vs. Z_2 - water recycled, in [ton/h].

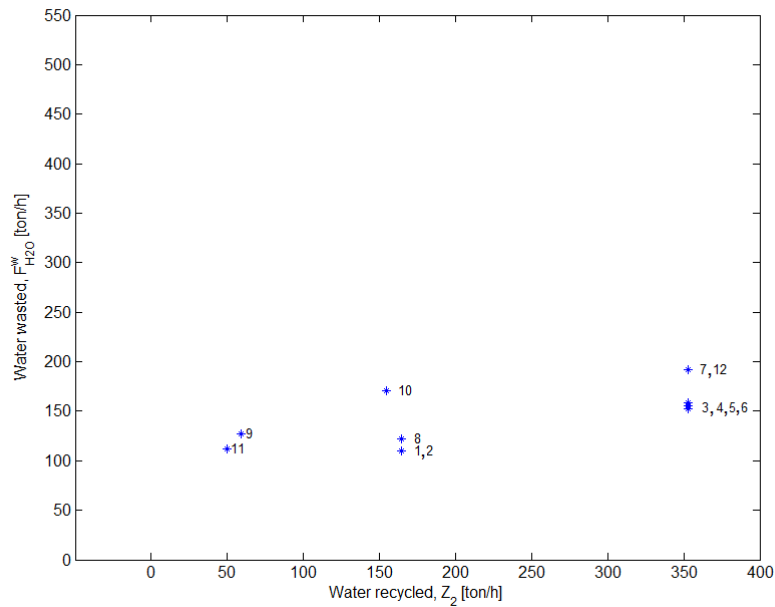


Figure 3.15 – Pareto plot for $\sum_{kk} F_{\text{H}_2\text{O},kk}^w$ - water wasted, in [ton/h] vs. Z_2 - water recycled, in [ton/h].

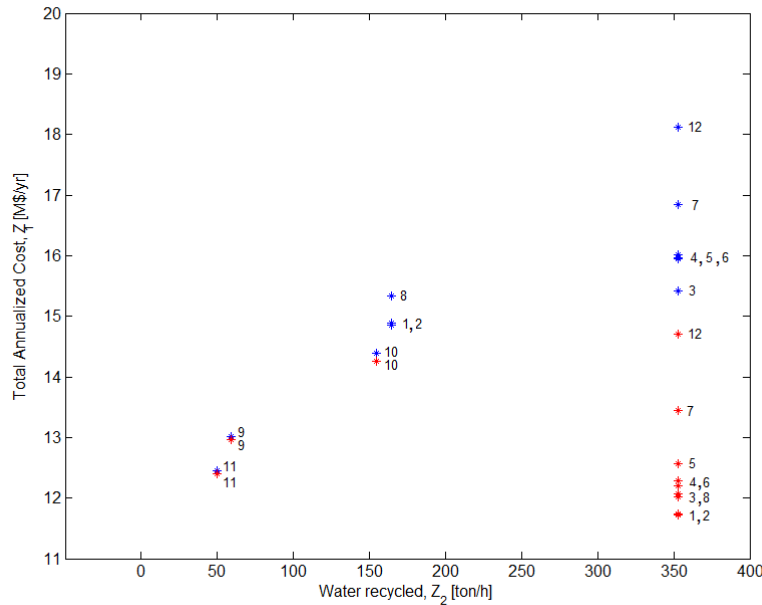


Figure 3.16 – Pareto plot for Z_1 - total annualized cost, in [M\$/yr] vs. Z_2 - water recycled, in [ton/h]; blue: base water cost; red: water cost five times higher.

The Pareto diagram looks different depending on the price of water: in water scarce areas, the price can be much higher than the one assumed so far. The value chosen for the price of freshwater, 0.28 \$/ton, is representative for example of China, Chongqing; the average value is 1.32 \$/ton and the extremes are 0.01 \$/ton in Cuba, L’Havana, and 7.71 \$/ton in Denmark, Copenhagen [5]. These prices are for end users in municipalities, thus the price of water for industrial use could differ depending on the agreement of the industrial complex with the water suppliers. Since the water cost can vary a lot, for purpose of comparison a scenario in which the price of freshwater is five times the value used in the previous simulations is considered, and the same analysis is done for this case. The Pareto diagram for the two scenarios is reported in Figure 3.16. For networks no. 9, 10 and 11, the difference is minimal due to the fact that the amount of water recycled is low. For the networks that already allowed for the maximum water recycle (no. 3, 4, 5, 6, 7, and 12), the annual cost is much lower due to the savings, which are five times higher. For configurations that could potentially lead to the maximum water recycle but led to a lower water recycle to contain the costs (networks no. 1, 2, and 8), this new value of water price makes the recycle of the maximum amount of water convenient. Table 3.19 compares the difference observed for a specific network (network no. 2): it can be seen that while the operating and the capital costs do not change significantly, the savings register a huge increase, thus switching the choice of treating the water in enough quantity to satisfy the requirements of the stricter sink.

Table 3.19 – Comparison of the effect of the water cost on the total annualized cost for the same network configuration (network no. 2 in Table 3.18): scenario 1 represents the base case for which all the other optimization problems were solved; scenario 2 represents a case in which the water price is five times higher.

	UOM	Scenario 1	Scenario 2	Relative variation
Z_1	[M\$/yr]	14.879	11.741	-21.1%
Capex	[M\$]	22.058	23.149	4.9%
Opex	[M\$/yr]	13.481	14.454	7.2%
Utility Cost	[M\$/yr]	8.726	9.632	10.4%
Waste Cost	[M\$/yr]	4.754	4.822	1.4%
Savings	[M\$/yr]	0.072	4.256	5835.5%
Water Saved (Z_2)	[ton/h]	164.54	353.10	114.6%
Water Discharged	[ton/h]	383.63	159.82	-58.3%
Water Wasted	[ton/h]	109.39	144.64	32.2%

3.6 Discussion of the results

In this section, the results obtained for the case study of oil refinery wastewater are summarized and discussed. Once the network is developed, it is solved as an optimization problem as a single-stream or multi-stream treatment problem.

The network obtained from the solution of the single-stream treatment problem for the objective of minimum total cost is shown in section 3.4 along with the relevant results. It is seen that the stream is overtreated with respect to various contaminants, thus suggesting that the flow could bypass the treatment operations at least partly with the effect of decreasing the cost associated with them; additionally, part of it could be recycled as cooling water with the effect of reducing the freshwater consumption and the associated costs. Consequently, this solution is judged not acceptable and it is considered worth to investigate the multi-stream treatment problem, which allows for the splitting of the stream but it is more complex from a mathematical point of view - the single-stream treatment problem is a MILP while the multi-stream treatment problem is a MINLP. Nevertheless, the solution of the single-stream treatment problem is useful for the solution of the multi-stream treatment problem because it provides a good starting point to initialize the solution algorithm of the MINLP, thus helping its convergence. Additionally, this solution provides a benchmark to evaluate the advantages introduced by the new solution.

The networks obtained from the solution of the multi-stream treatment problem and the relevant results are shown in section 3.5.

The results obtained if the objective function is the minimum total annualized cost are shown in section 3.5.1. If compared to the solution of the single-stream treatment problem, the solution found for the multi-stream treatment problem presents a lower value of the objective function, as well as of all the other entries of the costs - utility, waste and capital cost, and the limitations on the contaminant concentrations imposed on the water sinks are respected quite tightly. Thus, this solution is better than the one obtained for the single-stream treatment problem, and this highlights the advantages of a distributed wastewater treatment system with respect to a centralized wastewater treatment system. However, since the optimization problem associated with the multi-stream treatment problem is a MINLP, the convergence to

the global optimum is not guaranteed with the available solver; this is illustrated by solving the problem as a NLP for different feasible binary configurations: the solution of some of the NLPs produces a lower value of the objective function with respect to the situation in which the problem is solved directly as a MINLP. With the current assets, it is not possible to guarantee that the global optimality is reached; however, it is definitely possible to find a solution for the network design problem and possibly an improved solution with respect to an existing case, which can be for example one corresponding to the single-stream treatment. The results obtained if the objective function is the maximum water recycle are shown in section 3.5.2. In this case it is possible to prove that the global optimality is reached because the constraints are hit - the maximum amount of flow rate that can be accepted by any water sink associated to a recycle option is sent there. However, the treatment operation has a higher cost than the previous case because the stream must be treated down to stricter concentrations.

A trade-off between the two objectives is investigated in section 3.5.3. It is observed that a higher water recycle is associated with higher treatment costs and with a higher percentage of water wasted. However, the figures on the costs are quite dependent on the price of freshwater: if this is high enough, recycling a higher amount of water can be economically convenient. Since the global optimum for the minimum cost is not found, it is not possible to find the breakeven value of the water price which makes the maximum recycle of water economically convenient.

The concentrations of the contaminants in the wastewater sources present a huge range of variability, as shown in Table 3.10 in section 3.4.1. Thus, a sensitivity analysis is performed with respect to these parameters. This is done for the single-stream treatment only, because the solution found for the multi-stream treatment problem is not the global optimum, which is instead the case for the solution of the single-stream treatment problem. The solution of the stochastic programming for the single-stream treatment problem reveals that, if it is accounted for the expected content of the contaminants of the wastewater sources, an extra unit for removal of chromium is necessary to comply with the limitations at the discharge.

When the optimization problem is solved with the minimum total annualized cost as objective function, the specific cost of the wastewater treatment is 2.996 \$/ton for the multi-stream treatment versus 3.540 \$/ton for the single-stream treatment. The typical water treatment cost in refineries ranged between 0.52 and 1.04 \$/m³ in 1999 [17]. This can be considered a qualitative validation of the result obtained, since the order of magnitude is the same.

Independently on the type of optimization problem solved (single- or multi- stream, deterministic or stochastic), the results give a number of performance and economic metrics which are useful in the early stage of design of treatment processes - for example, the specific water saved, discharged and wasted; the specific cost of the treatment etc. The results include information on the streams involved and the evolution of each contaminant in the treatment train, as well as the total annualized cost, its breakdown in utility and waste costs, the total capital cost and the contribution of the various treatment units to each of these. Furthermore, it is also obtained information on the type and the amount of utilities needed for each treatment unit, as well as on the waste produced by each of them. This is possible thanks to the employment of a functional model of the treatment units.

Furthermore, the effect that different scenarios have on the results can be investigated, for example regarding different levels of contamination of the wastewater sources or different wa-

ter costs. The optimal network can be found with respect to any desired objective function, as it was exemplified for the minimum total annualized cost or for the maximum water recycle. Also, the effect of the uncertainties in the contamination level of the wastewater to treat and in the treatment performance can be evaluated through the use of stochastic programming.

If any refinery is interested in making evaluations similar to the ones presented here, the concentrations of the contaminants of the various wastewater sources and the limitations on the treatment objectives of the specific site can be assigned, and the problem can be solved for their specific data with the same superstructure and following the same steps illustrated here. If a refinery is interested in redesigning its treatment to comply with new environmental regulations or wastewater influents, it may be possible that some of the treatment units included in the superstructure are already implemented and it may be desired to keep them. In this case, the optimization problem can be solved forcing the solution to include these units. This is an example of solution of a retrofitting or expansion problem. The parameters for the aforementioned units can also be adjusted to the real parameters known from practice.

The present chapter additionally represents a successful application of the methodology presented in section 2.1 of Chapter 2 to a case study dealing with oil refinery wastewater. The methodology can be applied to a different industry going through its steps as it was done for the present case study and tailoring the input data on the basis to the network to be built: the wastewater sources and the treatment objectives will differ in number and in the type and number of pollutant considered, and different treatment technologies could be included depending on the specific pollutants to remove - most of the ones considered in the case study presented can be used for many types of wastewater, however the parameters which characterize them (removal efficiency, waste produced and even the utility consumption) can vary with the type of wastewater treated. Also the configuration of the superstructure can vary. Thus, it is necessary to go through the steps of the methodology and apply each of them having in mind the considerations which are peculiar for the type of industry chosen.

In conclusion, thanks to its flexibility and to the relevance of the information given, the methodology developed constitutes a useful tool to provide a guideline for the design of wastewater treatment systems for new plants or for retrofitting or expansion of existing plants.

Chapter 4

Conclusions

In this work, a systematic framework for the formulation and solution of water network problems is proposed. The methodology consists in the following steps. First, the scope is posed and the sources of wastewater and the treatment objectives are identified; the former are characterized in terms of total flow rate and concentration of the contaminants and the latter in terms of the limits imposed on the maximum total flow rate and on the concentration of the various contaminants. Second, a suitable superstructure is built to represent water network alternatives by connecting wastewater sources and treatment objectives through the treatment operation, which is organized in tasks on the basis of the pollutants to remove or on the principle of treatment, and for each task different alternative treatment technologies are proposed. Each treatment alternative is modeled according to a simple but functional general scheme which gives information on the type and amount of utilities consumed and on the waste produced, as well as on the extent of removal of the pollutant by reaction or separation. The mathematical model of the network is obtained considering the equations that characterize its various parts and features. Finally, the problem is formulated as a Mixed Integer Linear or Non-Linear Programming (MILP/MINLP), which is solved in GAMS to identify the best wastewater treatment network among all the possible process paths according to a selected optimum criterion - which is most commonly the minimum total cost or the maximum water recycle, which are of interest in water networks.

In order to highlight the features of the tool, a case study dealing with oil refinery wastewater is developed. Three wastewater sources are considered which have different level of contamination and flow rates and are representative of the types of wastewater found in this industry, and four treatment objectives are considered which include both discharge to an open surface and options of recycle to the major water using processes; the flow rate and the level of contamination of the wastewater sources and the limiting concentrations and flow rate of the treatment objectives are chosen on the basis of literature information. A superstructure containing technological alternatives for water purification is built considering the units commonly employed in the industry, and each treatment alternative is modeled according to the common framework choosing the relevant parameters; this is done on the basis of the performance reported in literature or obtained with a simple model of the process itself. Then, the optimization problem is formulated and solved choosing as objective function first the minimum total annualized cost, and then the maximum water recycle; for the first objective, it is investigated both the case in which the wastewater sources are mixed and treated as one single

stream which is not allowed to split (single-stream treatment problem) and the case in which the wastewater sources are not completely mixed and the streams are allowed to split (multi-stream treatment problem), while for the second objective only the second type of problem is solved due to the nature of the objective function. For each of the two objectives, the optimal treatment path is identified, and thanks to the stream table obtained it is possible to track the evolution of each specific contaminant in the treatment train. Additionally, information on the economic and performance parameters of the treatment is produced, such as the total capital cost, the operating cost, the cost associated with the waste, the cost associated with the utilities and its breakdown per type of utility; for any of this, the contribution of each treatment unit can be estimated. Statistics on the water discharged, wasted and recycled are also extracted. Finally, a trade-off solution between the two objectives was investigated, as well as the effect that different freshwater costs have on the solution. The effect that the uncertainty in the level of contamination in the wastewater sources to treat have on the network selection was also inspected. These results give an idea of the great amount of information that can be obtained from the employment of the methodology on a specific case study.

The methodology proposed allows the solution of any desired case study through the application of the indicated steps; furthermore, it allows for a comprehensive characterization of the wastewater flow and for a descriptive modeling of the treatment units, features which are absent in the networks proposed in literature. The advantage of proposing a complete characterization of the water stream is to enable the inclusion of a wide range of contaminants depending on the needs of the specific case study considered. The use of a more descriptive model of the treatment units gives insights on the type of utilities and wastes involved in the process, enabling to extract performance parameters of interest in the stage of design of wastewater treatment plants and decision making. Thus, the methodology is flexible for application to a wide number of case studies and can be of great help to solve problems of design of new water treatment plants as well as of retrofit, expansion or simple optimization of existing plants.

Even though the results obtained through the application of the proposed methodology are considered satisfactory, further work would benefit its predictivity.

In order to solve the inability to guarantee that the global optimum is found, the model could be reformulated with the help of some global optimization technique to avoid the problems associated to the non-convexities, so that it can smoothly lead to a solution of global optimality.

At a superstructure level, the possibility for the stream to move only through adjacent removal tasks may not be the best solution, since some undesired mixing could still take place. A modification that can prove useful is to allow the stream to split and go to tasks situated downstream without passing through all the train of tasks, thus providing an alternative to the use of the bypass and avoiding unneeded mixing with other streams. However, this would have the drawback of increasing hugely the problem complexity, since a higher number of split factors would have to be accounted for. Another modification that could be made on the network structure is the possibility of recycling back the water waste produced in the tertiary filtration units, which is a contaminated flow of water itself and was seen to amount to a quite significant fraction of the total stream treated. Another option that could be considered is the inclusion of a freshwater source to dilute the wastewater to treat or to discharge: in this way, the treatment objectives can be achieved not only with pure treatment. While this may prove convenient from an economical point of view depending on the price at which the

freshwater is available, it does not represent an environmentally friendly alternative.

In the type of network generated, the waste handling is not considered. The wastes and the sludges originated in wastewater treatment are often sent to treatment processes, and this could be the object of a further optimization problem.

For a generic water network, another objective function that may prove interesting to test apart from the total minimum cost and the maximum water recycle could be some kind of objective function which quantifies the environmental impact of the treatment, for example minimum waste with a relevant weight associated to each waste type.

With respect to the modeling of the single treatment units, the prediction can be improved on the basis of real industrial performance and expert review. For example, the treatment performance often varies depending on the inlet contaminant concentration and the units can reach down to a certain lower concentration regulating the size of the equipment and the utilities fed. This could be accomplished replacing the assumption of constant conversions and waste fractions with parameters which depend on the conditions of the inlet stream.

A further expansion could be done also with respect to the wastewater characterization used. Other two important characteristics of wastewater which can be included among the properties to monitor are the temperature and the alkalinity, which are relevant not only for the presence of discharge limits on them, but also because they represent important parameters for the correct functioning of most wastewater treatment processing units, especially the biological and the membrane treatments are effective only in a certain range of pH and temperature. If the wastewater stream is fully characterized in its chemical composition, the pH can be back calculated on that basis, while the temperature is an independent property.

Thus, this work represents a first step towards a more detailed representation of water networks to synthesize and optimize, but the synthesis of water networks through mathematical optimization still remains a problem were further studies are needed to achieve a completely satisfactory state of modeling.

Appendices

Appendix A

Water sources and sinks characterization

In this appendix, a short description of how the flow rates and the contaminant level of the wastewater sources and the water sinks included in the superstructure is given.

A.1 Flow rates

The flow rates of the various wastewater sources and water sinks are estimated on the basis of the data reported by Khor et al. [23] for a petroleum refinery in Malaysia.

The total of the wastewater sources flow rates reported is assumed to be the flow rate of oily wastewater (558.8 ton/h). The flow rates of the sour wastewater and the caustic wastewater are obtained using the proportion between the three according to what reported in [10] (where it is indicated that a refinery produces in general between 10 and 30 gal/bbl of wastewater, between 1.1 and 6 gal/bbl of sour water, and between 2 and 12.2 gal/1000bbl of spent caustic; thus the average proportion between the three are 20:3.55:7.10 $\cdot 10^{-3}$).

For the water sinks, the limitation on the flow rate for the desalter is chosen equal to the wastewater produced by that process, while for the recycle as cooling water and boiler feed water the sum of the flow rates sent to the relevant operation is used - see [23].

A.2 Contaminant level

Data on the level of contamination of the wastewater sources in terms of the pollutants selected are found in literature. Table A.1 shows the sources used for each type of the three wastewaters. The maximum, minimum and average values of these data is reported in Table 3.10 in section 3.4.1. The metals are assumed to be all Cr₆⁺, which is the most abundant and important metal present in refinery wastewater, and the FSS are assumed to be half of the TSS.

The references used for the characterization of the limitations on the concentrations of the various pollutants in the water sinks were already reported in section 3.2.3 of Chapter 3.

APPENDIX A. WATER SOURCES AND SINKS CHARACTERIZATION

Table A.1 – References for level of contamination of the three wastewater sources.

Wastewater Source	ID	Reference
Caustic	1	[12], [42], [43], [44], [45]
Sour	2	[12], [15], [43]
Oily	3	[12], [42], [46], [47], [39]

Appendix B

Models for process intervals

In this appendix, the process intervals are presented along with the data and the information used in order to model them. It will be evident how many factors are involved in the wastewater treatment operations and how important it is to take into account them in order to represent the operations in a meaningful way.

B.1 Gravity separation

In separation equipment based on gravity, components heavier and lighter than water are separated thanks to their weight difference: free oil floats to the surface and solids settle to the bottom, where they are skimmed and scraped off, respectively. While sedimentation is generally employed in all process industries, the following equipment for oil-water separation is typical of refineries.

B.1.1 American Petroleum Institute (API) separator

The basic design of an American Petroleum Institute (API) separator is a long rectangular basin with enough detention time for most of the oil to float to the surface and for most of the solids to settle on the bottom. They are usually equipped with scrapers to move the oil to the downstream end of the separator where it is collected. On their return to the upstream end, the scrapers travel along the bottom moving the solids to collection. The API separator is also used as a control device to protect downstream equipment against large oil slugs [48, 49]. An API separator is effective to remove emulsified particles down to 15 μm of diameter; levels of oil and total suspended solids in the effluents are usually down to 50 and 200 mg/L, respectively, and a well designed API separator should be able to achieve the same outlet performance despite the variability of the influent quality [49].

In the API separator no transformation occurs, so no reaction is present. The equipment acts only to remove the phases other than water, so floating oil and grease and settling solids. All the separated material goes as waste. No product separation is performed.

Removal efficiency

Removal efficiencies for API separators are reported in [12] and [50]; on the basis of this data, an average removal efficiency of COD (and BOD₅) of 30.5%, of 30.0% for TSS and of 79.5% for oil and grease.

Utility consumption

The utility consumption accounts for:

- Electricity necessary to pump fluid through the basin and move the scraper.

The utilities used are not added to the stream ($\alpha_i = 0$).

Correlation of operating costs as a function of the flow rate are reported in [51] for a specific API - depth of 1 m, width of 2 m, mean inlet particle diameter of 1 mm. It can be reasonably assumed that the operating costs are due to the electricity consumption only, so this value is back calculated with the relevant price of electricity and, since the relationship is almost linear, an average value is used to represent the electricity consumption of a generic API separator, as $\mu_{EL,H_2O}=0.22$ MJ/ton.

B.1.2 Corrugated/parallel plate (CPI/PPI) separator

Corrugated and parallel plate separators (CPI and PPI, respectively) rely on the same principle of the API separators. Their tilted plates increase the collection area while decreasing the overall size of the unit. As the water flows through the separator, the oil droplets coalesce on the underside of the plates and travel upwards to where the oil is collected, while the solids deposit in the bottom. Because of the coalescing action, these separators can separate oil droplets as small as 6 μm in diameter and produce effluent-free oil concentrations as low as 10 mg/L [12].

As in the API separator, no reaction is present and the oil and solids separated go as waste. No product separation is performed.

Removal efficiency

Removal efficiencies for CPI or PPI separators are reported in [52] for TSS and oil and grease as 60.0% and 90.0%. The removal efficiency for COD (and BOD₅) are estimated on the basis of the experimental data reported in [16].

Utility consumption

The utility consumption accounts for:

- Electricity necessary to pump fluid through the basin and move the scraper.

The utilities used are not added to the stream ($\alpha_i = 0$). Due to the lack of data, the electricity consumption is assumed to be the same as for an API separator.

B.2 Flotation

Flotation enhances the separation of very small or light particles that will settle slowly if separated by gravity, thus removing them more completely and in shorter time. The removal can be enhanced by the use of chemical additives: inorganic chemicals (aluminum and ferric salts and activated silica) bind particulate matter together and make bubble entrapment easier; polymers can be used to change the liquid-gas and/or solid-liquid interface properties [9]. With the addition of appropriate additives as needed, the flotation of refinery wastewaters reduced their oil content to less than 10 mg/L in pilot-plant operation [12].

B.2.1 Dissolved Air Flotation (DAF)

The Dissolved Air Flotation (DAF) consists in injection of air in water under pressure followed by pressure release. The fluid is compressed with a pump to 275-350 kPa [9]. The entire flow is held in a retention tank under pressure for several minutes to allow time for the air to dissolve, then it is admitted to the flotation tank through a pressure-reducing valve where the air comes out of the solution in very fine bubbles, dragging upwards the suspended material. In large units, a portion of the effluent is recycled, pressurized and semi-saturated with air, then it is mixed with the unpressurized influent before release in the tank; in this way, the energy for pumping is reduced.

No transformation occurs, so no reaction is present. The equipment acts only to remove the suspended phases lighter than water, so floating oil and solids. All the separated material goes as waste. No product separation is performed.

Removal efficiency

For a DAF unit, removal efficiencies for COD, O&G, TSS, and BOD₅ are reported in [50] as 35.0%, 77.5%, 82.5% and 45.0%, respectively. These values are used.

Utility consumption

The utility consumption accounts for:

- Electricity necessary to pump the fluid and and to keep operation.
- Air injected to float dissolved solids and emulsified particles.
- Chemicals for coagulation and flocculation.

The utilities used are not added to the stream ($\alpha_i = 0$).

The electricity necessary to pump the fluid is relative to the work necessary for compression. According to [37], this work can be expressed in specific terms as:

$$w_P = \frac{(P_{\text{out}} - P_{\text{in}})}{\rho_W \eta_p \eta_m} \quad (\text{B.1})$$

where P_{in} and P_{out} are the inlet and outlet pressures, respectively, and ρ_W is the density of the compressed fluid, water ($\rho_W = 1000 \text{ kg/m}^3$). The pump efficiency η_p is assumed to be 0.5 and the motor efficiency η_m is assumed to be 0.9. Assuming $P_{\text{out}}=312.5$ kPa as average operating pressure, it follows that the specific consumption is 0.47 MJ/ton. Data on global consumption or electricity needed to operate the whole equipment are reported in [53], as $\mu_{\text{EL,H}_2\text{O}} = 0.59$ MJ/ton. This data is used.

According to [9], the volume of air to the mass of solids ratio (A/S ratio, in [mL/mgTSS]) for systems without recycle can be estimated as:

$$\frac{A}{S} = \frac{1.3s_a (fP - 1)}{S_a} \quad (\text{B.2})$$

where s_a [mL/L] is the air solubility ($s_a = 18.7$ mL/L at 20°C), f is the fraction of air dissolved at pressure P (usually 0.5), P [atm] is the operating pressure, S_a [mL/L] is the influent

suspended solid. Thus, the volume of air to be introduced for mass of influent water, in [mL/L], is:

$$\frac{A}{S} \cdot S_a = 1.3s_a(fP - 1) \quad (\text{B.3})$$

The volume of air to be introduced is computed assuming an average pressure of 312.5 kPa and T=20°C. The corresponding mass is found assuming perfect gas behavior and a molecular weight of $MW_{air}=29$ g/mol, in consistent units:

$$\mu_{air,H_2O} = 1.3s_a(fP - 1) \cdot \frac{P \cdot MW_{air}}{RT} \cdot \frac{1}{\rho_W} \quad (\text{B.4})$$

being $R=8.314$ J/molK. The composition by weight of dry air are around 23.18 for O₂ and 75.47 for N₂ [9]. Rounding these values to 23 and 77, respectively, the corresponding oxygen and nitrogen are:

$$\mu_{O_2,H_2O} = 0.23\mu_{air,H_2O} \quad (\text{B.5})$$

$$\mu_{N_2,H_2O} = 0.77\mu_{air,H_2O} \quad (\text{B.6})$$

In numbers, $\mu_{O_2,H_2O} = 1.09 \cdot 10^{-2}$ kgO₂/ton and $\mu_{N_2,H_2O} = 3.65 \cdot 10^{-2}$ kgN₂/ton.

For refinery wastewater, it is reported that an alum dose of 15 mg/L can be used as a coagulant [54]. Thus, the utility added results $\mu_{Alum,H_2O}=1.5 \cdot 10^{-2}$ kgAlum/ton.

B.2.2 Induced Air Flotation (IAF)

The Induced Air Flotation (IAF) consists in injection of air in water through a revolving impeller. Advantages of IAF with respect to DAF are a more compact size, a lower capital cost, a higher removal of free oil and suspended solids; while disadvantages are higher power requirements and the fact that the performance is affected by hydraulic control [9].

Removal efficiency

For the IAF unit, the same removal efficiencies employed for the DAF unit are used, with the only difference of the O&G removal, which is reported to be higher [53], and this is assumed to be 90.0%.

Utility consumption

The utility consumption accounts for:

- Electricity necessary for impeller rotation.
- Air injected to float dissolved solids and emulsified particles.

Data on global consumption or electricity needed to operate the whole equipment are reported in [53] as $\mu_{EL,H_2O} = 0.66$ MJ/kg.

Due to lack of data, the air consumption of a IAF unit is assumed equal to the one of the DAF unit.

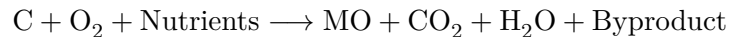
B.3 Biological treatment

Biological processes are essential for removing soluble, colloidal and suspended organic substances, for biological nitrification and denitrification and for biological phosphorous removal. This is done by means of microorganisms. At this stage, carbonaceous removal only is considered. Also, only aerobic biological treatment is considered.

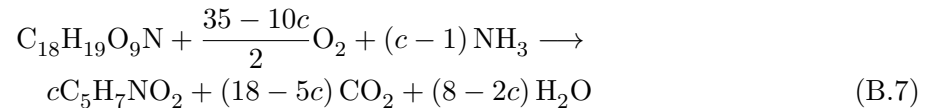
Microorganisms use the substrates for production of energy and synthesis of new cellular material and nutrients. The principal nutrients are nitrogen and phosphorus, but also other micro-nutrients must be present in traces (i.e., metal species etc.). Industrial wastewaters are known for being short of nitrogen and phosphorus. If they are not added, the treatment process will be very slow, incomplete or the settling and flocculation characteristics of the sludge will be bad [34]. In aerobic processes, oxygen is required for respiration and it can be supplied by means of an aeration system as pure oxygen or as air.

With a few exceptions, most organic compounds can be degraded biologically eventually, but in some cases the rates may be slow, unique environmental conditions may be required (e.g. pH, temperature) and specific bacteria may be needed. Complete biodegradation of toxic and recalcitrant compounds to harmless end products CO_2 and H_2O or CH_4 may not always occur, and biotransformation to different organic compounds is possible. The substrate to be degraded is quantified through the COD. However, only part of the COD is biodegradable (bCOD). Additionally, only part of the biodegradable material enters as soluble compounds thus in order to use the non soluble part of the degradable material the microorganisms need to hydrolyze it first. However, all these factors need to be considered in a detailed modeling of the biological process, but they are not relevant for a simple representation of the process unit. Detailed models can be found for each process in [9].

The only reaction taking place in a biological treatment unit is considered to be the bacterial synthesis, i.e. the conversion of the substrate into new biomass, which is responsible of carbonaceous removal (adapted from [9, 10]).



where C stands for the carbonaceous substrate and MO stands for the biomass synthesized. In terms of the pseudo-species identified (C as $\text{C}_{18}\text{H}_{19}\text{O}_9\text{N}$ and MO as $\text{C}_5\text{H}_7\text{NO}_2$) and neglecting the byproducts, the equation becomes:

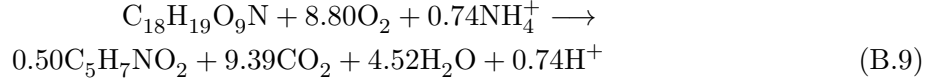


where only NH_3 has been considered as a nutrient in the stoichiometry. The parameter c is:

$$c = y \cdot \frac{MW_{\text{C}}}{MW_{\text{MO}}} \quad (\text{B.8})$$

being y the mass yield of substrate to biomass, with $MW_{\text{C}}=393$ g/mol and $MW_{\text{MO}}=113$ g/mol. The value of y varies with the process conditions. For aerobic growth of microbial biomass, the amount of organic material that is converted to biomass is generally around

0.5 on a COD basis [34], thus it is assumed $y = 0.5$. Considering that in aqueous solution ammonia is considered completely ionized, reaction B.9 becomes:



where the stoichiometric coefficients have been rounded to the second decimal position. For carbonaceous removal, pH in the range of 6.0 and 9.0 is tolerable, while optimal performance occurs near a neutral pH. Wide fluctuation in pH is known to be detrimental in plants of conventional design. A reactor dissolved oxygen concentration of 2.0 mg/L is commonly used, and the aeration equipment should have adequate capacity to maintain at least this concentration of dissolved oxygen in the aeration tank under normal loading conditions. Additionally, care must be taken to assure that sufficient nutrients (N and P) are available for the amount of biodegradable soluble COD to be treated. Nutrient deficiency is a classic problem in the treatment of industrial wastewaters [9]. Nutrients are provided to the system as ammonia for N and as phosphoric acid for P [10]. With industrial wastewaters some of the contaminants may be inhibitory or toxic to the microbes [10].

The utilities necessary for biological treatment processes are:

- Electricity to run the equipment
This is computed as specified for each unit.
- Oxygen supply
Air is chosen as oxygen supply, since it is cheaper and readily available rather than pure oxygen. The oxygen supplied from the aeration system must satisfy the requirements for biodegradation of the substrate for cell growth, respiration of the microorganisms, and for maintaining a minimum dissolved oxygen concentration in the aeration tank. In the model used, the oxygen needed is computed as the oxygen requirement from reaction B.9 with the relevant conversion and a transfer efficiency of $\eta_{\text{O}_2}=15\%$ is assumed, thus the effective amount of oxygen to be fed is:

$$\mu_{\text{O}_2,\text{C}} = \frac{1}{\eta_{\text{O}_2}} \cdot \nu_{\text{O}_2,\text{B.9}} \cdot \theta_{\text{C,B.9}} \cdot \frac{MW_{\text{O}_2}}{MW_{\text{C}}} \quad (\text{B.10})$$

The amount of nitrogen is adjusted according to the air composition.

$$\mu_{\text{N}_2,\text{C}} = \frac{0.77}{0.23} \mu_{\text{O}_2,\text{C}} \quad (\text{B.11})$$

- Nutrients
Ammonia is added as a source of nitrogen only if not present in enough quantity in the wastewater with respect to the stoichiometric amount (equation 2.4 for ammonia and biological treatment is $R_{\text{NH}_3,kk} \leq \mu_{\text{NH}_3,\text{C},kk} \cdot F_{\text{C},kk}^{\text{in}}$). Only the difference needed to perform the reaction is fed. For ammonia, the transfer efficiency is unitary since it is assumed that all the ammonia added is dissolved into the water. Thus:

$$\mu_{\text{NH}_3,\text{C}} = \nu_{\text{NH}_4^+,\text{B.9}} \cdot \theta_{\text{C,B.9}} \cdot \frac{MW_{\text{NH}_4^+}}{MW_{\text{C}}} \quad (\text{B.12})$$

The rule of thumb according to which nutrients should be added is N:P=5:1 [34, 10]. Thus, the amount of phosphoric acid to add is:

$$\mu_{\text{H}_3\text{PO}_4, \text{C}} = \frac{1}{5} \cdot \mu_{\text{NH}_3} \cdot \frac{MW_{\text{N}}}{MW_{\text{NH}_3}} \cdot \frac{MW_{\text{H}_3\text{PO}_4}}{MW_{\text{P}}} \quad (\text{B.13})$$

Electricity and H_3PO_4 are not added to the stream ($\alpha_{\text{EL}}, \alpha_{\text{H}_3\text{PO}_4} = 0$), while NH_3 , O_2 and N_2 are added completely ($\alpha_{\text{NH}_3}, \alpha_{\text{N}_2}, \alpha_{\text{O}_2} = 1$). Other specific utilities are discussed for each particular process in the relevant section.

The waste consists in the unreacted O_2 and N_2 , the bacteria formed, as well as the solid and the oil and grease separated. Removal efficiencies of the carbonaceous material in the biological units is quantified through the conversion of reaction B.9, $\theta_{\text{C,B.9}}$; the value assigned to it is discussed for each unit, as well as the waste fraction of the other components removed.

In the following, the various biological treatments considered are discussed.

B.3.1 Activated sludge

The physical design of activated sludge plants may vary considerably. Irrespective of the design, a plant must consist of two elements: an aeration and reaction tank, where microorganisms convert the substrate, and a settling tank, which separates the biomass from the purified water. Then, part of the biomass is recycled in order to keep the desired concentration of microorganisms and the excess biomass is wasted along with part of the suspended solids present in the influent. Activated sludge should be able to reach an outlet concentration lower than 20 mg/L for total suspended solids and lower than 25 mg/L for BOD_5 [10].

Parameters of interest in an activated sludge system are:

- Mixed Liquor Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS):
Concentration of the solids of recycled sludge.
- Solid Retention Time (SRT):
Average period of time the sludge stays in the system; $1/\text{SRT}$ represents the fraction of solids wasted per unit time.
- Hydraulic Retention Time (HRT):
Average period of time the water stays in the system.
- Volumetric organic loading rate:
Amount of COD or BOD_5 per aeration tank volume per day.
- Food to microorganism ratio (F/M ratio):
Ratio between the mass of substrate (usually quantified as BOD_5) fed per day and the mass of biomass.

All these parameters must be considered for a detailed design of the activated sludge unit, but they are not considered here. When representing the activated sludge as a process interval, the aeration and clarification tanks are lumped together in the reaction section, with the waste positioned according to the process interval model (see Figure B.1).

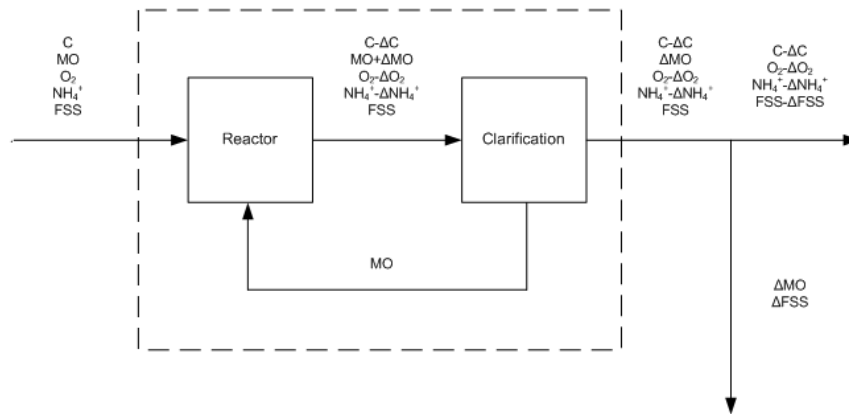


Figure B.1 – Representation of activated sludge as a process interval.

Removal efficiency

The conversion for reaction B.9 is conservatively assumed $\theta_{C,B.9} = 0.725$ on the basis of the removal efficiency of COD reported in [50], even if experiments proved higher efficiency - for example Merlo et al. [55] report a conversion up to 93% in a pilot activated sludge for refinery wastewater. On the basis of what reported in [50], the removal efficiency for BOD₅ is 89.5%, for TSS is 72.5%, and for O&G is 89.5%.

Utility consumption

The utility consumption accounts for:

- Electricity necessary for the aeration equipment and for the solid recycle.
- Air to supply the necessary amount of oxygen.
- Nutrients necessary to maintain the proper environment for microorganism growth.

The electricity consumption of the activated sludge unit is estimated as an average of the power consumption reported in [56] as 2.02 MJ/ton.

The air and the nutrients necessary to operate the system are computed as described for the generic biological unit, with equations B.10, B.11 and B.12, B.13 respectively.

B.3.2 Trickling filters

The trickling filter is a packed bed of rock or plastic covered with biological slime through which the wastewater is passed. Wastewater is sprinkled onto the medium through a rotating distribution system above the bed. As the wastewater passes through the slime, organics and oxygen diffuse into the microbial mass where they are oxidized to carbon dioxide, water, and metabolic byproducts. The trickling filter is followed by a clarifier to settle sloughed-off slimes and recycle flow may be taken either before or after clarification [12, 9].

Trickling filters are often used as roughing devices before the wastewater is fed to an activated sludge system, especially in refineries. Thus, data for roughing trickling filter will be used. Trickling filters used for secondary treatment present an effluent with BOD₅ and total suspended solids in the range of 15-30 mg/L [9].

Removal efficiency

The conversion for reaction B.9 is obtained from the COD removal efficiency experimentally registered for roughing trickling filters; for example, Qasim [57] reports a conversion of 50% while the General Electric Wastewater Treatment Handbook [50] reports a conversion of 70%, thus it is assumed an average of $\theta_{C,B.9} = 0.60$. Removal of O&G is reported as 65.0%, while for TSS is 72.5% [50].

Utility consumption

The utility consumption accounts for:

- Electricity necessary for operation.
- Air to supply the necessary amount of oxygen.
- Nutrients necessary to maintain the proper environment for microorganism growth.

The electricity consumption of a roughing trickling filter is estimated as an average of the power consumption reported in [56], as 0.51 MJ/ton. One of the advantages of roughing filters is the low energy consumption for BOD removal of higher strength wastewaters as compared to the activated sludge [9].

The air and the nutrients necessary to operate the system are computed as described for the general biological unit, with equations B.10, B.11 and B.12, B.13 respectively.

B.3.3 Rotating Biological Contactor (RBC)

Rotating biological contactors (RBC) generally consist of rows of polymeric discs mounted on horizontal shafts that turn slowly (1.0 to 1.6 rpm) keeping the disc about 40% immersed in a shallow tank containing wastewater. Microorganisms attach and grow on the surface of the disk producing a film which removes organic matter from the wastewater, and accumulate on each disc. Aeration occurs while a section of disc is above water level. The RBC process application typically consists of a number of units operated in series. The number of units depends on the treatment goals, with two to four stages for BOD₅ removal and six or more for nitrification [12, 9].

RBCs designed for BOD removal only have hydraulic retention time between 0.7 and 1.5 hrs and present an effluent with BOD₅ in the range 15-30 mg/L [9]. Treatment efficiency can be improved by increasing the number of RBCs in series, and by temperature control, sludge recycle, and chemical addition. Advantages of RBCs include the ability to sustain shock loads because of high microorganism concentrations, ease of expansion because of modular design, and low power consumption, which may be particularly attractive for industrial application. Full-scale RBC installations in refineries have performances in removal of oxygen-demanding pollutants comparable to activated sludge systems. [12]

Removal efficiency

The conversion for reaction B.9 is obtained from the COD removal efficiency experimentally registered for rotating biological contactors operating with refinery wastewater; for example, Tran et al. [58] report a COD conversion of 85.7%, however previous experiments reported a lower conversion. Thus, it is conservatively assumed that $\theta_{C,B.9} = 0.80$. The same

source provides an estimation of the removal of BOD₅ and TSS, which for the same reason are chosen as 80.0%.

Utility consumption

The utility consumption accounts for:

- Electricity necessary for operation.
- Air to supply the necessary amount of oxygen.
- Nutrients necessary to maintain the proper environment for microorganism growth.

The electricity consumption of a rotating biological contactor is estimated as an average of the power consumption reported in [56], as 2.37 MJ/ton.

The air and the nutrients necessary to operate the system are computed as described for the general biological unit, with equations B.10, B.11 and B.12, B.13 respectively.

B.3.4 Powdered Activated Carbon Treatment (PACT)

The powdered activated carbon treatment (PACT) is basically an activated sludge enhanced with the addition of powdered activated carbon, which is effectively used for removal of pollutants in wastewater treatment as discussed in section B.4.1. By merging biological and physical/chemical treatment into a single process step, the system is able to buffer toxic loads which might otherwise impair a straight biological system and reduce the amount of carbon otherwise needed by a straight adsorption treatment system. Advantages of the PACT system are: possibility to control the performance of the system adjusting the carbon dose; metal removal and no need of up-front metals precipitation, since toxic metals that would otherwise poison a conventional biological system are removed due to their affinity for carbon; less sludge volume than an activated sludge system due to a drier cake (50% solid vs $\leq 20\%$) [59]. Carbon dosages may vary from 20 to 200 mg/L, depending on the results desired [10, 9]. An operating PACT was able to stand COD up to 4,000 mg/L, sulfides up to 300-500 mg/L and phenols up to 900 mg/L still meeting the effluent quality (design values: COD around 1,500 mg/L, sulfides around 150 mg/L, phenols around 70 mg/L) [59].

PACT can be integrated into existing activated sludge facilities at minimum capital cost [10]. When there is a small or intermittent application of PAC, the carbon is disposed of with the excess sludge. Continuous application at larger plants, however, requires regeneration of the carbon.

Removal efficiency

The conversion for reaction B.9 is obtained from the COD removal efficiency experimentally registered for PACT systems; for example, Meidl [59] reported influent and effluent refinery wastewater treated with PACT for which the conversion was up to 94.8%. Thus, $\theta_{C,B.9} = 0.948$. The same source provides an estimation of the removal of BOD₅ and TSS as 99.0% and 92.0%, respectively. For O&G, a removal of 90.0% can be reached [10].

Utility consumption

The utility consumption accounts for:

- Electricity necessary for operation.
- Air to supply the necessary amount of oxygen.
- Nutrients necessary to maintain the proper environment for microorganism growth.
- Powdered activated carbon (PAC).

The utility consumption has the same entries as the activated sludge system, with the additional power required to handle the make-up carbon feeding system if small plant or the carbon regeneration if big. Here it is assumed that the carbon is not regenerated. The electricity consumption of a PACT system is assumed to be the same as the one of an activated sludge - the electricity associated to the PAC feed is neglected. The active carbon is added as GAC rather than PAC. It is added to the stream as an average of 110 mg/L, which equals 0.11 kg of GAC per ton of water. This overestimates the consumptions since the residence time of the activated carbon is higher than the residence time of water, but this is neglected in first instance and could compensate the additional costs not considered.

B.3.5 Membrane bioreactor (MBR)

The membrane bioreactor (MBR) has the same configuration as an activated sludge unit, but the sedimentation tank is replaced by a membrane unit. This has many advantages such as a higher biomass concentration in the reactor, a reduced reactor volume and an improved product quality. Two different MBR process configurations have been applied: external, where the membrane modules are situated outside the bioreactor, and submerged where the membranes are directly immersed in the reactor tank. Most submerged MBRs are applied under aerobic conditions where aeration is also used to create cross-flow along the membrane to reduce fouling. Aeration is used both for scouring the immersed membrane and for suspending the biomass.

Removal efficiency

The conversion for reaction B.9 must be chosen so that also the removal of COD by action of the membrane is taken into account, thus, the conversion must be higher than the one for activated sludge and microfiltration unit; it is chosen $\theta_{C,B.9} = 0.90$. The same removal is assumed for the BOD₅, while for the O&G and TSS removals the same value chosen for the microfiltration unit is used.

Utility consumption

The utility consumption accounts for:

- Electricity to pump fluid and to run the blower.
- Air to supply the necessary amount of oxygen and to scour the membrane.
- Nutrients necessary to maintain the proper environment for microorganism growth.

- Chemicals for membrane maintenance.

The energy requirement for submerged membrane bioreactor is usually much lower than for the side stream ones (at least for aerobic systems) [9]. Energy consumptions for the first type are reported as 0.92 kWh/m³ [60], which corresponds to 3.31 MJ/ton. This value is used for the computations.

The air and the nutrients necessary to operate the system are computed as described for the general biological unit, with equations B.10, B.11 and B.12, B.13 respectively. In addition to the air required for oxygen supply for the biological reaction, air is needed for membrane scouring. In many cases the suppliers recommend a proper aeration rate in terms of the specific aeration demand (SAD), either with respect to the membrane area (SADm) or the permeate volume (SADp). Values of SADp can range between 10 and 100 Nm³ of air per m³ of permeate. Assuming an average value of 55 Nm³ of air per m³ of permeate, and a recovery of water of 14.5% (see section B.10), it is obtained 0.054 kgair/kg, which equals to 12.38 kgO₂/ton and 41.46 kgN₂/ton.

Membrane bioreactors also require utilities for backwashing of the membrane. Physical and chemical backwashing requirements are dependent primarily on the membrane and process configurations and the feed water quality; protocols for specific technologies are normally recommended by the membrane and/or process suppliers and sometimes further adapted for specific applications. For industrial applications the range of candidate cleaning chemicals may include detergent and chelating or anti-scaling chemicals at a pre-defined temperature and duration of application. The protocol of a clean in place can involve repeated short backflush intervals (or pulsing) and hence resemble a chemically enhanced backflush. The sequence of cleaning agents is usually alkaline solution (with sodium hypochlorite) followed by organic acid. A typical membrane cleaning protocol and frequency, required for chemical demand determination, comprises a weekly cleaning in place (CIP) with 500 mg/L NaOCl and 2000 mg/L citric acid (C₆H₈O₇) supplemented with biannual cleaning out of place (COP) using 1000 mg/L NaOCl and 2000 mg/L citric acid [60]. On this basis, the consumptions estimated are $\mu_{\text{NaOCl},\text{H}_2\text{O}}=0.30\cdot 10^{-2}$ kgNaOCl/ton and $\mu_{\text{C}_6\text{H}_8\text{O}_7,\text{H}_2\text{O}}=1.24\cdot 10^{-2}$ kgC₆H₈O₇/ton.

B.4 Adsorption

Many industrial wastes contain refractory organics which are difficult or impossible to remove by conventional biological treatment processes, for example heterocyclic organics. These compounds can frequently be removed by adsorption.

The most commonly used adsorbent is activated carbon. Activated carbon is able to remove a broad range of adsorbates, including many synthetic organic chemicals and inorganics such as heavy metals. Activated carbons are made from a variety of materials including wood, lignin, bituminous coal, lignite, and petroleum residues. Two types of carbon are usually employed: powdered activated carbon (PAC, 200-400 mesh) and granular activated carbon (GAC, 10-40 mesh); the granular form is more expensive but it is easier to regenerate and to use in a counter current contactor [61]. The carbon adsorbent is loaded in columns through which the wastewater is passed. After the column has been saturated, breakthrough occurs. Breakthrough is said to happen when the effluent concentration reaches 5% of the influent value. Exhaustion of the adsorption bed is assumed to have occurred when the effluent concentration is 95% of the inlet. Two or more columns are usually put in series and rotated

as they become exhausted so that the unit remains in operation while one column is taken out of service for regeneration or maintenance [9].

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and the concentration of the adsorbate and the temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called adsorption isotherm. The most common adsorption isotherm are Freundlich, Langmuir and Brunauer-Emmett-Teller (BET). Freundlich is the most used to describe the adsorption characteristics of the activated carbon used in wastewater treatment. The coefficient of the adsorption isotherm vary over a wide range depending on the substance to adsorb. In case of mixtures, it is possible to obtain adsorption isotherms for the specific mixture. However, this is left to consider for a more detailed design of the unit.

Activated carbon should be able to reach an outlet concentration lower than 1 mg/L for TSS, lower than 2 mg/L for BOD₅ and lower than 10 mg/L for COD [10].

It is generally economical advantageous to regenerate the spent carbon. In the regeneration process, the previously adsorbed materials are removed from the carbon pore structure by thermal regeneration, steam, or solvent extraction, acid or base treatment, or chemical oxidation [10]. For wastewater treatment applications in which a large number of pollutant present in low quantity must be removed, thermal regeneration is favored [61], thus this regeneration method is suitable for carbon adsorption used as a tertiary treatment. Thermal regeneration is the process of drying, desorption, and high temperature heat treatment (650 to 980°C) in the presence of steam, flue gas, and oxygen. Usually, for each regeneration cycle 5 to 10 percent by weight of the carbon regenerated is lost due to attrition and burning [10].

B.4.1 Granulated Activated Carbon (GAC)

Typically, a GAC bed treats flow rates between 50 and 400 m³/h and has cross sectional area between 5 and 30 m² and length between 1.8 and 4 m, with a void fraction between 0.38 and 0.42; the approach velocity is 5-15 m/h and the operation time between 100 and 600 days [9]. The empty bed contact time (EBCT) is a measure of the time in which water is in contact with the carbon; for filter adsorbers to be effective, an EBCT of at least 5 minutes is generally required [62] and it is usually between 5 and 30 min [9]. The EBCT and the design flow rate define the amount of carbon in a GAC contactor. For treatment of tertiary effluent, regeneration is expected if the flow treated is higher than 3.0 mgd (0.47 kg/h) [56]. Given this low value, it is chosen to include regeneration.

Removal efficiency

On the basis of what given in [50], the removal efficiencies for COD, BOD₅, TSS, O&G, and ammonia are estimated as 80.0%, 83.0%, 75.0% and 85.0%, respectively.

Utility consumption

The operating costs include:

- Electricity necessary for pumping and running the equipment.
- Make-up carbon.

- Steam, flue gas rich in CO₂ and natural gas as fuel to the regeneration furnace.

The power required to run the equipment is assumed equal to the energy consumption in absence of regeneration and it is estimated as an average of the power consumption reported in [56] as an average value of 3.72 kJ/kg.

Carbon exhaustion rates for refinery wastewater treatment are known to be in the range of 1.1 to 141 lb/1000gal [10], which equals to 0.13 to 16.92 kgGAC/ton. This corresponds to the amount that is treated in the regeneration furnace. Assuming that an average of 7.5% of this carbon is lost, the make-up carbon is $\mu_{\text{GAC,H}_2\text{O}}=0.64$ kgGAC/ton.

In a municipal wastewater treatment plant, the GAC regeneration uses from 0.259 to 0.375 kg of steam and from 0.475 to 0.687 kgCO₂ per kg of GAC regenerated [63]. Average values of these consumptions are assumed also for industrial wastewater treatment, and the values found are $\mu_{\text{LPS,H}_2\text{O}}=12.70 \cdot 10^3$ GJ/ton and $\mu_{\text{CO}_2,\text{H}_2\text{O}}=4.96$ kgCO₂/ton. The regeneration heat required is 7,000 Btu per lb of carbon regenerated [56] (16,282 kJ/kgGAC). This heat is supplied to the furnace through natural gas; with a heating value of 62,238.4 kJ/kgNG [61], the natural gas per ton of wastewater treated is $\mu_{\text{NG,H}_2\text{O}}=2.27$ kgNG/ton.

B.5 Stripping

Stripping operations are used for cleaning wastewater from certain compounds which are transferred to the gas phase. The ability of a contaminant to be stripped increases with increasing temperature and decreases with increasing solubility. Henry's constant is a parameter which can be used to determine the easiness with which a certain compound can be stripped - the higher Henry's constant, the easier it is to strip the compound. The two most prevalent pollutants which are found in refinery wastewaters which are susceptible to stripping are H₂S and NH₃ (or NH₄⁺). This is usually performed with steam, which removes also other aromatics, including phenols and cyanides. Air stripping is also used for volatile organic compounds. There are many different types of strippers, but most of them involve a downward flow of water through a trayed or packed tower while an ascending flow of stripping steam or gas removes the pollutants. The stripping medium can be steam or any inert gas.

B.5.1 Steam stripping

Three steam stripping equipments are considered:

1. Two combined columns for stripping of both hydrogen sulfide and ammonia
2. Hydrogen sulfide stripping
3. Ammonia stripping

B.5.1.1 Steam stripping in two columns

Owing to its higher efficiency, the majority of installed refinery water strippers employ steam as both a heating medium and a stripping gas [12]. Since H₂S tends to be stripped by water more easily than NH₃, if both components need to be stripped, the removal efficiency is enhanced using two columns: in the first, NH₃ is fixed with mineral acid or flue gas and H₂S is stripped, then the ascending steam is condensed and the gas is sent to a sulfur recovery

plant; in the second, NH_3 is stripped and recovered as high purity ammonia. The first column is operated at around 40°C and the second at around 110°C [10]. The cooled water bottoms from the system contains less than 5 mg/L for H_2S and 50 mg/L for NH_3 [10, 12].

Removal efficiency

The removal efficiencies of H_2S and NH_3 observed in sour water strippers can reach up to 0.98 and 0.82, respectively [10]. This performance can be assumed valid for the operation of one single column. Since two columns are used and H_2S is more easily removed than NH_3 , part of H_2S will be removed also in the second column, thus to make the options comparable with the single columns described later the removal of H_2S is assumed to be 0.98^2 .

Utility consumption

The utility consumption accounts for:

- Electricity necessary to operate the unit.
- Steam as a stripping medium and for temperature regulation.
- Cooling water for temperature regulation.
- Acidifying mineral acid (H_2SO_4) for ammonia fixing.

It is reported that a stripping column for both H_2S and NH_3 has a power consumption of 9.83 MJ/ton [54], so it is assumed that two columns would consume 19.66 MJ/ton.

The steam consumption can be estimated applying a material balance to the column:

$$LC_{i,0} + Gy_{i,0} = LC_{i,e} + Gy_{i,e} \quad (\text{B.14})$$

where L is the descending liquid phase and G the ascending gas phase (assumed constant), C and y indicate the concentration of pollutant i in the liquid and gas phase, respectively, and the subscripts 0 and e indicate the inlet and outlet, respectively. Assuming that the exiting gas phase is in equilibrium with the inlet liquid phase:

$$y_{i,e} = \frac{H_i(T)}{P} C_{i,0} \quad (\text{B.15})$$

where $H_i(T)$ is the Henry constant of component i at the operating temperature of the column. The values of $H_i(293\text{K})$ and of the coefficients to calculate it at different temperatures are reported in Table B.1 for the two key components, H_2S and NH_3 . The minimum steam-water ratio is found as:

$$\left(\frac{G}{L}\right)_{\min} = \frac{P}{H_i} \left(1 - \frac{C_{i,e}}{C_{i,0}}\right) = \frac{P}{H_i} \cdot r_i \quad (\text{B.16})$$

where r_i is the removal of component i . The actual steam-water ratio is found as:

$$\left(\frac{G}{L}\right) = 2.2 \left(\frac{G}{L}\right)_{\min} \quad (\text{B.17})$$

Assuming a removal of H_2S and NH_3 of 0.98 and 0.82, respectively, it results that 0.003 kgLPS/kg are necessary for H_2S removal and 0.102 kgLPS/kg are necessary for NH_3 removal,

for a total of 0.105 kgLPS/kg. Assuming that the steam is available at 500 kPa and 150°C, its enthalpy of evaporation is $\Delta H_{vap}=2,081.4$ kJ/kg, which gives 218.23 MJ/ton - the enthalpy of evaporation is computed as the difference between vapor and liquid enthalpies of saturated water at the temperature and pressure of saturation, as reported in [64]. This is in the range of the steam consumption with acidifying medium reported, which is between 8 and 32 SCF/gal [10], which equals to 91.65 and 366.59 MJ/ton.

Cooling water and steam are needed also to regulate the temperature of the wastewater to the desired level. The amount of water as cooling medium is computed as:

$$\mu_{CW,H_2O} = \frac{c_{P,w} \cdot (T_{in} - T_{out})}{c_{P,w} \cdot \Delta T} \quad (B.18)$$

where $q = c_{P,w} \cdot (T_{in} - T_{out})$ represents the specific heat subtracted to the wastewater to take it from T_{in} to T_{out} , $c_{P,w} = 4.186$ kJ/(K·kg) is the specific heat of water, and ΔT is the temperature variation of cooling water, assumed to be 20°C. The amount of steam as heating medium is computed as:

$$\mu_{LPS,H_2O} = \frac{c_{P,w} \cdot (T_{out} - T_{in})}{\Delta H_{vap}} \quad (B.19)$$

where $q = c_{P,w} \cdot (T_{out} - T_{in})$ represents the specific heat given, ΔH_{vap} is the latent heat of the steam, and the other symbols have the same meaning as above. A simplified scheme of the process which can help to compute the heating and cooling utilities is shown in Figure B.2; the scheme is derived assuming a minimum temperature approach of 10°C and that the inlet wastewater is available at 20°C and must be returned to the following equipment at this same temperature. Of course, the figures on consumption would change if this assumption is not valid anymore, but at the moment temperature is not considered as a variable of wastewater to treat. According to it, steam is needed to heat the water stream from 65°C to 100°C, and this corresponds to 146.51 MJ/ton. Thus, the total amount of steam necessary would be 364.74 MJ/ton. However, it is assumed that due to further integration for example with the condensers (in which steam is cooled to recover H_2S and NH_3), this amount is one third lower, thus $\mu_{LPS,H_2O}=243.16$ MJ/ton. The amount of cooling water is instead computed as $\mu_{CW,H_2O}=1.75$ kgCW/kg, which is almost in agreement with what reported in [54], which gives a consumption of 0.51 kgCW/kg for one column, so two columns would consume 1.02 kgCW/kg. The value computed is used.

The consumption of acidifying mineral is related to the pH variation of the solution, thus it is not considered so far.

Table B.1 – Henry constants at 293 K and coefficients to calculate them at various temperatures [9].

i	$H_i(293K)$ [atm]	A_i ¹	B_i ¹
H ₂ S	483	884.94	5.703
NH ₃	0.75	1887.12	6.315

¹ $H_i(T) = 10^{\left(-\frac{A_i}{T} + B_i\right)}$, with T in K

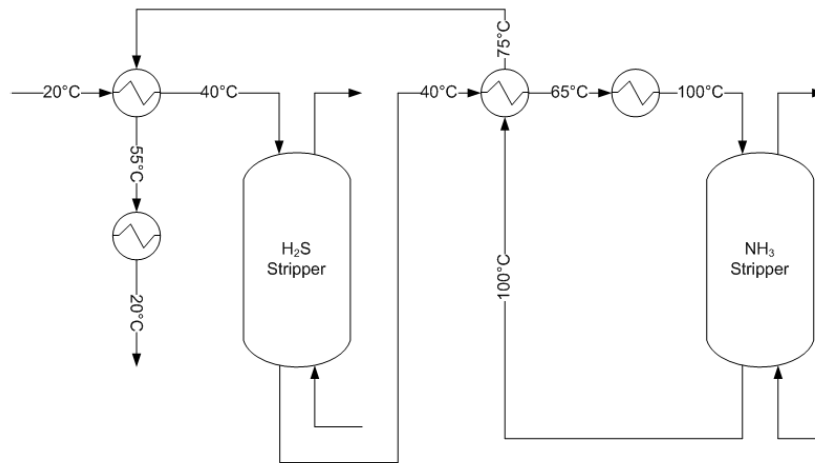


Figure B.2 – Scheme of the sour water stripper.

B.5.1.2 Steam stripping of hydrogen sulfide

The stripping steam consumption is only the one for hydrogen sulfide. The cooling water for cooling and the steam for heating are computed with equations B.18 and B.19 following the integration scheme in Figure B.3, as $\mu_{CW,H_2O}=1.00$ kgCW/kg and $\mu_{LPS,H_2O}=83.72$ MJ/ton, respectively. Thus, the total amount of steam is $\mu_{LPS,H_2O}=89.81$ MJ/ton.

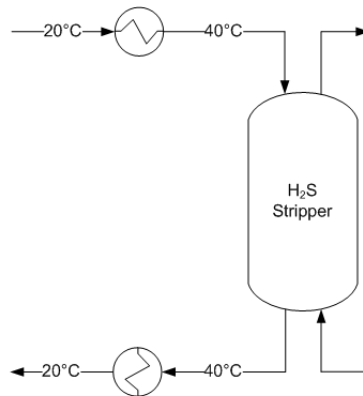


Figure B.3 – Scheme of the hydrogen sulfide stripper.

B.5.1.3 Steam stripping of ammonia

The steam consumption is only the one for ammonia. The cooling water for cooling and the steam for heating are computed with equations B.18 and B.19 following the integration scheme in Figure B.4, as $\mu_{CW,H_2O}=2.25$ kgCW/kg and $\mu_{LPS,H_2O}=188.37$ MJ/ton, respectively. Thus, the total amount of steam is $\mu_{LPS,H_2O}=400.51$ MJ/ton.

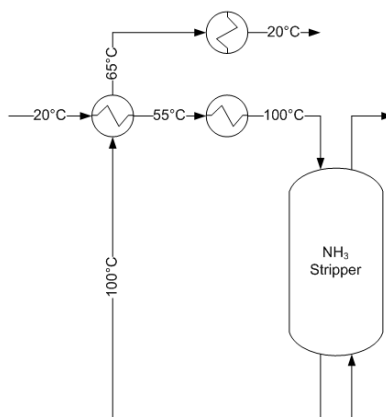


Figure B.4 – Scheme of the ammonia stripper.

B.5.2 Air stripping

Air stripping works on the same principle as the steam stripping. In wastewater treatment, air strippers are usually used for removing ammonia. The amount of air can be computed in the same way as for the steam. Since H_2S is more easily stripped than NH_4^+ , a removal of 98% is assumed for H_2S . The amount of air needed for stripping is computed in the same way as for steam, and thus amounts to 0.102 kg of air per kg of water, which corresponds to $\mu_{\text{N}_2, \text{H}_2\text{O}} = 78.48 \text{ kg}_{\text{N}_2}/\text{ton}$ and $\mu_{\text{O}_2, \text{H}_2\text{O}} = 23.44 \text{ kg}_{\text{O}_2}/\text{ton}$.

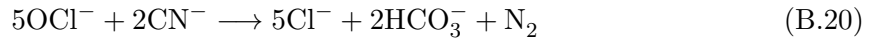
B.6 Chemical oxidation

Chemical oxidation is employed when organic compounds which are refractory, toxic, or inhibitory to microbial growth are present in the wastewater. Due to the large amount of side reactions that consume the oxidant, the efficiency of removal of a specific target compound is low and often the oxidation is not completed to full extent. Thus, the quantity of oxidant required is low enough to allow an economically feasible operation only when the concentration of the target compound is very low. Partial oxidation can be sufficient to improve the treatability of the wastewater. For these reasons, chemical oxidation is usually employed before the biological units or sometimes after them to further reduce the pollutant content. Commonly used oxidants include ozone, permanganate, chlorine, chlorine dioxide, and ferrate. Oxidation is often done in combination with a catalyst, which include simple pH adjustment, UV light, transition metal cations, enzymes and a variety of proprietary catalysts. Standard mixed reactors with contact times between several minutes to an hour are used [61]. While the total COD decreases, the BOD_5 and the soluble fractions increase due to the conversion from long chain biologically refractory organics to biodegradable compounds. The TOC does not decrease unless the compounds are completely oxidized. However, this is neglected, and the oxidation is considered only to target specific compounds. To estimate the quantity of oxidant needed for the ultimate conversion of an organic compound to CO_2 and H_2O , it is important to define the stoichiometry of the oxidation reaction for the compounds to be oxidized. However, this is difficult because of the huge number of reactions involved.

In refinery wastewater, cyanides are often removed by oxidation. Thus, the oxidation of cyanides is considered here.

B.6.1 Cyanide oxidation

Cyanides are oxidized with hypochlorite (OCl^-). The oxidation of cyanide by chlorine proceeds through several reactions that are highly pH-dependent and a two-step process is typically practiced: in the first step, cyanide reacts with hypochlorite to form cyanogen chloride which is subsequently hydrolyzed to form cyanate (pH 11.5); in the second step, cyanate is oxidized to form bicarbonates and nitrogen gas (pH 8.0 to 8.5). The overall reaction is:



If chlorine is used as a source of hypochlorite, the following dissociation reaction must be considered:



The oxidant needed is mixed with the stream. Only reaction B.20 (and B.21) is considered. The waste separated is the N_2 produced.

Removal efficiency

Theoretically, any removal efficiency can be achieved depending on the amount of oxidant fed. It is reasonable to assume that a conversion of $\theta_{\text{CN}^-, \text{B.20}} = 0.99$ can be easily achieved.

Utility consumption

The utility consumption accounts for:

- Electricity to run the equipment.
- Oxidant.

The power consumption is estimated on the basis of what reported in [56] for breakpoint chlorination facility. The power consumption is seen to vary significantly with the flow rate, thus an average value around the inlet flow rate is assumed, which is 3.37 MJ/ton.

The dosages of chlorine depend heavily on the identity of the metals complexed with the cyanide ion and the presence of other background constituents in the wastewater. Cyanide wastewaters containing nickel, silver or iron are difficult to treat by alkaline chlorination because of the slow reaction rate of these chemical processes [10]. Usually the amount of oxidant needed to achieve a certain performance is tuned experimentally for each wastewater. For simplicity, it is assumed that a 50% excess is supplied with respect to the stoichiometric amount:

$$\mu_{\text{Cl}_2, \text{CN}^-} = 1.5 \cdot \frac{\nu_{\text{OCl}^-, \text{B.20}} \cdot MW_{\text{Cl}_2}}{\nu_{\text{CN}^-, \text{B.20}} \cdot MW_{\text{CN}^-}} \quad (\text{B.22})$$

In numbers, $\mu_{\text{Cl}_2, \text{CN}^-} = 20.19 \text{ kg}_{\text{Cl}_2} / \text{kg}_{\text{CN}^-}$. Only the oxidant which actually reacts is added to the stream, thus $\alpha_{\text{Cl}_2} = 0.66$.

B.7 Hydrothermal processes

Hydrothermal processes refer to treatment of wastewaters at elevated temperatures and pressures. They include wet air oxidation (WAO), hydrothermal hydrolysis and supercritical water oxidation (SCWO). To date, only wet air oxidation has achieved some degree of commercial success [10], thus, only this one is considered.

B.7.1 Wet air oxidation (WAO)

Wet air oxidation (WAO) is an attractive treatment for waste streams which are too dilute to incinerate and too concentrated for biological treatment. It basically consists in the oxidation of organic and inorganic substances in an aqueous solution with oxygen or air at elevated temperatures and pressures. Typical conditions for wet oxidation range from 180°C to 315 °C and 20 to 150 bar; residence times may range from 15 to 120 min, and the COD removal may typically be from 75 to 90% [65]. Insoluble organic matter is converted to simpler soluble organic compounds which are in turn oxidized and eventually converted to carbon dioxide and water. Inorganics are partially oxidized to NH_4^+ , N_2 , SO_3^- or completely oxidized to NO^{3-} , SO_4^{2-} or PO_4^{3-} .

The wastewater is pumped to the system pressure and air is added to the reactor using a compressor. Preheating may be necessary to raise the temperature of wastewater. The feed temperature is adjusted such that the exothermic heat of reaction raises the mixture temperature to the operating temperature, and the preheating can be done using the treated effluent. The reactor effluent can be cooled by cooling water (to produce steam) or by the inlet wastewater-air mixture. Liquid and non-condensable gases are then disengaged in a separator and the clean water is sent to further processing.

In most applications, WAO is not used as a complete treatment method, but only as a pretreatment step where the wastewater is rendered non-toxic and the COD is reduced sufficiently so that biological treatment becomes applicable for the final treatment; this strategy means that extreme oxidation conditions are no longer necessary [66]. Thus, in the superstructure, the WAO unit is positioned as a first possible treatment to decrease the COD in the high COD source, i.e. caustics.

For simplicity, only reactions of complete oxidation are considered, both for COD and H_2S . For COD, the reaction is as in 2.1, while for H_2S :



The waste consists in the gas produced (CO_2) and the eventual unreacted air, while the other species produced by the oxidation reaction remain dissolved in the water stream.

Removal efficiency

The conversion of the two reaction is assumed to be an average of the data reported in [65]: $\theta_{\text{C},2.1}, \theta_{\text{H}_2\text{S},\text{B.23}}=0.825$.

Utility consumption

The utility consumption accounts for:

- Air for oxidation.

- Electricity to pump the water, compress the air and run the equipment.
- Heating medium to raise the reactor temperature.
- Cooling medium.

In order to compute the utility requirements, average operating conditions of 247.5°C and 85 atm are chosen.

The necessary amount of oxygen required for COD oxidation is:

$$\mu_{O_2,C} = \theta_{C,2.1} \frac{\nu_{O_2,2.1} \cdot MW_{O_2}}{\nu_{C,2.1} \cdot MW_C} \quad (B.24)$$

If oxygen is supplied along with air, as it is often the case, also nitrogen is introduced as:

$$\mu_{N_2,C} = \frac{0.77}{0.23} \cdot \mu_{O_2,C} \quad (B.25)$$

In numbers, $\mu_{O_2,C}=1.18 \text{ kg}_{O_2}/\text{kg}_C$ and $\mu_{N_2,C}=3.94 \text{ kg}_{N_2}/\text{kg}_C$. The total kg of air per kg of COD is 5.11 kg of air per kg of C.

Similarly, for oxidation of H_2S :

$$\mu_{O_2,H_2S} = \theta_{H_2S,B.23} \frac{\nu_{O_2,B.23} \cdot MW_{O_2}}{\nu_{H_2S,B.23} \cdot MW_{H_2S}} \quad (B.26)$$

$$\mu_{N_2,H_2S} = \frac{0.77}{0.23} \cdot \mu_{O_2,H_2S} \quad (B.27)$$

In numbers, $\mu_{O_2,H_2S}=1.55 \text{ kg}_{O_2}/\text{kg}_{H_2S}$ and $\mu_{N_2,H_2S}=5.20 \text{ kg}_{N_2}/\text{kg}_{H_2S}$. The total kg of air per kg of H_2S is 6.75 kg of air per kg of H_2S .

The energy necessary to pump the water is expressed in specific terms as in equation B.1, with P_{out} equal to the operating pressure. This amounts to 18.66 MJ/ton. The energy necessary to compress the air can be expressed in specific terms according to [37]:

$$w_C = \frac{\gamma}{\gamma - 1} \cdot R \cdot (T_{out} - T_{in}) \quad (B.28)$$

being T_{in} the initial gas temperature (20°C) and T_{out} the final gas temperature; for an ideal system, $\gamma=1.4$ and if the expansion is assumed ideal and isotropic:

$$T_{out} = T_{in} \left(\frac{P_{out}}{P_{in}} \right)^{\frac{\gamma-1}{\gamma}} \quad (B.29)$$

With the given conditions, $T_{out}=765.71^\circ\text{C}$ and $w_C=63,299.66 \text{ MJ}$ per ton of air, which considering the air/COD and the air/ H_2S ratios equals to 323.54 MJ/kg_C and 427.39 MJ/kg_{H₂S}.

The water-air mixture must be heated up to the reaction temperature. Integration can be done using the outlet reactor stream as a heating medium. The oxidation reactions taking place in the reactor are exothermic and the process becomes self-sustaining with no auxiliary fuel requirement when the COD is above 20,000 mg/L and the operating costs are almost entirely for power to compress air and high pressure liquid pumping [66], otherwise heating supply is needed. Here it is assumed that the utilities for heating and cooling can be neglected due to integration; and this assumption can be re-evaluated if the process is selected.

B.8 Chemical precipitation

Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solid and facilitate their removal by sedimentation. Chemical precipitation is most commonly employed for removal of most of metals, but it can be employed also for phosphorous removal. A great amount of sludge is produced in chemical precipitation operation, and its disposal is an issue. Many competing reactions take place which cause the amount of precipitation agents to be higher than the stoichiometric ratio; its dosage is generally based on test performed on the specific wastewater.

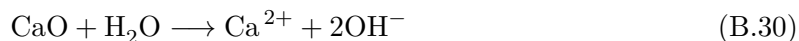
If both phosphorous and metal precipitations are selected, the possibility of fusing them must be evaluated. This allows for a reduction in capital costs.

B.8.1 Phosphorous precipitation

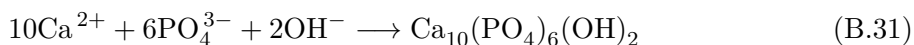
Phosphorous can be precipitated mainly with lime or alum. Polymers have been used effectively in conjunction with them as flocculant agents. Phosphorous can be removed by adding a precipitating agent at various points in the wastewater treatment plant - before, during or after the biological treatment. However, orthophosphorous is more easily removed than other forms of phosphorous, thus the precipitation treatment is added after biological treatment, where most of the phosphorous has been converted to orthophosphorous [9].

Here, phosphorous precipitation with lime is considered. Lime precipitation is suitable for wastewater with low alkalinity and high and variable phosphorous content [10]. Other precipitants are formed and the sludge to handle is higher than the metal precipitation; however, lime is cheaper than metal salts [9].

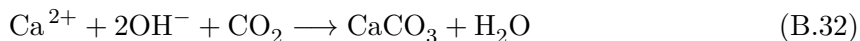
When lime is added to water, it is hydrolyzed as:



Sufficient lime is provided to raise the pH above 11 to precipitate the soluble phosphorous as calcium phosphate:



The excess soluble calcium is removed in the second stage clarifier as calcium carbonate adding carbon dioxide:

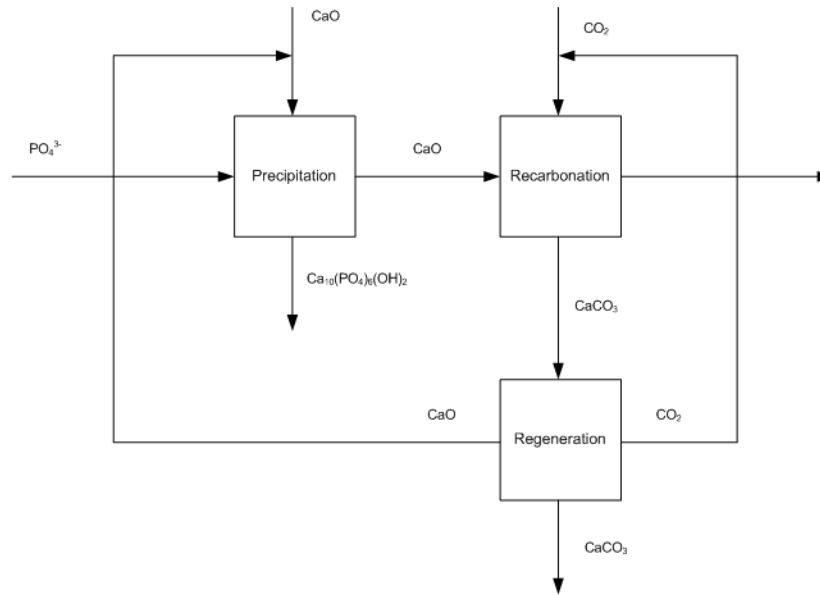


The calcium carbonate formed acts as a coagulant for TSS removal. The lime can be recovered with thermal regeneration, where calcium carbonate in the sludge is converted to lime by heating to 980°C; the carbon dioxide formed in this process is generally used as a source for recarbonation for pH adjustment of wastewater. The reaction is:



A simplified scheme of the process is shown in Figure B.5. It can be seen that the inputs are represented by the feed lime CaO and by the make-up CO₂. As a simplification, the lime regeneration is not considered and the process scheme in Figure B.5 is reduced to precipitation and recarbonation. Thus, reaction B.33 is not considered and all the CaO and CO₂ needed supplied by an external source.

Figure B.5 – Scheme of the lime precipitation process.



Removal efficiency

If the removal of PO_4^{3-} is $\theta_{\text{PO}_4^{3-}} = 0.90$, the conversion of Ca^{2+} in reaction B.31 is $\theta_{\text{Ca}^{2+}, \text{B.31}} = 0.60$, while the rest is converted in B.32, so $\theta_{\text{Ca}^{2+}, \text{B.32}} = 0.40$. The solid material formed is completely removed while it is assumed that in the clarification the TSS are reduced by 80.0%.

Utility consumption

The utility consumption accounts for:

- Power to run the equipment.
- Feed CaO.
- Make-up CO_2 .
- Fuel to regenerate the lime.

Since regeneration is not considered, all the CaO and CO_2 needed are supplied by an external source and no fuel is needed.

The power consumption can be estimated on the basis of what reported in [56] for a two-stage lime treatment. The power consumption is found to vary greatly with the flow rate; in proximity of the maximum design flow rate, the average value is around 5.74 MJ/ton.

The amount of lime to be fed varies greatly with the feed wastewater content and its alkalinity [9]. As an approximation, it is assumed that an extra 50% is added to the stoichiometric amount assuming complete conversion:

$$\mu_{\text{CaO}, \text{PO}_4^{3-}} = 1.5 \cdot \frac{\nu_{\text{Ca}^{2+}, \text{B.31}} \cdot MW_{\text{CaO}}}{\nu_{\text{PO}_4^{3-}, \text{B.31}} \cdot MW_{\text{PO}_4^{3-}}} \quad (\text{B.34})$$

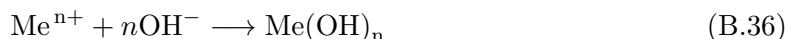
Also carbon dioxide is fed in stoichiometric amount:

$$\mu_{\text{CO}_2, \text{PO}_4^{3-}} = \mu_{\text{CaO}, \text{PO}_4^{3-}} \cdot \theta_{\text{Ca}^{2+}, \text{B.32}} \cdot \frac{MW_{\text{CO}_2}}{MW_{\text{CaO}}} \quad (\text{B.35})$$

In numbers, $\mu_{\text{CaO}, \text{PO}_4^{3-}} = 1.47 \text{ kg}_{\text{CaO}}/\text{kg}_{\text{PO}_4^{3-}}$ and $\mu_{\text{CO}_2, \text{PO}_4^{3-}} = 0.46 \text{ kg}_{\text{CO}_2}/\text{kg}_{\text{PO}_4^{3-}}$.

B.8.2 Metal precipitation

For metal precipitation, common precipitants include hydroxide (OH^-), sulfide (S^{2-}) and carbonate (CO_3^{2-}). The precipitation is often conducted in pH range in which the solubility is at minimum. Here, lime precipitation is considered. The general reaction is:

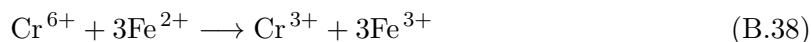


The reactions of metal precipitation are governed by equilibrium, which is influenced by the metal concentration and the pH of the solution. For simplicity, it is assumed that it is attained an equilibrium condition which allows for precipitation of 95% of the metal in solution.

Almost any metal can be precipitated according to B.36. In refinery wastewater treatment, a metal of concern for emissions is hexavalent chromium Cr^{6+} . In order to remove chromium by precipitation, hexavalent chromium, Cr^{6+} must first be reduced to the trivalent state, Cr^{3+} , and then precipitated with lime. A reducing agent commonly used for chromium wastes is ferrous sulfate, FeSO_4 , which in water is dissolved as:



Then, Cr^{6+} is reduced and Fe^{2+} is oxidized according to the following reaction:



This reaction occurs rapidly at pH levels below 3.0; acid must therefore be added for pH adjustment.

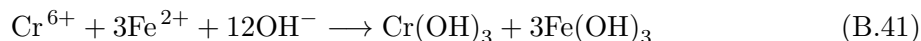
Then, Cr^{3+} is precipitated:



The use of ferrous sulfate as a reducing agent has the disadvantage that a contaminating sludge of $\text{Fe}(\text{OH})_3$ is formed:



The overall reaction is then:



Two units are considered: one for generic metal removal and the other one for chromium removal. This is done because of the difference in the utility use: the addition of FeSO_4 , which is needed for chromium precipitation but not for the precipitation of other metals, and the chemicals needed for pH regulation.

Removal efficiency

The removal efficiency of metal removal are highly dependent on the solubility equilibrium which rules at the conditions of the solution. For simplification, it is assumed that a conversion of $\theta_{\text{Cr}^{6+},\text{B.41}}=0.95$ is achieved. The solid material formed is completely removed while it is assumed that in the clarification the TSS are reduced by 80.0%.

Utility consumption

The utility requirement is:

- Electricity to run the equipment.
- Lime.
- Chemicals for pH regulation.
- In case of hexavalent chromium precipitation, reducing agent FeSO_4 .

The electricity necessary to run the equipment is assumed equal to the one for lime precipitation.

The stoichiometric amount of lime to be fed for the unit mass of each metal to precipitate is:

$$\mu_{\text{CaO},\text{Me}^{n+}} = n_{\text{Me}^{n+}} \cdot \frac{MW_{\text{CaO}}}{MW_{\text{Me}^{n+}}} \quad (\text{B.42})$$

where $n_{\text{Me}^{n+}}$ is the valence of the metal. If only chromium is considered as a metal pollutant, the amount of lime supplied must be enough to precipitate all Cr^{3+} and Fe^{3+} according to equation B.41, thus:

$$\mu_{\text{CaO},\text{Cr}^{6+}} = \frac{\nu_{\text{OH}^-, \text{B.41}} \cdot MW_{\text{CaO}}}{\nu_{\text{Cr}^{6+}, \text{B.41}} \cdot MW_{\text{Cr}^{6+}}} \quad (\text{B.43})$$

In this latter case, $\mu_{\text{CaO},\text{Cr}^{6+}}=6.46 \text{ kg}_{\text{CaO}}/\text{kg}_{\text{Cr}^{6+}}$.

The chemicals for pH regulation need to lower pH at 3.0 to conduce reaction B.38 and then raise pH at 11.0 to conduce reaction B.39 and B.40. However, this is not considered as for now.

If it is necessary to remove the hexavalent chromium, ferrous sulfate must be added. In order to obtain a complete reaction, an excess dosage of 2.5 times the theoretical addition of ferrous sulfate must be used [10]. Thus, the amount of reducing agent to be fed is:

$$\mu_{\text{FeSO}_4,\text{Cr}^{6+}} = 2.5 \frac{\nu_{\text{Fe}^{2+}, \text{B.41}} \cdot MW_{\text{FeSO}_4}}{MW_{\text{Cr}^{6+}}} \quad (\text{B.44})$$

In numbers, $\mu_{\text{FeSO}_4,\text{Cr}^{6+}}=21.92 \text{ kg}_{\text{FeSO}_4}/\text{kg}_{\text{Cr}^{6+}}$.

B.9 Electrostatic separation

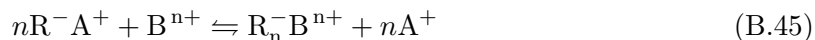
Two wastewater treatment processes are considered which rely on electrostatic forces for separation: the ion exchange and the electrodialysis. These are described in the following.

B.9.1 Ion exchange (IE)

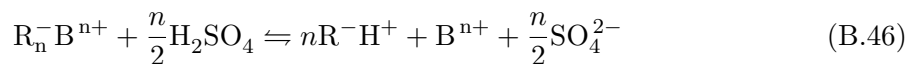
The ion exchange is a process in which ions of a given species are displaced from an insoluble exchange material by ions of a different species in solution. Typically, cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Thus, there are two types of membranes: cation exchangers, which release hydrogen cations, or anion exchangers, which release hydroxyl anions. The process can be operated in batch or continuous: in a batch the resin is stirred with water until the reaction is complete and then the spent resin is removed, regenerated and reused; in a continuous process the resin is placed in a bed or packed column and the water is passed through, then the resin is regenerated when exhausted.

Ion exchange has been used for removal of total dissolved solids, heavy metals, and nitrogen. The most wide application is in water softening, where sodium ions from a cationic-exchange resin replace the calcium and magnesium ions in the treated water, thus reducing the hardness. The economic feasibility of the ion exchange process for metal removal greatly improves when the process is used for removal and recovery of valuable metals. For nitrogen control, the ions normally removed from the waste stream are ammonium, NH_4^+ , and nitrate, NO_3^- .

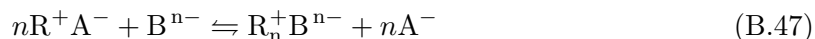
For a cationic membrane, the general equation according to which the ion exchange mechanism can be represented as:



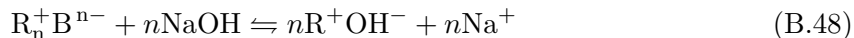
where R^- is the anionic group attached to membrane matrix, B^{n+} is the cation to be removed, and A^+ is cation released in solution, which is typically H^+ . The regeneration is done with H_2SO_4 :



For an anionic membrane instead:



where R^+ is the cationic group attached to membrane matrix, B^{n-} is the anion to be removed, and A^- is anion released in solution, which is typically OH^- . The regeneration is done with NaOH :



The process interval is modeled without reaction, which is used only to compute the amount of regenerant needed. The ions are considered as a waste.

Removal efficiency

Removal of all the ions is estimated to be 95%.

Utility consumption

The utility consumption accounts for:

- Electricity to run the equipment.
- Chemicals for regeneration - NaOH or H_2SO_4 .

- Chemicals for pH adjustment.

The power consumption is assumed equal to the power consumption of running a GAC adsorption bed, given the similarity of their structure.

The chemicals needed for regeneration are stoichiometrically related to the anion or cation removed, no matter how often the regeneration is done.

If a cation membrane is used, equation B.46 states that for each mole of cation B^{n+} removed, $n/2$ moles of H_2SO_4 are needed. Thus:

$$\mu_{H_2SO_4, B^{n+}} = \frac{n}{2} \cdot \frac{MW_{H_2SO_4}}{MW_{B^{n+}} \cdot wt} \quad (B.49)$$

where n is the valence of the ion to remove and wt is the weight purity of H_2SO_4 .

If an anion membrane is used, equation B.48 states that for each mole of cation B^{n-} removed, n moles of NaOH are needed. Thus:

$$\mu_{NaOH, B^{n-}} = n \cdot \frac{MW_{NaOH}}{MW_{B^{n-}} \cdot wt} \quad (B.50)$$

where n is the valence of the ion to remove and wt is the weight purity of NaOH.

Chemicals for pH adjustment are not considered here.

B.9.2 Electrodialysis (ED)

Ionic components of a solution are separated through the use of semipermeable ion-selective membrane thanks to application of an electric potential between two electrodes. The electric current causes the ion to migrate, and because of the alternate spacing of anion and cation permeable membranes cells of concentrated and diluted solutions are formed. Wastewater is pumped in through the membranes and it is usually retained for 10 to 20 days. Temperature, amount of electrical current, type, number and configuration of the membrane, fouling and scaling potential of the wastewater influence the ion recovery. Typical problems are precipitation of salts on the membrane surface and clogging of the membrane by residual colloidal organic matter, thus it is useful to precede the membrane with adsorption on active carbon and precipitation.

Removal efficiency

The product recovery is between 75% and 85% [9], thus around 20% of water is wasted in the retentate. Removal of all the ions is estimated to be 50%.

Utility consumption

As for the membrane separation processes described in section B.10, the utilities consumed are:

- Electricity for feed, permeate and concentrate pumping and backwashing.
- Chemicals for backwashing and washing.
- Pretreatment chemicals - acid or basic solution for pH regulation.

The power consumption of an electro dialysis unit has been reported by [9] to be 9.5 kWh/m³, which equals to $\mu_{EL,H_2O}=34.20$ MJ/ton.

Chemicals for backwashing and washing are assumed to be as for the other membranes - see section B.10.

Often, H₂SO₄ is used to keep a low pH and minimize scaling. However, chemicals for pH regulation are not considered as for now.

B.10 Membrane filtration

In this type of process, the wastewater is passed through a membrane which retains some of its components - suspended and dissolved solids, colloids, metals or other ions. The feed solution is pressurized with a pump and and it is circulated through the module, the permeate is withdrawn at atmospheric pressure and the concentrate or waste stream is disposed of or recirculated to other wastewater treatment units. As constituents in the feed water accumulate on the membranes the permeate flux and the percentage of rejection start to decrease and when the performance has deteriorated to a given level the membrane is backwashed, cleaned and subsequently replaced.

There are different types of membrane filtration, depending on the driving force and the sieve size. Filtration technologies that relies on hydrostatic pressure difference can be seen in Table B.2. The membrane process to be chosen depends on the size of the pollutant to be removed. Colloidal and particulate matter are approximately 75 μm , subcolloidal organics are between 0.2 and 10 μm , soluble organics between 0.005 and 0.2 μm and ions between 0.001 and 0.01 μm [10]. The selection of the best membrane is done on pilot studies, since every wastewater is unique with respect to its chemical characteristics. The criteria of membrane performance are the degree of impermeability (how well the membrane rejects the flow of the solute) and the degree of permeability (how easily the solvent is allowed to flow through the membrane). Cellulose acetate membranes provide an attractive combination of these criteria and thus this is the material with which most of the membranes are built [10].

The feed wastewater often needs to be pretreated. The type of pretreatment required depends on the feed water quality and membrane type, but usually consists of pH regulation and, if necessary, disinfection to minimize or limit the bacteria growth on the membrane. Membrane fouling indexes exist to assess the need for pretreatment. The need of pretreatment is particularly important for the nanofiltration and reverse osmosis units.

The disposal of the concentrated waste stream represents the major problem of membrane applications processes. The concentrate will contain heavy metals, high molecular weight organics and the pH is usually high due to the concentration of alkalinity, which increase the likelihood of metal precipitation in disposal wells. Disposal options are ocean or surface water discharge, land application, evaporation ponds or deep well injection, while discharge to wastewater collection system is suitable only for small discharges [9].

Microfiltration (MF) membranes are the most numerous on the market and are the least expensive. They are commonly made of acrylonitrile, nylon, and polytetrafluoroethylene and they need to be replaced each 3 to 5 years [9]. Microfiltration removes suspended solids, reduces bacteria to condition the water for effective disinfection and can be used as a pre-treatment step for reverse osmosis.

Ultrafiltration (UF) membranes are used for almost the same applications described for micro-

Table B.2 – Membrane filtration processes relying on hydrostatic pressure difference [9].

Process	Pore size	Permeate	Constituents removed
Microfiltration	Macropores (≥ 50 nm)	Water, dissolved solutes	TSS
Ultrafiltration	Mesopores (2-50 nm)	Water, small molecules	Macromolecules, colloids
Nanofiltration	Micropores (≤ 2 nm)	Water, very small molecules, ionic solutes	Small molecules, some hardness
Reverse osmosis	Dense (≤ 2 nm)	Water, very small molecules, ionic solutes	Very small molecules, hardness, sulfates, nitrate, sodium, other ions

filtration. Some UF membranes with small pore size have also been used to remove dissolved compounds with high molecular weight, such as colloids, proteins and carbohydrates, but the membranes do not remove sugars or salts [9].

Given the similar application and performance of the technologies, MF and UF are lumped in the same interval.

Nanofiltration (NF) is used to remove selected dissolved constituents in wastewater such as metallic ions, inorganics, organics, bacteria and viruses; membranes are usually made of polyamide or cellulose acetate [9].

In reverse osmosis (RO), the natural osmotic process is reversed by applying a feed pressure which forces water through a membrane against the natural osmotic gradient (i.e., water flows from the more concentrate solution to the less concentrate solution rather than the opposite, which would occur naturally). Reverse osmosis is usually preceded by microfiltration and the feed water is pretreated to minimize membrane fouling. Membranes consisting of cellulose acetate are subject to hydrolysis at high and low pH values; the optimum pH is approximately 4.7, with operating ranges between 4.5 and 5.5 [10]. Nanofiltration and reverse osmosis require very high quality feed, because the membrane elements in these units can be fouled by colloidal matter and constituents in the feed stream. They are usually preceded by microfiltration or ultrafiltration, which remove colloidal matter.

Given the similar application and performance of the two technologies, NF and RO are lumped in the same interval.

The membrane processes are modeled as a process interval allowing for no mixing with utilities ($\alpha_i = 0$) and no reaction. The permeate stream passes, while the concentrate stream can be treated either as a waste (in which case a cost is associated to it) otherwise it can constitute a secondary stream which is recirculated towards other equipment. In this work, only the first option is considered while the second is left for further studies.

Removal efficiency

The fraction of water retained in the waste stream is assumed to be an average of the water retained by the two units lumped as reported in Table B.3; thus, 0.145 for MF/UF and 0.200 for NF/RO. The loss of permeate for cleaning leaves this fraction almost invaried, but it is anyways accounted for.

The performance of the tertiary membrane units is highly site specific, both with respect to fouling and pollutants removal, and it depends on the type of membrane chosen and on the influent wastewater. Performance of removal of different ions are reported in [9] for a MF and for a NF systems in use in a municipal wastewater treatment plant. As an approximation, it is assumed that the membranes could at least reach these indicated values, thus the performance

reported for MF is used for MF/UF and the performance reported for RO is used for NF/RO. For the unit NF/RO, a removal efficiency of 97.5% is assumed, with the claim that this can be achieved through the selection of a proper membrane. This is not too far from what observed experimentally: a ion rejection of 95% is typically observed for reverse osmosis units [10]. It is further reasonably assumed that the oil and grease and the suspended solids are totally removed.

Utility consumption

For membrane separation processes, the utilities consumed are:

- Electricity for feed, permeate and concentrate pumping and backwashing.
- Chemicals for backwashing and washing.
- Pretreatment chemicals - acid or basic solution for pH regulation.

Power consumption of the various membrane processes are summarized in Table B.3, along with the product recovery. The electricity consumption is assumed to be an average of the two units lumped, $\mu_{EL,H_2O}=6.12$ MJ/ton for MF/UF and $\mu_{EL,H_2O}=35.10$ MJ/ton for NF/RO.

Table B.3 – Power consumption and product recovery of various membrane technologies - adapted from [9].

Technology	MJ/ton	r
Microfiltration	1.44	0.96
Ultrafiltration	10.80	0.75
Nanofiltration	19.08	0.83
Reverse Osmosis	51.12	0.78

It is very important to know which components of the feed stream could cause fouling, in order to develop an effective cleaning strategy, which could also involve a succession of different chemicals or different operating conditions. As a rule, mineral deposits are removed by acidic solutions and organic compounds by alkaline solutions. A variety of agents can be employed for the chemical cleaning of membranes, including detergents, acids, bases, oxidizing agents, sequestering agents, and enzymes; where the membrane material is not sensitive to chlorine, it can be employed in doses ranging from 2 to 2,000 mg/L [67]. Approximately 1 to 1.5 percent of the process water goes to waste as a part of the cleaning operation, with the cleaning cycle being every 24 to 48 h [10]. On the basis of these information, as a simplification, it is assumed that the cleaning takes place each 48 h and 1.25% of the permeate water is used as cleaning solution, with Cl_2 as a cleaning agent in the maximum concentration reported. Thus, the cleaning utility is estimated as $\mu_{Cl_2,H_2O} = 4.45 \cdot 10^{-4}$ kg Cl_2 /ton for MF/UF and $\mu_{Cl_2,H_2O} = 4.17 \cdot 10^{-4}$ kg Cl_2 /ton for NF/RO. The decrease of permeate flow due to cleaning is also accounted for.

The regulation of pH is performed with NaOH and H_2SO_4 . In NF and RO, the pH is usually adjusted within the range from 4.0 to 7.5 with sulfuric acid in order to reduce scaling potential [9]. The removal of bicarbonate and alkalinity to varying degrees causes depression of the pH of the treated water, which can impact corrosion control and scale stability in the distribution system; for this reason, pH and/or alkalinity adjustment may be necessary

in post-treatment to maintain effective corrosion control downstream of these processes [62]. However, the pH regulation is not considered at this stage. Park et al. [68] report a value of 0.0225 \$/ton for utilities to run a reverse osmosis unit, which is far above the estimation of the model ($0.1 \cdot 10^{-3}$ \$/ton), which considers only Cl_2 for cleaning as chemical utility. This clearly indicates that the utility costs of the membrane processes are underestimated, and this may be attributed to the negligence of the utilities for pH regulation. It is thus assumed that the difference in the utility cost is associated to H_2SO_4 for pH pre-regulation and to NaOH for pH post-regulation in equal measure. This leads to consider $\mu_{\text{H}_2\text{SO}_4, \text{H}_2\text{O}} = 0.17 \text{ kg}_{\text{H}_2\text{SO}_4} / \text{kg}_{\text{H}_2\text{O}}$ and $\mu_{\text{NaOH}, \text{H}_2\text{O}} = 0.02 \text{ kg}_{\text{NaOH}} / \text{kg}_{\text{H}_2\text{O}}$. The same values are used for MF/UF. This does not address the pH regulation problem, and it must be re-evaluated when a good prediction of the utilities for pH regulation is needed.

The average operation cost (utilities and waste) of the membrane processes predicted by the model are 0.152 \$/ton for MF/UF and 0.713 \$/ton for NF/RO, which are in the range reported by [10] - between 0.15 and 1.10 for MF/UF and between 0.2 and 0.8 \$/ton for NF/RO.

B.11 Parameter summary

In the following, the parameters used for the modeling of the processing equipment are reported.

The following assumptions were done:

1. The removal of the pseudospecies C is assumed equal to the removal of COD found.
2. When the removal of BOD_5 is observed to be lower than the removal of the COD (as waste or C converted), the removal of the BOD_5 is assumed to be equal to the one found for the COD. This is done to avoid inconsistencies of the type $\text{BOD}_5 \geq \text{COD}$, which does not have any physical sense.
3. The removal of the FSS is assumed to be equal to the removal of the TSS.

APPENDIX B. MODELS FOR PROCESS INTERVALS

Table B.4 – Specific utility consumption $\mu_{i,t,kk}$.

i	t	201	211	212	221	222	101	102	111	112	121	131	132	133	134	141	151	161	171	172	181	182	191a	191b
EL	H ₂ O	18.66	19.66	9.83	9.83	9.83	0.22	0.22	0.59	0.66	0.51	2.37	2.02	2.72	3.31	3.72	3.37	5.75	5.75	5.75	3.72	34.20	6.12	35.10
EL	C	323.54																						
LPS	H ₂ S	427.39														0.01								
CW	H ₂ O		0.24	0.09	0.40	0.19			0.04	0.04					41.46									
N ₂	H ₂ O		1.75	1.00	2.25	2.25			0.01	0.01	9.70	12.93	11.72	15.32	12.39									
N ₂	H ₂ O					78.48					2.90	3.86	3.50	4.58	14.55									
N ₂	C					23.44								4.34										
O ₂	H ₂ O	18.47																						
O ₂	C	7.92																						
N ₂	H ₂ S	12.20																						
O ₂	H ₂ S	5.23									0.02	0.03	0.02	0.03	0.03									
NH ₃	C										0.01	0.02	0.02	0.02	0.02									
H ₂ SO ₄	H ₂ O																							
H ₂ SO ₄	H ₂ O															0.64								
NaOH	H ₂ O														4.95									
GAC	H ₂ O														2.23									
GAC	H ₂ O																							
CO ₂	H ₂ O																							
NG	H ₂ O																							
CaO	PO ₃ ⁻																							
CO ₂	PO ₃ ⁻																							
ReSO ₄	Cr ⁶⁺																							
Cr ₂ O ₃	Cr ⁶⁺																							
NaOCl	Cr ⁶⁺																							
Cl ₂	Cr ⁶⁺																							
Na ₂ O	Cr ⁶⁺																							
Alum	Cr ⁶⁺																							
H ₂ O	Cr ⁶⁺																							
Cl ₂	Cr ⁶⁺																							
Alum	Cr ⁶⁺																							
H ₂ SO ₄	Cr ³⁺																							
H ₂ SO ₄	Cr ³⁺																							
H ₂ SO ₄	Cr ³⁺																							
H ₂ SO ₄	Ca ²⁺																							
H ₂ SO ₄	Ca ²⁺																							
H ₂ SO ₄	Fe ²⁺																							
H ₂ SO ₄	Fe ³⁺																							
H ₂ SO ₄	NH ₄ ⁺																							
H ₂ SO ₄	NH ₄ ⁺																							
NaOH	PO ₃ ⁻																							
NaOH	SO ₄ ²⁻																							
NaOH	Cl ⁻																							
NaOH	CO ₃ ²⁻																							
NaOH	CO ₃ ²⁻																							
NaOH	Cl ⁻																							
NaOH	Cl ⁻																							
NaOH	NO ₂ ⁻																							
NaOH	NO ₂ ⁻																							
NaOH	HCO ₃ ⁻																							

Table B.5 – Waste fraction $SW_{i,k,k}$.

i	201	211	212	221	222	101	102	111	112	121	131	132	133	134	141	151	161	171	172	181	182	191a	191b	
H ₂ O																					0.20	0.15	0.20	
C						0.31	0.42	0.35	0.35						0.80							0.78	0.90	
N ₂	1.00							1.00	1.00	1.00	1.00	1.00	1.00	1.00										
O ₂	1.00							1.00	1.00	1.00	1.00	1.00	1.00	1.00										
CO ₂								1.00	1.00	1.00	1.00	1.00	1.00	1.00										
H ₂ S ₂		1.00	0.98	0.98	0.98																			
NH ₄ ⁺		0.82		0.82	0.82										0.20					0.95	0.50	0.10	0.98	
OH ⁻						0.80	0.90	0.78	0.93	0.65	0.80	0.90	0.90	0.90	0.85							1.00	1.00	
Ca ²⁺						0.30	0.60	0.83	0.83	0.73	0.80	0.73	0.92	0.97	0.75							0.97	0.98	
PSS										1.00	1.00	1.00	1.00	1.00										
MgO																								
PO ₄ ³⁻																								
Cr ⁶⁺																								
Cr ³⁺																					0.95	0.50	0.98	
Cr ²⁺																					0.95	0.50	0.91	
C ₃₀ (OH) ₆																					0.95	0.50	0.98	
C ₃₀ CO ₃																					0.95	0.50	0.98	
SO ₄ ²⁻																						1.00	1.00	
Fe ₂ ³⁺																					0.95	0.50	0.98	
Fe ₃ ⁺																					0.95	0.50	0.98	
Cr(OH) ₃																					0.95	0.50	0.98	
Fe(OH) ₃																					0.95	0.50	0.98	
Cl																					1.00	1.00	1.00	
CO ₃ ²⁻																					0.95	0.50	0.98	
OCl ⁻																					0.95	0.50	0.98	
CN ⁻		0.30	0.30	0.30	0.30																0.95	0.50	0.98	

Table B.6 – Conversion of reactions $\theta_{react, kk, rrr}$.

react	kk	Eq. B.9	Eq. 2.1	Eq. B.23	Eq. B.20	Eq. B.31	Eq. B.32	Eq. B.41
C	121	0.60						
C	131	0.80						
C	132	0.73						
C	133	0.95						
C	134	0.90						
CN ⁻	151				0.99			
Ca ²⁺	161					0.60		
Ca ³⁺	161						0.40	
Cr ⁶⁺	172		0.83					0.95
C	201			0.83				
H ₂ S	201							

Table B.7 – Coefficient of variation of the properties $RM_{j,kk}$.

t	201	211	212	221	222	101	102	111	112	121	131	132	133	134	141	151	161	171	172	191a	191b
BOD ₅	0.31	0.42	0.45	0.45	0.45	0.73	0.73	0.80	0.80	0.80	0.73	0.90	0.99	0.90	0.83	0.80	0.80	0.80	0.80	0.83	0.90
TSS	0.30	0.60	0.83	0.83	0.83	0.73	0.73	0.80	0.83	0.80	0.73	0.92	0.92	0.97	0.73	0.80	0.80	0.80	0.80	0.97	0.98

Appendix C

Costs

In this appendix, the base information regarding the utilities used and the way the waste was treated is described.

C.1 Utility cost

Table C.1 reports the data for the utilities used in the simulations. The prices retrieved from ICIS are updated between 2006 and 2008. Air is assumed to be available for free, and also carbon dioxide, due to the fact that it can be available as a flue gas from other parts of the plant. In the simulation, the price of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is corrected to give the price per unit mass of FeSO_4 , as $4.572 \cdot 10^{-2}$ \$/kg.

Table C.1 – Utility data.

Utility	Unit	Unit cost	Purity	Heat content [kJ/kg]	Source
Electricity	[\$/MJ]	$1.889 \cdot 10^{-2}$	-	-	[69]
LP steam, 6 bar, 160°C	[\$/MJ]	$4.269 \cdot 10^{-3}$	-	2,081.4	[70]
MP steam, 20 bar, 210°C	[\$/MJ]	$6.349 \cdot 10^{-3}$	-	1,899.3	[70]
CW, 10°C increment	[\$/kg]	$2.642 \cdot 10^{-5}$	-	-4.186	[70]
Natural Gas	[\$/kg]	0.696	-	62,238.4	[69], [61]
NH_3	[\$/kg]	0.602	1.00	-	[71]
H_3PO_4	[\$/kg]	0.809	0.75	-	[71]
H_2SO_4	[\$/kg]	0.067	0.93	-	[71]
NaOH	[\$/kg]	0.726	1.00	-	[71]
GAC	[\$/kg]	2.000	-	-	[72]
Alum	[\$/kg]	0.370	0.17	-	[71]
Lime	[\$/kg]	0.610	1.00	-	[71]
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	[\$/kg]	$2.500 \cdot 10^{-2}$	1.00	-	[71]
$\text{C}_6\text{H}_8\text{O}_7$	[\$/kg]	1.213	1.00	-	[71]
NaOCl	[\$/kg]	$1.942 \cdot 10^{-4}$	0.13	-	[71]
Cl_2	[\$/kg]	0.258	1.00	-	[71]

C.2 Waste cost

A cost penalty is associated with the waste. Liquid, solid and gaseous waste cannot be released to the environment as they are originated but often need to be pretreated before disposal or release, and this is especially true for solids. In the model the cost associated with solid and liquid wastes is considered only. The processes considered which originate solid waste are the gravity separation equipment (API and CPI/PPI), the biological treatments (AS, RBC,

PACT, TF), and the precipitation units (PhPrec, MePrec, CrPrec), while the processes which originate liquid waste are the membrane separations (MBR, RO, ED, MF/UF and NF/RO).

Sludge contains between 0.25 to 12% of solids [9]. It must be treated to reduce its water and organic content and to make the processed solids suitable for reuse or final disposal. Thickening, conditioning, dewatering, and drying are used to remove moisture from the solids, while digestion, composting and incineration are used primarily to treat or stabilize the organic material in the solids. The methods used for sludge treatment are highly variable with the type and the composition of the sludge, and also the cost associated to the treatment. The treatment equipment is not considered in the cost of the processing units considered; this may constitute quite a big expense, but it is left for further studies. It is assumed that the water flow rate through the processing units remains unvaried due to the water entrapment in the sludge.

In 1993, the average cost of the pre-treatment of sludges in refinery wastewater treatment has been reported as 45 €/ton while the average cost of sludge disposal (of all sludges) has been reported as 60.5 €/ton; in 1999, the average cost of disposal of oily sludge was reported as 105 €/ton and for biosludge 55 €/ton, with an average of 95 €/ton for a generic sludge [73]. Due to lack of more up to date data and based on the observed cost increase, it is estimated a +50% higher cost of sludge pretreatment (cost of 1993) and disposal (costs of 1999) due to inflation and the more stringent regulations. Assuming that the sludge is disposed dry and that the pretreatment includes dewatering, the cost associated to the waste, $w_{C,s}$, is computed as:

$$w_{C,s} = \frac{C_p}{x_s} + C_{d,s} \quad (\text{C.1})$$

where C_p is the cost of pretreatment, C_d is the cost of disposal, and x_s is the solid fraction in the sludge (assumed as an average of 6%); s stands for the sludge type considered (oily, biological, or other). Table C.2 summarizes the sludge cost obtained. The waste cost is based on the fixed solids for the oily waste, and on the fixed solids and the bacterial mass created for biological waste.

Liquid wastes are rich in salts, metals and other dissolved solids. The cost of brine disposal depends on brine characteristics and amount, level of treatment before disposal, disposal method and environment. Current disposal methods include direct sea discharge, well injection and evaporation ponds. The cost of the former two options has been reported to be between 0.05 and 0.06 \$/m³ of product water while that for the latter option is estimated at 0.56 \$/m³ [74]. Since the last one is the only one who allows for direct discharge of the sludge, that method is chosen and an average cost of 0.252 \$/ton of water retentate is assumed - this was computed on the basis of the retentate percentage reported in Table B.3 in Appendix B.10. For the ion exchange unit, the waste is the washing water containing the ion exchanged on the resin in solution with the washing water. The washing solution contains 45% of H₂SO₄ in water [10], thus the amount of solution leaving the process unit is assumed to be 2.22 times the amount of acid or base fed. The oil and grease removed in the primary treatment is not considered as a liquid waste because once recovered it can be recycled to the process units.

Table C.2 – Solid and liquid waste cost.

Solid Waste	
s	\$/kg
Generic sludge	1.618
Oily sludge	1.637
Biosludge	1.540
Liquid Waste	
Retentate	25

C.3 Capital cost

The parameters A_C and B_C are found by regression on correlation of data found in literature or estimated on the basis of the process. The parameters A'_C and B'_C are found by linear regression of the function in the neighborhood of the flow rate (if f is the total flow rate, eight points are taken between $0.01 \cdot f$ and $1.99 \cdot f$). As an example, the case of the activated sludge unit is reported: Figure C.1 reports the real capital cost function and its approximation obtained with a linear function in the neighborhood of the flow rate considered. Table C.3 reports the values used to obtain the capital costs in k\$ from the flow rate expressed in ton/h.

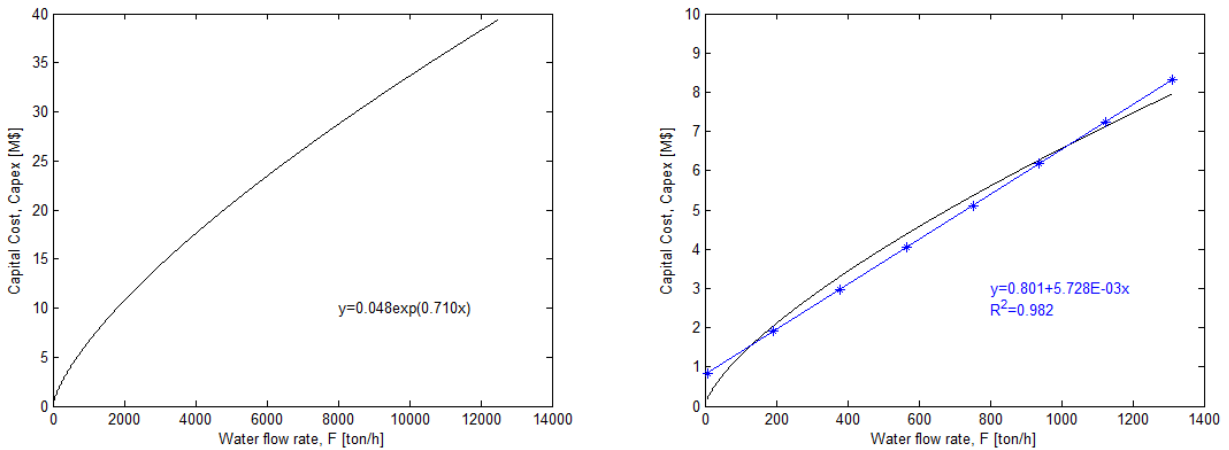


Figure C.1 – Capital cost as a function of the water flow rate and linear approximation in the neighborhood of the flow rate treated - activated sludge.

In the following, details for each specific process are discussed.

Correlation of capital costs as a function of various parameters (flow rate, characteristic of the oil and grease to be removed and the size of the vessel) are reported in [51]. One curve is taken. Due to lack of data, the price of a CPI/PPI separator is assumed to be 10% more of the API designed for the same flowrate.

The costs of a flotation unit vary widely, depending on the purpose [48]. Construction costs for a DAF unit are reported in EPA 1976 [56]. Capital costs include the basic unit, flow splitting device, drive equipment, piping, pumps, air tank and miscellaneous equipment. It has been reported that IAF equipment designed to treat a flow rate between 300 and 800 m³/h has a capital cost between 0.5 and 2.1 M€, while a DAF equipment designed to treat the

same flow rate has a capital cost between 1.6 and 1.8 M€ [48]. Assuming an average of these values, the ratio between the two is 0.68, which is used to scale the DAF cost function in order to obtain the IAF cost function.

Construction costs for an activated sludge, a high rate trickling filter, a biological contactor are reported in EPA 1976 [56]. For a conventional activated sludge aeration with diffused air, cost include cost of basins, air supply equipment, piping, blower building, flocculator type clarifier, sludge return and waste pumps. For an trickling filter, they include circular filter units with rotating distributor arms, synthetic media, under drains, sludge pumps, effluent recycle pumps, clarifier mechanisms and internal piping. For a rotating biological contactor, they include RBC shafts, standard media, molded fiberglass covers, reinforced concrete basins, sludge return, waste pump. The capital costs of a powdered activated carbon treatment are the same as the activated sludge system, with the addition of the initial carbon present in the sludge, the feeding system of the carbon make-up or the regeneration system. At this stage, these additional items are neglected. For the membrane bioreactor, the capital costs are estimated as the sum of an activated sludge and a microfiltration unit. The cost associated to membrane replacement is considered as accounted by the capital cost amortization.

The capital costs of a GAC adsorption bed are also reported in [56] and are based on an EBCT of 30 minutes and a regeneration furnace loading of 80 lb/(ft²·day) (390 kg/(m²·day). They include carbon columns (minimum 3), virgin and spent carbon storage tanks, feed and backwash pumps, piping, multiple heart regeneration furnace, slurry tank and steam generator.

The capital costs of a stripping column are estimated on the basis of those reported in [56] for an ammonia stripping column. For the sour water stripper, two columns are involved and consequently the costs are doubled.

The capital costs of the chemical oxidation are estimated on the basis of those reported in [56] for a breakpoint chlorination equipment. They include chlorine storage and feed system, lime storage and feed system (lime is often used to regulate the pH), and a chlorine contact tank of 30 minutes detention.

The capital costs of a WAO unit can be estimated as the sum of the cost of a pump, a compressor and a reactor vessel dimensioned for the proper flow rate. The approximate costing method suggested in [37] is used. Capital costs are computed for three different flow rates (100, 170 and 300 ton/h) and the coefficients A_C and B_C are obtained by regression on these three data.

For phosphorous and metal precipitation, the capital costs are estimated on the basis of those reported in [56]. Construction costs include lime storage and feed facilities, rapid-mix facilities, flocculator/clarifiers, flow and pH controls, recarbonization.

The capital cost of a ion exchange unit is given in [62]. Capital costs include the addition of ion exchange or adsorption beds, chemical storage, associated piping and valves, instrumentation and controls. The capitals costs of an electrodialysis unit is estimated on the basis of the correlation reported by Sajtar and Bagley [75]: $1,052,000 + 14,340Q_f + 6.06Q_f^2$, where Q_f is the flow rate treated in m^3/h .

Data on capital costs of MF/UF and NF/RO are given in [62]. They include membranes, feed pumps, associated chemical feed equipment, and electrical and instrumentation, but they do not include pre-treatment or post-treatment processes because they are highly dependent on the specific source water quality.

Table C.3 – Coefficient for capital cost.

	201	221	211	212	222	101	102	111	112	121	131	132
A_c	80000.00	458.86	917.72	458.86	458.86	0.95	1.04	242.56	167.37	677.97	524.86	801.37
B_c	8.56	4.73	9.47	4.73	4.73	0.01	0.01	1.32	0.91	4.87	15.49	5.73
	133	134	141	151	161	171	172	181	182	191a	191b	
A_c	801.37	1686.62	743.06	426.99	801.14	801.14	801.14	216.17	0.00	1258.37	626.06	
B_c	5.73	11.42	7.42	1.38	3.50	3.50	3.50	3.32	21.82	7.71	5.99	

C.4 Water cost

The cost associated to the water sinks can be seen in Table C.4. The price of the boiler feed water (sink 92) for producing high pressure steam is roughly twice the price of freshwater, which in lack of data could be estimated as 0.5 \$/1000 lb [70], which equals to 1.10 \$/ton. If this value is compared with the cost of freshwater in various countries reported in [5], it results to be close to the average, which is 1.32 \$/ton. However, as discussed in section 3.5.3, the price of water presents a wide range of variation - from 0.01 \$/ton to 7.71 \$/ton. A base case scenario in which the price of freshwater is in the low range is used (one fourth of the suggested value, 0.28 \$/ton), and the effect of the price of the freshwater on the solution is then investigated. The price of cooling water (sink 93) is the same reported in Table C.1. The price of the water to the desalter (sink 94) is assumed to be equal to the one for cooling water, since water of no high grade is required.

Table C.4 – Water sink cost.

kk	[\$/ton]
92	0.551
93	0.026
94	0.026

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