Improvement of the demin water plant for steam production with AquaSPICE Project

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Vist i plau pel lliurament i defensa del TFG del grau d'Enginyeria Química.

TÍTOL DEL TFGEQ: IMPROVEMENT OF THE DEMIN WATER PLANT FOR STEAM PRODUCTION

SUBTÍTOL WITH AQUASPICE PROJECT

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ABSTRACT

Organic acid anions are formed in boilers by hydrothermolysis due to the presence of organic carbon in the boiler water[1]. This generates corrosion on the steam-water cycle components, increasing the amount of condensate generated, and reducing the lifetime of the components and the boiler efficency[2].

Optimizing water production and specifications are key to avoiding water losses in industrial processes. The Dow Böhlen processes are highly dependent on water, both for cooling and steam production. Fresh water is taken from primarily two sources, Lake Witznitz and River Elster. This is further processed to achieve the required specifications to use as cooling tower make-up (CTMU) and supply for the Demin water production. Dow key water-stressed sites, such as Böhlen, have set a global target to reduce freshwater intensity by 20% by 2025 [4]. This thesis evaluates how to enhance the existing Demin Water production plant with the objective of obtaining the required water specifications to meet site needs and future demand. This reduces the corrosion formation in the equipment downstream while avoiding unnecessary losses in the form of condensate.

Two mobile research facilities (IMPROVED containers) from the University of Gent are used to perform pilot tests and select the most appropriate technology train. These containers comprise several water treatment technologies which can be configured in different sequences and equipped with smart controls and online sensors that ensure a safe and stable continuous operation. Six different technology trains have been evaluated. A technology train composed of a pre-treatment of coagulation/flocculation followed by rapid sand filtration and ion exchange resins has been selected. The proposed train adds into the current demin water system an organic scavenger SCAV4 Cl resins column, this presents affinity within specific hydrophobic organic compounds and biopolymers that are not removed within the current treatment. The fact of adding this step allows Dow to reuse most of the assets in the existing demin water plant (lower CapEx) while meeting the desired specifications, thus, resulting in the most cost-effective solution.

A full-scale design is proposed to modify the existing demin water, including the design of the new column and pumping system. This will help the Dow Bohlen site to have a first general estimation for further evaluate the implementation of this project. Total capital of 3.5 million euros[1] is estimated through TURTON's methodology to modify current assets.

[1] Note: this cost estimation does not consider Dow's guidelines for project estimations.

LIST OF ABBREVIATON AND NOMENCLATURE

BB	Building Blocks
CDOC	Chromatographic Dissolved Organic Carbon
CEPCI	Chemical Engineering Plant Cost Index
CoC	Cycles of Concentration
CPS	Cyber Physical Systems
CTBD	Cooling Tower Blowdown
CTMU	Cooling Tower Make-Up
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
DOP	Dissolved Organic Phosphorus
GAC	Granulated Activated Carbon
HOC	Hydrophobic Organic Compound
IEX	Ion Exchange
LC-OCD	Liquid Chromatography – Organic Carbon Detection
LMW	Low Molecular Weight
MB	Mix Bed
NOM	Natural Organic Matter
OCD	Organic Carbon Detector
OH	Hydroxide
OND	Organic Nitrogen Detector
POC	Particulate Organic Carbon
RO	Reverse Osmosis Membrane
RSD	Relative Standard Deviation
RSF	Rapid Sand Filter
SAC	Strong Acid Cation Exchange Resin
SBA	Strong Base Anion Exchange Resin
SCAV	Organic Scavenger Exchange Resin
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
UF	Ultrafiltration Membrane
UVD	Ultra Violet Detector of 254 nm
VER	*Vorentcarbonisiertes Rohwasser* – Pre-Decarbonated Raw Water
WBA	Weak Base Anion Exchange Resin

1. INTRODUCTION

1.1. Dow and Dow Olefinverbund GmbH

The Dow Chemical Company, commonly referred as Dow, is a company of innovators, believers and solutions providers. It was founded by Herbert H. Dow in 1897 in Midland (USA) and is one of the largest chemical manufacturers in the world by revenue. Dow offers technology-based products and services to clients in about 160 countries and high-growth sectors like food and specialty packaging, industrial and consumer packaging, health and hygiene, electronics, energy, architectural and industrial coatings, home care and personal care, as well as infrastructure.

Dow Olefinverbund GmbH is a subsidiary of Dow Chemical established in central Germany since 1995, making it one of the first international investors in the region. As the last major privatization of the Treuhandanstalt, the Olefinverbund was formed from the three locations Buna-Schkopau, Leuna and Böhlen[3].

Nowadays, the company's German headquarters are in Wiesbaden (Hessen), and the largest production sites are in Lower Saxony (Stade) as well as in Saxony (Böhlen) and Saxony-Anhalt (Schkopau) [3]. Dow is involved in a variety of ways in the economic, social and cultural development of the regions.

Dow's processes are heavily dependent on water. Engineering Dow's facilities to better withstand acute impacts of severe weather and addressing water availability, especially at Dow water-stressed sites, such as Böhlen, are of particular importance to enabling continued, safe operation of the facilities. Dow has set a global target to reduce freshwater intensity by 20% at the key water-stressed sites by 2025[4].

1.2. AquaSPICE

AquaSPICE stands for Advancing Sustainability of Process Industries through Digital and Circular Water Use Innovations. AquaSPICE is a European-funded project with a duration of 3.5 years (01/12/20-31/05/24) that has received funding from the European Union's Horizon 2020 research, an innovation program (under grant agreement No 958396). This is a project supported by 29 partners from around 12 different countries. The project is divided into 6 case studies, with different companies around Europe interested in eco-efficient and sustainable industrial water management to reduce the freshwater intake in their sites[5].

The project aims at materializing circular water use in European Process Industries. AquaSPICE's goal is the development and validation of water efficiency management and optimization methodologies, technologies and tools that will carry process industries forward to a near-zero water footprint target with minimum freshwater consumption and water-borne emissions[5]. This is pursued through a set of scientific and technical objectives, motivated by real industrial needs and a set of impact-related objectives.

Two mobile research facilities (IMPROVED Project containers) from the University of Gent are used to perform pilot tests and select the most appropriate technology train for the different legs. The containers from IMPROVED Project, comprise several water treatment technologies, equipped with online sensors.

In addition, within AquaSPICE, Dow is also looking into implementing Cyber-Physical Systems (CPS) to reduce the water losses by creating a next level of site water management by using smart monitoring, algorithms, and control on raw water, discharge, and recycle streams.

Dow carries out the first case study of the project, in which the experimental phase is carried out in two of the sites: (A) Terneuzen (Netherlands) and (B) Böhlen (Germany). This first Case Study is focused on three main areas:

(1) Reuse of cooling tower blowdown (Terneuzen leg 1, Böhlen leg 2)

(2) Reuse of different heavy polluted condensates (Terneuzen leg 2)

(3) Optimize production of demi water (Böhlen leg 1)

1.2.1 AquaSPICE – Case Study 1 (B): Dow Böhlen,Germany

The location of Dow Böhlen is one of Dow's key water-stressed sites[4], this counts with a global target to reduce freshwater intensity by 20% by 2025[4]. To reach this global target is necessary to implement improved handling of the raw water and wastewater streams.

The current feed streams used are two water sources: Lake Witznitz and River Elster, these are used in varying fractions to produce cooling tower make-up (CTMU) and supply for the Demin water production. The pre-treatment for the raw water streams is called "pre-decarbonated raw water" (VER), this pre-treatment is done in parallel and it consists of the same technologies. The pre-treatment consists in a coagulation/ flocculation step done in re-circulators, then the water is sent to a rapid sand filter.

Nowadays, this water is directly used in the Cooling Towers and its cooling tower blow down (CTBD) is discharged directly into the river and the off-spec condensate is treated in the wastewater treatment plant without further reuse.

For the steam generation and process water, there is a further treatment, besides the VER treatment, the water is sent to the Demin Water Plant. The demin water is produced by ion exchange (IEX), using cation and anion IEX and mixbed (MB). A general diagram of the actual water treatment of the site can be found below:

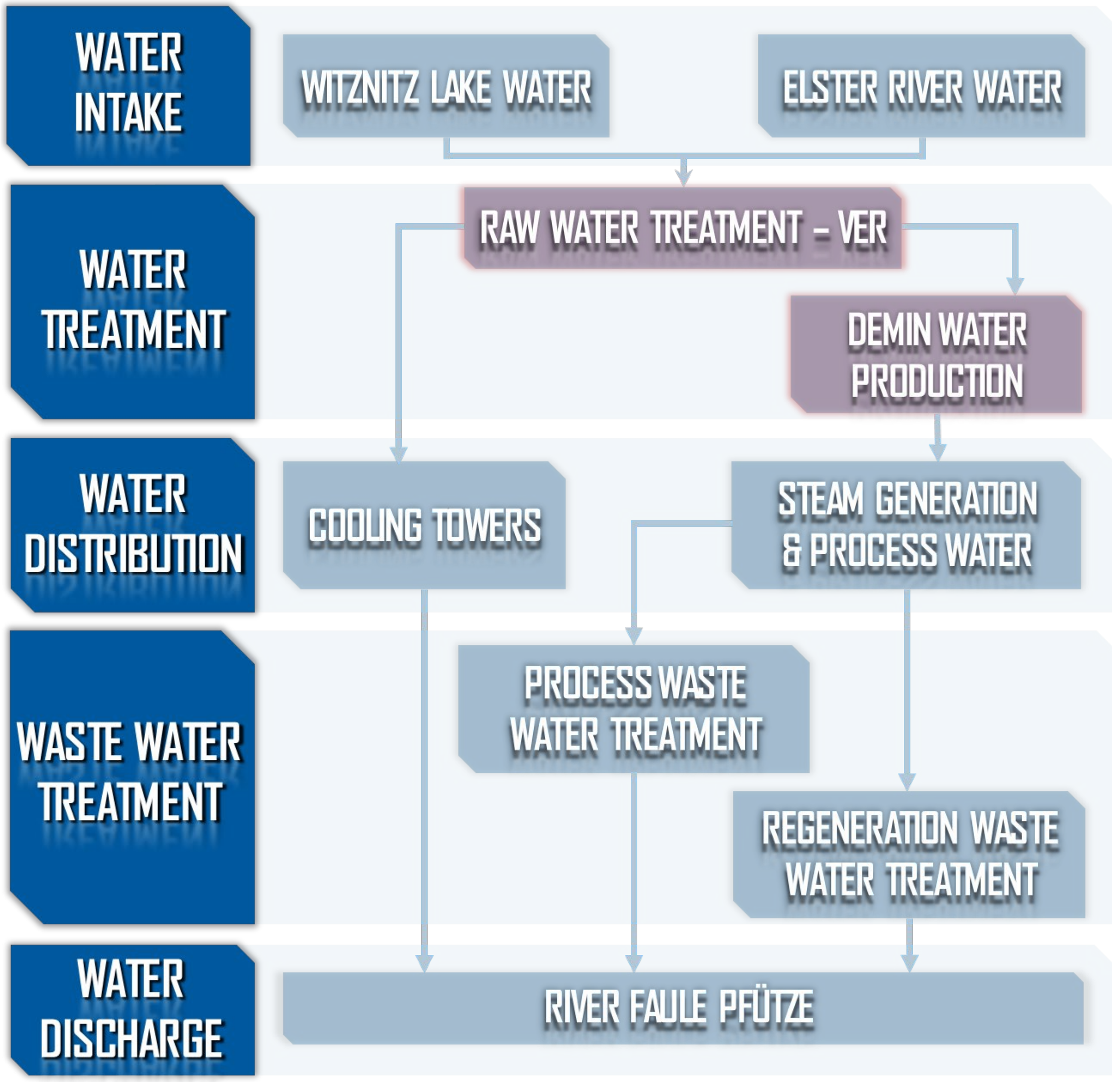


Figure 1.1 – General bloc diagram of the water system in Dow´s Böhlen site

1.3. Project goals

The project will be focused on finding the most suitable technology train and operating conditions to upgrade the demi water quality at Dow Böhlen, considering minimum footprint, capital and operational cost. Research is done for 5 months in a real-time pilot plant to find the most appropriate technology and operational conditions. In addition, this bachelor thesis evaluates the feasibility of scaling up the preferred technology train for further full-scale implementation at Dow Böhlen.

Demin water (for steam production) wants to be upgraded to avoid possible severe corrosion downstream and minimize water losses. During steam production, high-purity water is required to feed the boilers because of the susceptibility of the steam-water cycle in front of corrosion[1]. While being heated, some organic contaminants undergo a process called **hydrothermolysis**, forming organic acid anions, which are suspected to cause corrosion of steam-water cycle components[1].

By improving the demin water quality at Dow Böhlen, the amount of organics present will be reduced. Resulting in a longer lifetime and reducing the required maintenance of the equipment. Also, better quality in the boiler feed water will represent a higher recovery of the boiler by the reduction of condensate.[6]

1.3.1 Project KPI's Definition for the Demin plant

To monitor the performance and success of the project, Key Performance Indicators (KPIs) have been defined. These set up the minimum quality that the product water needs to achieve for optimal downstream process performance.

In order to control the amount of organics entering the feed water for the boilers, the Total Organic Carbon (**TOC**) is frequently checked in the plant to ensure the long-term performance of the boilers. The organic matter can be also estimated with the measurement of the Dissolved Organic Carbon (**DOC**). The DOC is defined as the totality of organic carbon-based compounds that are capable of passing through a filter of 0.45 μm. Another type of analysis, the DOC Fractionation offers a more detailed report, allowing the classification of the organics present. To understand which organics are not removed after the actual treatment, the DOC Fractionation was done two times during 2021:

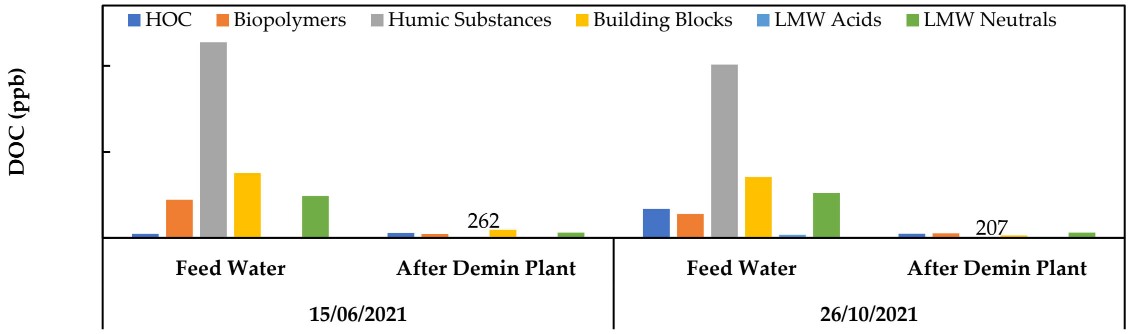


Figure 1.2. Evolution of the DOC through the water treatment process on the 15th of June and the 26th of October of 2021, DOC plotted numerically after the Demin Plant

Through the water treatment process, the organics present in the feed water are mostly removed but there is a small part of the HOC (Hydrophobic Organic Compound), Biopolymers, Building Blocks, and LMW (Low Molecular Weight) Neutrals that is not removed by the current water treatment. These species increase the conductivity after cation exchange measurements, confounding the utility of this measurement for monitoring sulphate and chloride. Besides, organic acids can also lead to corrosion in the steam cycle. That is why in AquaSPICE the degradation of TOC in the pre-treatment and IEX technology must be analyzed and evaluated to find opportunities of **lowering the TOC at the Demin water plant below 200 ppb.**

Total dissolved solids (TDS) are also an important parameter to take into account in the boiler feed water. High content of TDS in the water reduces the boiler efficiency due to the reduction of heat transfer rates, increasing the heat losses and scale deposits. The electrical conductivity of the water also depends on the type and amount of dissolved solids that's why this is also analyzed and controlled. Within the AquaSPICE Project, the goal is to reduce the **electrical conductivity under 0.1 μS/cm for future processes in the site**. A summary of the main KPIs can be observed in the table below:

Table 1.1. Summary of the KPIs to reach within the AquaSPICE Project

KPI	Specification	Units
TOC	≤ 200	ppb
Electrical conductivity	≤ 0.1	μS/cm

1.4. Thesis Objectives

This thesis focuses on selecting the right technology train to evaluate its full-scale implementation. Three main goals are defined:

1. Analyze and compare the different water treatment technologies alternatives within the IMPROVED Containers to produce Demin Water quality suitable for steam production (TOC ≤ 200 ppb and EC ≤ 0.1 μS/cm)
2. Present a first design for the proposed changes in the actual Demin Plant for a production of 330 m^3/h of Demin Water under the desired spec
3. Give a first cost estimation for the proposed modification of the current system

2. THEORETICAL AND LITERATURE REVIEW

A literature review has been performed to define the baseline of this project. The below chapter contain a summary of the literature review with subsequent references.

2.1. Corrosion Mechanisms Affecting the Steam Production

Boiler corrosion is a non-desired effect that may develop deep holes and cavities on the metal due to oxidation reactions of the dissolved oxide and the iron-rich boiler metal [8]. The size of the holes may increase over time, to the point that the boiler/tubing is destroyed. There are many causes of boiler corrosion that can be found in the literature[9], the one affecting this study is presented in the following subsection:

2.1.1 Organic Matter

As mentioned in the previous Chapter 1.3 the organic matter present in water suffers hydrothermolysis with the presence of heat, transforming it into organic acids (acetic acid mainly and formic acid and galactic acid on the boiler. The corrosion produced by hydrothermolysis can be explained by the following equations[7]:

$$n \cdot H^+ + n \cdot e^- \leftrightarrow \frac{n}{2} \cdot H_2 \quad (2.1)$$

$$M \leftrightarrow M^{n+} + n \cdot e^- \quad (2.2)$$

$$\boldsymbol{n \cdot H^+ + M \leftrightarrow M^{n+} + \frac{n}{2} \cdot H_2} \quad (2.3)$$

Defining a Hydrogen Proton as H^+, an electron as e^- and M as the metal of interest. The expression (2.3) describes the dissolution of the metal in the presence of Hydrogen Ions, explaining the corrosion under acidic conditions as metal degradation[10].

As is presented in the study of W.Y. MAENG and D.D. MACDONALD[10] in Figure 2.1 below, there is a dependence of the acetic acid concentration on the elongation and maximum stress. These values are decreased as the pH of the solution is decreased (with a major concentration of acetic acid, a lower pH is obtained)

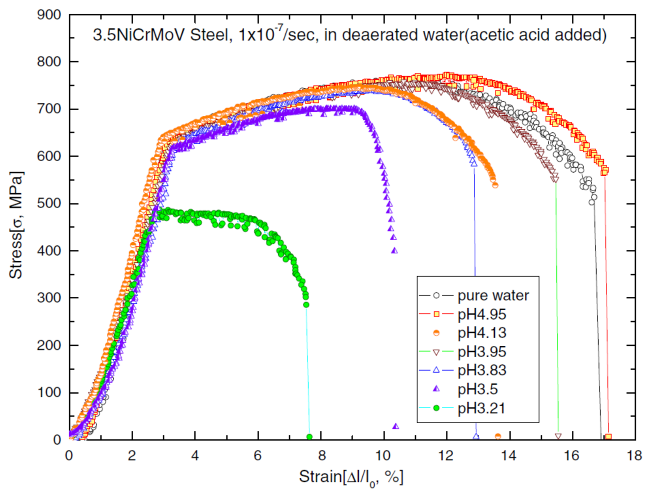


Figure 2.1. Strain-stress curves of 3.5NiCrMoV Steel for different acetic acid concentrations at 150°C [10]

As shown in Figure 2.1, the Fracture point decreases dramatically from the curves under 3.5 pH, compared to the curves between 3.83-4.95 pH. Comparing it with the 4.95

pH curve, the decrease is about 40%. Within the 3.21 pH curve, it can be observed a reduction of more than 50%.

The maximum stress is decreased from 772 MPa to 487 MPa with the 4.95 and 3.21 pH curves respectively. It corresponds to a 37% reduction with the addition of Acetic Acid in concentrations between 1.10×10^3 to 1.32×10^6 ppb. The fracture mechanism in the 3.21 pH solution is the ductile fracture with uniform corrosion, possibly reflecting crack blunting due to dissolution[10].

2.2. Determination of the Organic Matter

Quantifying organic matter remains a challenge due to the complex nature and the variability from the different sources. Natural Organic Matter (NOM) can be detected using advanced spectroscopic, chromatographic, and mass spectrometric means[11]. The different forms of the organic matter found in natural water can be found in the following representation:

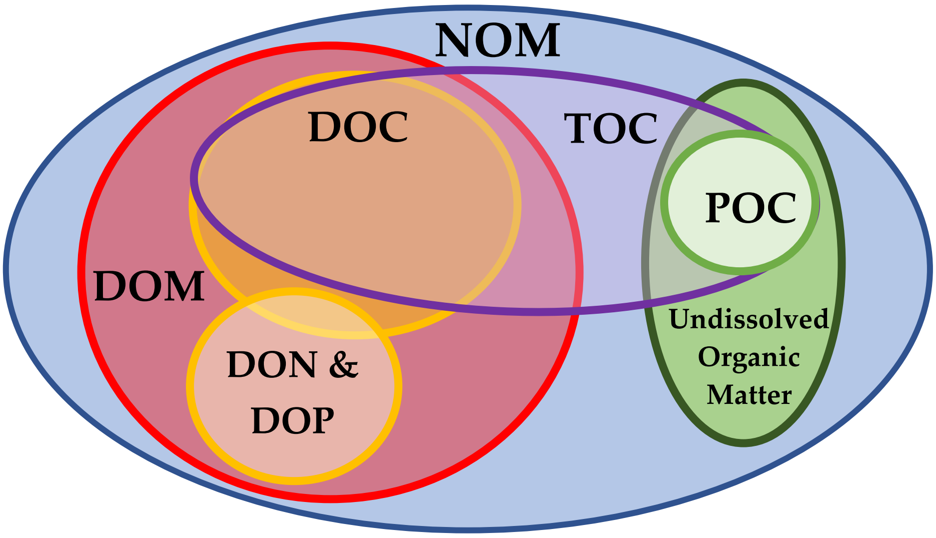


Figure 2.2. Stacked Venn diagram of the various forms of organic matter present in natural water. Natural Organic Matter (NOM), Dissolved Organic Matter (DOM), Dissolved Organic Carbon (DOC), Total Organic Carbon (TOC), Particulate Organic Carbon (POC), Dissolved Organic Nitrogen (DON), and Dissolved Organic Phosphorus (DOP)[11].

In water treatment, the typical quantification of the organic matter is done by the measurement of the TOC and the DOC. The DOC represents the total organic carbon smaller than 0.45 μm in diameter while the POC represents the rest of the organic carbon that is not able to pass through the filter, this is a minor fraction below 10% [12]

2.2.1 TOC Online Measurement

The research facility of the IMPROVED Containers counts with the Sievers M5310C TOC Online analyzer[13] in order to be able to analyze the different water at the sample points with grab samples or have the Mix Bed (MB) TOC continuously monitored. This analyzer counts with the Membrane Conductometric Detection technology, giving reliable results for measuring TOC in the drinking water industry or water treatment processes and an easy calibration that has to be done once a year. Its range of operation is from 4ppb to 50ppm with a precision of 1% Relative Standard Deviation (RSD) and accuracy of ±2% or 0.5ppb (the greater one) [13].

2.2.2 DOC Fractionation

The Fractionation of the DOC is done by the external company of DOC-Labor GmbH[14] by Liquid Chromatography – Organic Carbon Detection (LC-OCD). This fractionation presents a detailed report of the TOC, obtaining the overall value of the TOC, DOC and the Particulate Organic Carbon (POC) as the difference between TOC and DOC measurement and the different parameters of the Chromatographic DOC (CDOC).

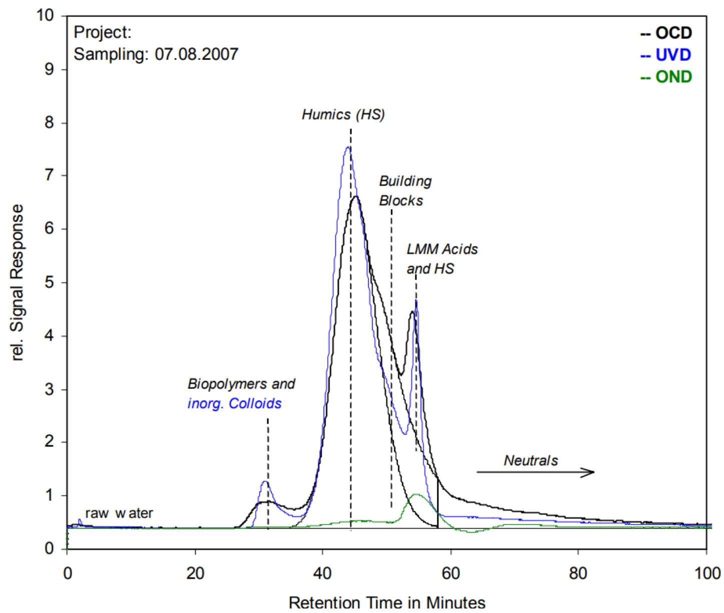


Figure 2.3. LC-OCD signal response for the Organic Carbon Detector (OCD), Ultra Violet Detector of 254 nm (UVD) and the Organic Nitrogen Detector (OND) from DOC-Labor Sample Reports [14]

As is presented in Figure 2.3 above, the different compounds of the DOC are presented within the peaks detected by the chromatography along the residence time. The following Table 2.1 lists the types of compounds represented:

Table 2.1. Definition and molecular size[15] of the compounds detected at the LC-OCD of Figure 2.3

Compound	Description
Biopolymers, > 20 000 g/mol	Defined as polymers produced from natural sources, can be chemically synthesized from material or entirely biosynthesized by living organisms. They are an important factor at wastewater treatment in the formation and settlement of sludge flocs in aerobic and anaerobic treatments.[16]
Humic Substances (HS), ~ 1 000 g/mol	Is the most predominant compound of natural organic matter present in water. Humic substances should be removed because of its harmful effects, they can cause the formation of carcinogenic compounds and their presence in water can decrease the capacity of the adsorbent as a basis of the target pollutant.[17]
Building Blocks (BB) 350-500 g/mol	Assumed breakdown products that appear during hydrolysis of the HS, its structure is similar to humics but a smaller molecular size.[18]
LMW Acids, < 350 g/mol	All aliphatic low-molecular-mass organic acids co-elute due to an ion chromatographic effect. [18]
LMW Neutrals < 350 g/mol	A complex fraction dominated by LMWs of weakly, or uncharged hydrophilic, or slightly hydrophobic ("amphiphilic") compounds that slowly approach baseline. Fraction is dominated by non-biodegradable, branched natural LMWs. [18]

2.3. Coagulation/Flocculation (Coag/Floac)

The coagulation process consists of the addition of a positively charged chemical (normally ferric chloride) known as the coagulant. Its positive charge neutralizes the negative charge of the dissolved and suspended particles in water. Within this process, the suspended particles are attached together formatting small coags. [19]

The flocculation process allows the formation of bigger suspended particle blocks, called flocs. Due to the bigger dimensions, these are easier to sediment. [19]

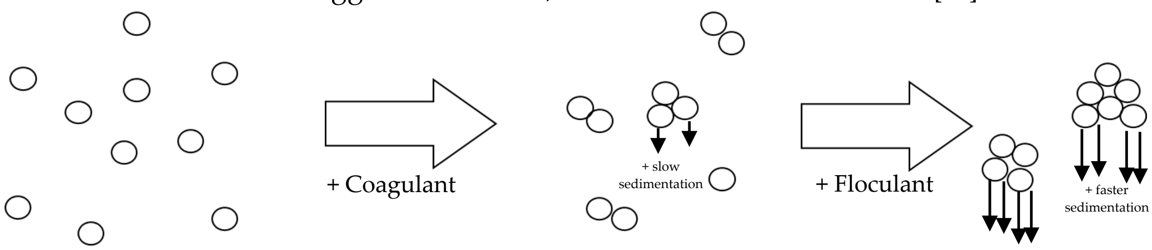


Figure 2.4. Visual representation of the sedimentation due to the addition of coagulant and flocculant

2.4. Rapid Sand Filters (RSF)

The sand filter is a relatively simple and affordable method of treating ecological effluents. Its principle consists of filtering water through a block of sand.

Schematically, the grains of sand form a layer crossed by the water and which, by a simple sifting effect, stops particles larger than the spaces between said grains. If along their progress they touch a grain, the smaller particles will also be retained on the surface of these by the wall effect. This is a typical post-treatment after coagulation-flocculation pretreatment. [20]

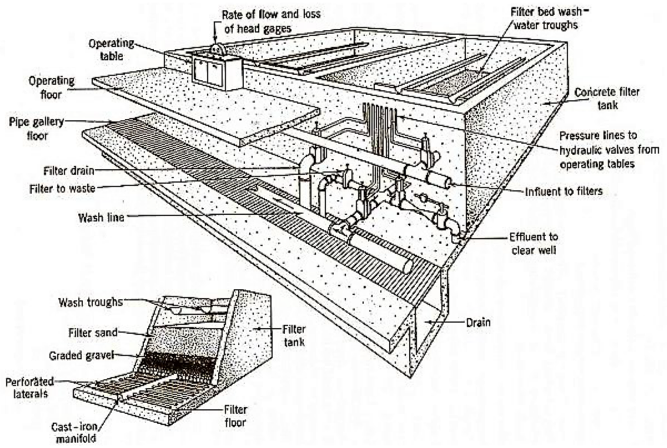


Figure 2.5. Components of an open rapid sand filter, TWT (n.y.) [20]

2.5. <u>Ultrafiltration (UF)</u>

Ultrafiltration (UF) is a membrane separation technique, which allows the mechanical separation of suspended or dissolved solids through a sieve, using hydrostatic pressure to force the passage of solids.

The two phases in contact with the membrane are liquid and at different hydrostatic pressure. Specific components of the liquid phase will transfer from the high-pressure side to the low-pressure side.

Small dissolved particles in the liquid pass through the porous membrane, while large dissolved molecules, colloids, and suspended solids, which do not pass through the pores, are retained. Ultrafiltration membranes have a pore size that allows the separation of particle sizes of different natures (suspended solids, fine particles, colloids, algae, and microorganisms such as bacteria) within the range of 0.01 and 0.1 μm. [21]

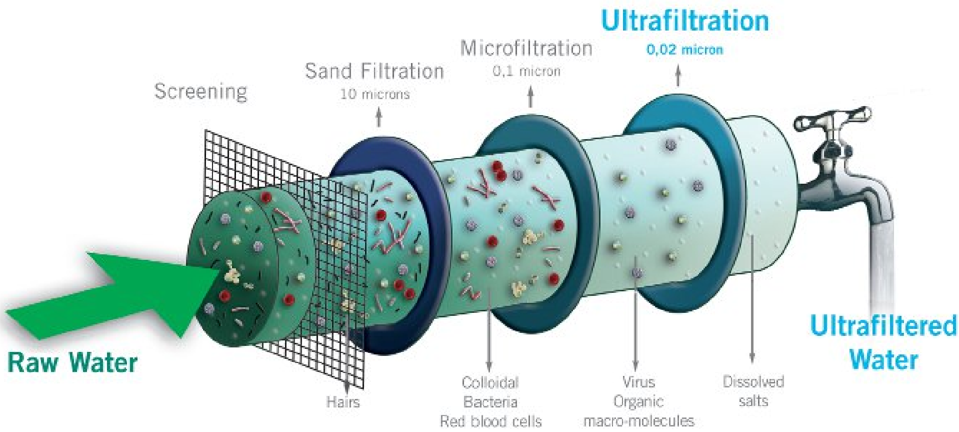


Figure 2.6. Components of an open rapid sand filter, TWT (n.y.) [21]

2.6. Reverse Osmosis (RO)

RO is a pressure-driven semi-permeable membrane that removes ionic and organic contaminants in the water. With the application of pressure to the salt water, it flows through the semi-permeable membrane removing 95-99% of the dissolved salts. These salts are retained before the membrane gets concentrated. [22]

The most relevant measurements reverse osmosis are total dissolved solids[22] (being a combination of the organic and inorganics presented dissolved in the water).

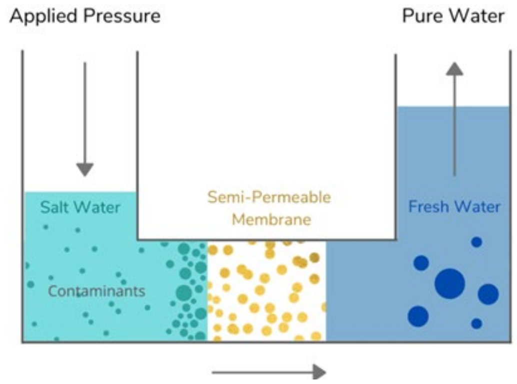


Figure 2.7. Visual representation of the salt water flow through the semi-permeable membrane[22]

2.7. Electrodialysis Reversal (EDR)

Electrodialysis Reversal (EDR) is a high-recovery brackish water desalination technology able to treat challenging waters by applying energy to the membranes. Membranes have a high density of fixed ionic groups, which allow the selective transport of ions through the membrane depending on their charge. Counter ions (opposite charge) are allowed to pass while co-ions (same charge) are prevented due to Donnan repulsion.[23] the polarity of the electrodes is reversed periodically (approximately 3 to 4 times per hour) and, using valves automatic outlets of the concentrated solution and the diluted solution are exchanged. In this way, the ions are transferred in opposite directions, which makes more difficult the scaling formation and allows the membrane to be washed[24].

According to the literature, electrodialysis is a technology that operates at low pressure, achieving lower concentrations of salts than other physical membranes that count with osmotic pressure limitations and also allows to reduce the fouling effect by applying a high electrical current through the membrane[34]

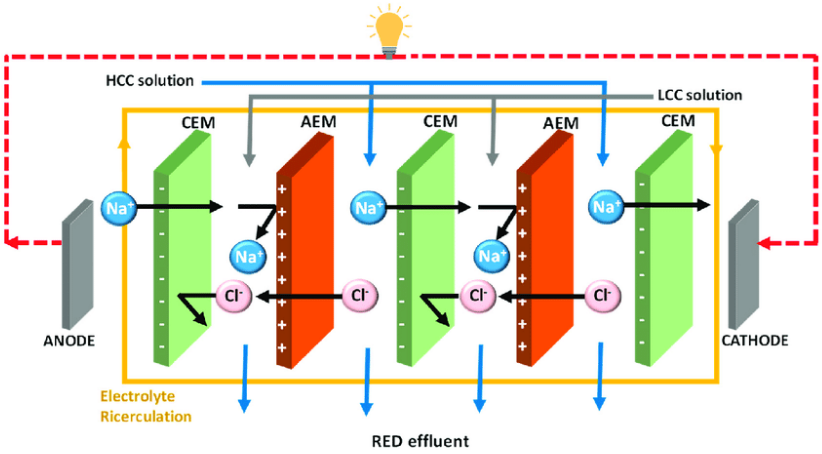


Figure 2.8. Visual Representation of the EDR Process [24]

2.8. <u>Ion Exchange Train (IEX)</u>

IEX is a cyclical electrochemically driven process where the exchange of ions between the solid and liquid phases is done reversible, adsorbing predominantly dissolved and colloidal ionic matter and not insoluble material. In this technology, ions are removed from the solution when they are exchanged with ions already present in the IEX solid resins.[25]

Important resin factors that must be duly considered include the resin type, porosity/polymeric framework of the resin, suitability of the reaction, regeneration/recyclability, economic/commercial effects of employing resins, type of reactor, and reaction operating conditions. [25]

IEX is used for the removal of calcium and magnesium in the water softening, also it can also remove various charged atoms or molecules such as nitrates, fluoride, sulfates, perchlorate, iron and manganese ions as well as toxic metals (radium, uranium, chromium, etc.) from water. The most typical application of ion exchange is where the production of high-purity water is needed. Mainly it is in industrial applications, water softening, recovery or removal of metals in the chemical industry. [25]

While the ions are exchanged, the resins are getting exhausted. At this point, a regeneration is required to refill the resins with renewed ions to exchange. [25]

2.8.1 Ion Exchange Resins

Ion exchange resins are produced by the polymerization of styrene or acrylic monomers. During this process, the addition of a divinylbenzene-DVB is needed to give physical strength to the resin, depending on the amount added the pores can be larger or smaller[27]. Optionally, porogen can be added in the reaction of the mixture if creating larger porous in the resins is needed, resulting a macroporous structure for the resin, otherwise, its structure is gelular. [27]

The key chemical characteristics of the ion exchange resins are:

Table 2.2. Definition of the different Chemical Properties of the Ion Exchange Resins[28]

Property	Description
Capacity	The total volume available for the exchange of ions (Total Capacity) or the useful performance of the resins when they are being operated in the defined operational conditions (Operating Capacity). This operational capacity has several factors. It depends on the level of regeneration, the composition of the solution, and flow rates on the column.
Swelling	The hydration of the fixed ionic groups increases with an increase of capacity to the limits of the resin's polymer network. The occupied volume of the resins is changed by the conversion to ionic forms.
Selectivity	The affinity of a resin for specific ions, depends on the ions' charge and size of the ion hydrated form
Kinetics	The speed of the process of exchanging ions. This exchange process is done by diffusion
Stability	The rate of degradation of strong oxidizing agents (rapid degradation) and slower degradation with oxygen and chlorine.

A classification of the functionalization of the resin is done to define the ability to attach ionized groups to the resin bead, depending on the functional group of the ions:

- Strong or weak acid cation exchangers
- Strong or weak basic anion exchangers

This strong and weak classification is done because of the difference in the influence of the degree of ionization. The selectivity of the different resins (in decreasing order of preference) is summarized as[29]:

- **Acid Cation Resins:** Barium, Lead, Calcium, Nickel, Cadmium, Copper, Zinc, Magnesium, Potassium, Ammonia, Sodium and Hydrogen.
- **Basic Anion Resins:** Iodide, Nitrate, Bisulphite, Chloride, Cyanide, Bicarbonate, Hydroxide, Fluoride and Sulphate.

2.8.2 Standard Operational Steps in a Filtration Cycle of IEX

The exchange of ions is a reversible process. Every different resin is rich in some specific ions, these are exchanged with the ones with higher affinity present in the water. As they are being exchanged, the amount of available ions is reduced to the point the resins are completely exhausted. At this point the resin is saturated with the exchanged ions present in the water, stopping the exchange of ions.

Before it happens, a regeneration solution has to be introduced to the columns in order to remove the saturated ions extracted from the water during the filtration and restore the resin's capacity. The cycle described takes place in the following order:

- **Filtration Step (Exhaustion of the Resins):** In this step, water passes through the resins system and the exchange of ions takes place on the different resins. Through this process, the resins are being exhausted progressively. This process is stopped when it reaches a certain determined value of key exhaustion identification parameters (normally conductivity or silica), when this value overcomes the limit indicates that regeneration is required.

The velocity of exhaustion and the exchange speed is different for every resin due to the resin type used, their total exchange capacity and the operational conditions (linear velocity of the water, temperature).

- **Backwash:** This is a previous step of the regeneration in order to avoid excessive compaction and remove the accumulated suspended solids and broken resin particles on the bed surface.
- **Regeneration:** The regenerant solution (specific acids for the acid cations resins and specific base for the basic anions resins) is slowly introduced into the column. This process can be done in co-current flow, where the flow goes in the same direction as in the filtration step and the counter-current, where the flow goes on the opposite direction of the filtration. The chemical dosing is done in excess in order to flow the same regeneration solution in the other acid or basic resin.
- **Rinse:** the objective of this step is to remove the chemicals added into the regeneration by flowing demin water in the same direction as in the filtration step but in this case being discharged to the drain. This is done in two steps, a first slow rinse (displacement) where the flow is the one used in the regeneration until most of the chemicals are removed. Then the last step is a fast rinse where the column is under the same flow as in the filtration step.

The representation shows a completed cycle of a counter current regeneration:

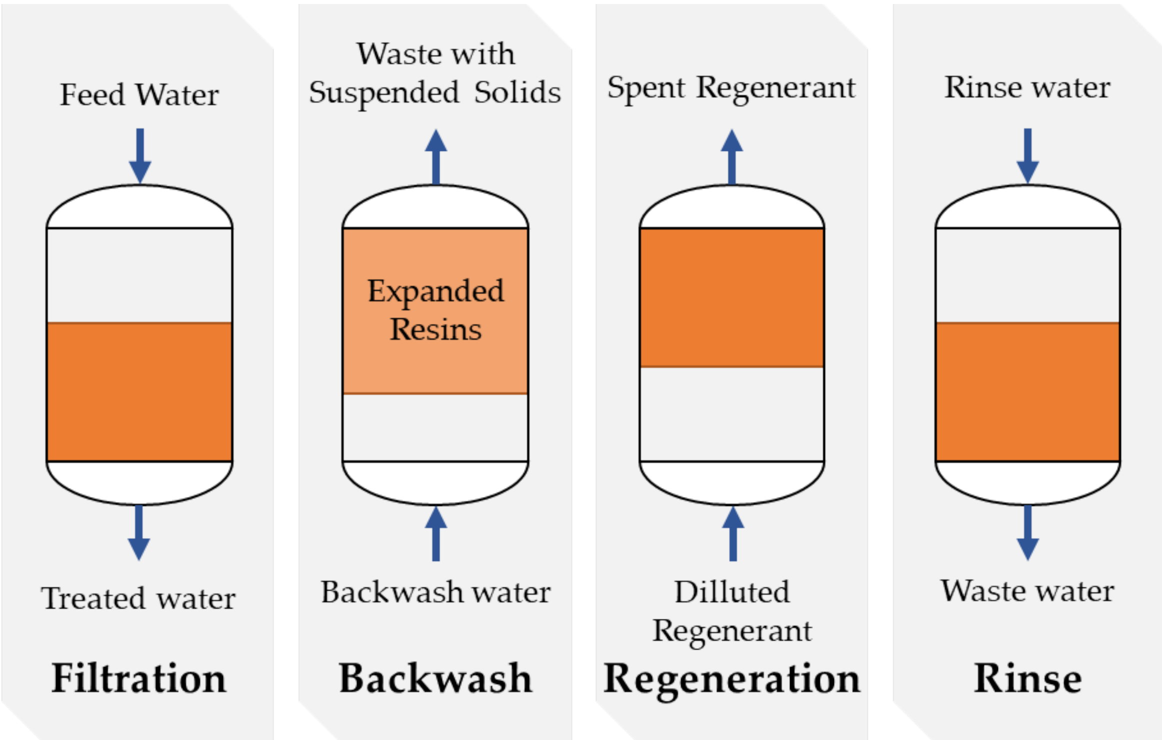


Figure 2.9. Steps description for a IEX cycle with counter current regeneration

3. DEMIN WATER PRODUCTION PROCESS DESCRIPTION AND EXPERIMENTAL PLAN

3.1. As-is treatment process

The demin water production process is composed by two steps: a pre-treatment and purification (so-called demi-water plant). The raw water coming from the Witznitz Lake and/or Elster River is decarbonized using coagulation and flocculation followed by sand filtration. Among the available technologies to remove carbon content, this technological train represents one of the most economically and commonly feasible methods [31].

The coagulant is added to the feed water, suspended solids are attached together forming small coags. With the addition of flocculant, bigger flocs are formed which are easier to settle in the recirculators. Then the water is sent to the rapid sand filtration in order to remove the remaining suspended solids present in the raw natural sources.

After the pre-treatment, the treated water is sent directly to feed the cooling towers or is sent to the Demin Plant for steam (demin) water production. This demin plant consists of a group of four different IEX resins. Firstly, the water flows through a strong acid cation (SAC) column where the cations are exchanged with Hydrogen Ions. This is followed by weak (WBA) and strong (SBA) basic anion resins where the anions are exchanged with hydroxide anions, removing most of the silica and organic matter present in the water. Last, a Mix Bed (MB) is used as a last purification step to remove the remaining contaminants, reduce its conductivity and bring water into the specification for steam production.

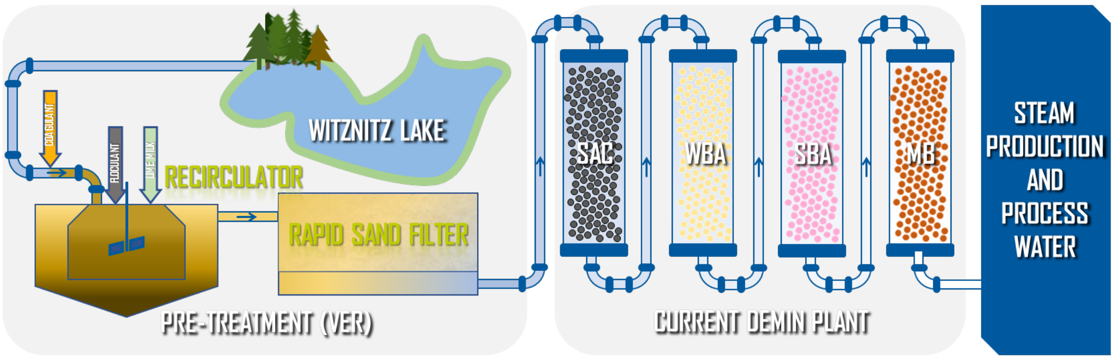


Figure 3.1. Schematic representation of the actual water treatment for the steam production and process water (in the overall water treatment, part of the VER Water is sent directly to the Cooling Towers)Quality specifications at the Demin Plant

An outranged quality (mainly TOC and electroconductivity) can cause severe corrosion and scaling in the downstream boilers and turbines[2]. Indirectly, it also results in inefficient water usage as the recovery rate in the demin water plant becomes lower. Current water recovery at the boilers results in approximately BWR%, it is expected that enhanced water quality can result as well in an enhanced water recovery, expected up to 95%[32]. In addition, a higher corrosion rate reduces the lifetime of the equipment and increases maintenance and turnaround frequency and early replacement. Ideal water characterization for demin water production found in the literature is about TOC < 500 ppb and EC < 0.2 µS/cm[33].

Table 3.1. Average encrypted results on the objectives in the product water quality on the last 3 years due to possible confidentiality

Parameter	Average value	Desired specs
TOC (ppb)	A-TOC	≤ 500 ppb
EC (μS/cm)	A-COND	0.2 μS/cm desired FL μS/cm future limit

Current TOC and EC data over the past three years is shown in the figure below. Straight doted lines determine the desired minimum Demin water quality and analytical limit. Due to confidential issues, this version is presented with different letters on the sensible values.

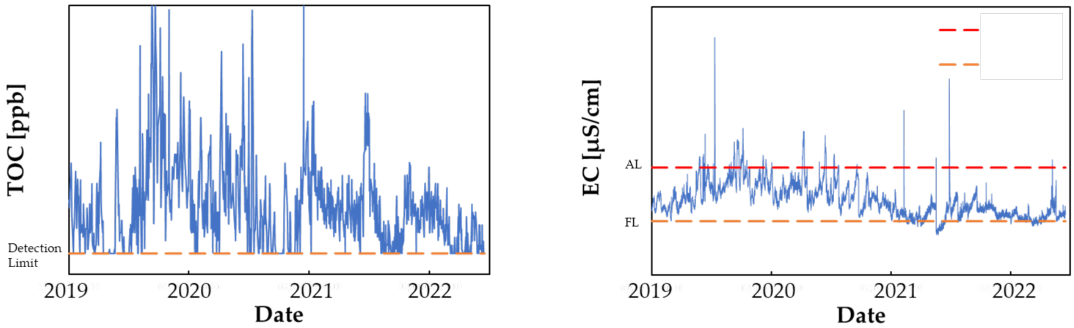


Figure 3.2. Online monitoring at Dow Böhlen from 01/01/19 to 10/07/22 for the TOC and Electroconductivy on the Demin Tank. AL represents the Actual Limit and FL a future limitation

Further analysis has been done about the historical values but has been removed in this version due to confidentiality limitations.

3.2. Study of different technology train alternatives

AquaSPICE Project aims to enhance the Demin Water quality by finding a sustainable and feasible technology train. FirstSearch is done through literature to determine the most promising technology trains. This thesis focuses on testing the pre-selected technology trains in continuous pilot plant experiments at the scale of 250 L/h~, to determine the most suitable solution for the Dow Böhlen case. In addition, a full-scale design is done and CapEx is estimated.

To evaluate the different possibilities, the different technologies have been evaluated through simulations with different water treatment software (WAVE, Water Analysis Software, Aquion Hydrochemistry).

The decided experiments have been studied in a continuous operation for 5 months in the UGent IMPROVED Containers[26]. The different technologies available and further information about the functionality can be checked in the virtual tour[26].

These containers give the opportunity to test and evaluate in a pilot scale in real-time the effectiveness of the different water treatment technologies in front of different waters used in the industry. Due to the limitations of the containers, the determination of the optimal operating conditions cannot be carried out with the research facility.

Below block diagram shows the existing situation at the Demi water production process followed by the different alternative technology trains that have been studied. The goal is to find out the most feasible technology train which achieves the specification required while having a minimal footprint and an acceptable capital/operational cost.

First, alternatives respecting the existing decarbonization pre-treatment (conventional coagulation and flocculation step followed by filtration) were studied (Alternative 1 and 2). Later breakthrough processes were added, changing completely the existing water treatment using alternative technologies such as BACF as pre-treatment, RO, UF, IEX (alternatives 3 and 4). Last, Electrodialysis was proposed (alternative 5). This technology was considered during the technology research and discussed with the supplier. It was decided not to test it, as the EDR was not foreseen as a feasible alternative, so it was discarded from the alternatives studied (alternative 5 in figure below).

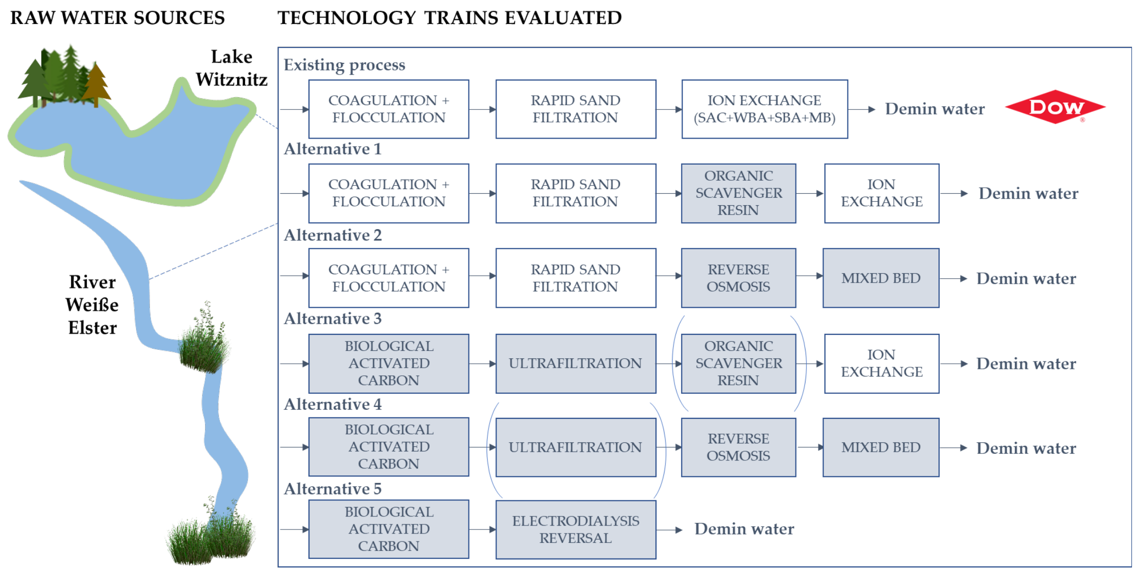


Figure 3.3. Research plan for testing different technology trains for Demin water production. Actual water treatment technologies highlighted with a white box. Ion Exchange refers to SAC+WBA+SBA+MB Resins.

3.2.1 VER-SCAV-Current IEX (alternative 1)

This group of technologies respects the current pre-treatment performed at Dow with an addition of organic scavenger resins between the current pre-treatment (VER) and the current demin plant. The current treatment consists in four different ion exchange resins: Strong Acid Cation resins (SAC) where most of the cations present in water are exchanged by hydrogen ions, Weak Basic Anion resins (WBA), strong basic anion resins (SBA) where the ions present are exchanged with hydroxide anions, removing most of the organic matter and silica present in the water and the mix bed resins (MB) behaving like a combination of SAC and SBA resins as a last purification step. Further information about the different resins can be found in Appendix A.1.

As described in Appendix A.1.7, the **organic scavenger** is a type of SBA resins that can be operated in the Cl- or OH- form and is able to **adsorb a high load of organic matter**, giving the possibility to remove specific organics that are not removed with the current technologies.

The application of this possibility will affect in the addition of an extra column on the different streets of the demin plant and in increase of the acid dosing at the SAC column in order to regenerate also the Organic Scavenger Resins.

3.2.2 VER-RO-MB (alternative 2)

The application of this train of technologies will replace the current SAC-WBA-SBA resins for a physical semipermeable membrane of reverse osmosis. As described in Chapter 2.6, is a powerful technique for concentrating the organic carbon present in the water with a high recovery, at the same time is a technology that requires expensive costs in terms of CAPEX/OPEX [30]

3.2.3 GAC-UF-(SCAV)-Current IEX (alternative 3)

The third train of technologies described is the ones explained in the first Chapter 3.2.1 with a different pretreatment. Instead of the current pre-treatment of coagulation/recirculation and rapid sand filter, granular activated carbon is used. The GAC presents a better affinity in the removal of organics than the current pre-treatment, meaning a smaller load in organic content for the Ion Exchange Columns with Organic Scavenger. Also, the addition of a physical membrane of ultrafiltration to the train will be tested. UF gives the possibility to remove particulates and macromolecules present after the GAC without the addition of chemicals in its operation, only on the Cleaning in Place (CIP) of the membrane in order to avoid destructive irreversible effects like scaling and particulate fouling In order to remove some organics that are not actually removed within the GAC and the Organic Scavenger Resins, a physical membrane of Ultrafiltration is added in front of the Organic Scavenger Column.

3.2.4 GAC-UF-(RO)-MB (alternative 4)

The second alternative will be also evaluated within the different pre-treatment already described in the previous alternative 3.

4. EXPERIMENTAL RESULTS AND COMPARISON WITH THE CURRENT DEMIN PLANT

4.1. Alternative 1: VER+(SCAV)+IEX

This first alternative has been evaluated approximately during two months of operation. Ion exchange columns in the containers were operated in a higher ratio of Bed Volume per hour than in the demin plant, meaning a smaller residence time inside the column and less time for the kinetics of exchange of ions. With this higher flow, it can be ensured that the results with a lower flow (as the demin plant), due to a longer residence time, will allow more exchange of ions for the same amount of water, obtaining better results.

The IEX columns available in the IMPROVED Containers counted with some limitations:

- Rinse to waste step was not possible to do: instead of that, a long displacement with Demin water was done in order to remove the acid/base present in the resins used during regeneration.
- The SCAV resins were filled in the SAC column and their volume was smaller than the other ion exchange columns, this resulted in a higher load of water per L of resin and a smaller amount of available ions to be exchanged.

In order to prove the effectiveness of the SCAV on the current configuration of IEX technologies. The current process at the demin plant was tested for from the 19/04 to the 04/05 then, the SCAV resins were implemented before the current IEX columns.

Figure 4.1. Daily data obtained through the ion exchange train from 19/04 to 09/06

Within the application of the organic scavenger SCAV4 Cl resins (vertical red line in the charts), the values for TOC at the WBA are smaller than those obtained without the SCAV even though the feed TOC was 250ppb higher on average. The period between the 2 black vertical lines represents a period a problem with the base dosing was occurring, leaving the resins exhausted without any regeneration.

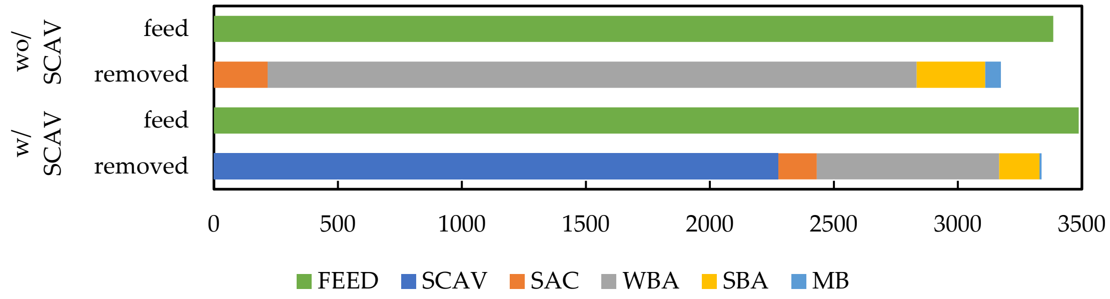


Figure 4.2. Summary of the daily results for TOC removal in absolute value from 19/04/2022 to 09/06/2022

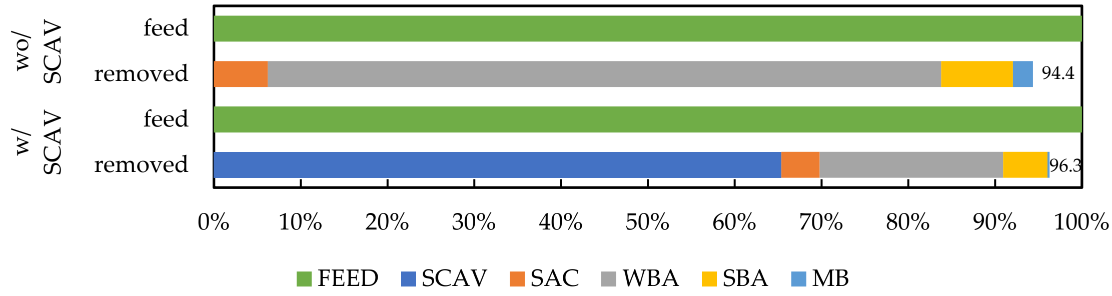


Figure 4.3. Summary of the daily results for TOC removal in relative value from 19/04/2022 to 09/06/2022, total removal for each period represented numerically in % in the chart

As can be observed in the bar charts of Figure 4.2 and Figure 4.3, during these 2 months of operations, the addition of the SCAV resins to the current train represents a higher removal of TOC in absolute values but an increase in the TOC content of the VER water is also observed. Looking at the relative values, it can be seen that TOC removal is increased by 2% in the SCAV trials.

The addition of the scavenger to the current resins train will represent a reduction of load charged on the WBA, SBA and MB resins. The WBA takes most of the organics (78%) of the pre-treated water. When the SCAV is added, it takes 65% of the organics, reducing the load on the WBA, to only 21%.

To understand the behavior of the organic scavenger resins in terms of total organic carbon and electroconductivity a continuous evaluation of the SCAV behavior during a filtration cycle was done on 03/06/2022.

As mentioned, the available column for the organic scavenger is 38% smaller than the other ion exchange resins used in the containers, meaning a smaller number of available ions to exchange.

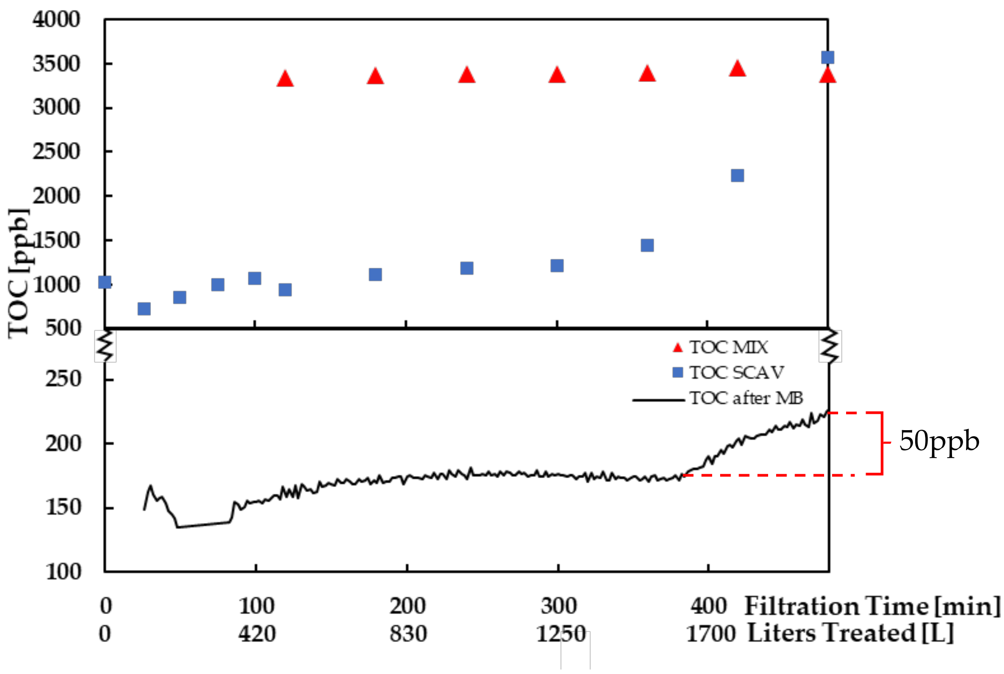


Figure 4.4. Evolution of the TOC within a filtration cycle of 480min

As can be observed in the representation of Figure 4.4, the TOC of the SCAV, increases rapidly from 350 minutes of filtration / 1500 Filtrated Liters, achieving the values of the inlet water. Within the SCAV TOC increase, a small increase of 50ppb is also observed at the end Mix Bed, meaning that there was 50 ppb of specific organics that the current ion exchange treatment is not able to remove.

To corroborate the results obtained in the trials, an extra week at the end of the experimental period (19/07/2022 to 26/07/2022) was done to compare the current process (19th and 20th of July) against the current process with SCAV resins in front within a more similar feed water (20th of July till 26th of July). On the 26th of July, a DOC Fractionation was done in order to identify the different types of dissolved organic carbons removed with SCAV4 Cl resins.

The main results obtained within these experiments are presented below, further details can be found in Appendix 0.

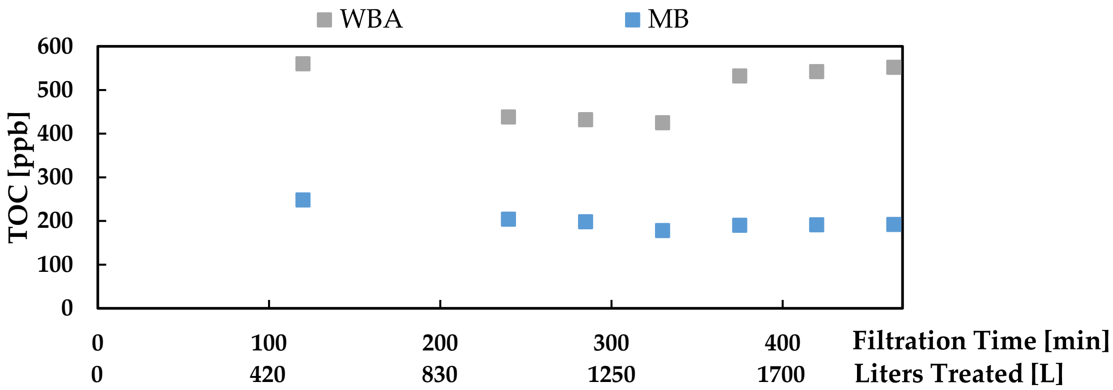


Figure 4.5. Evolution of the TOC for a ion exchange train of SAC+WBA+SBA+MB during 20/07/2022

As can be seen in the Figure 4.5, an increase in the WBA TOC occurs around 350 min of filtration time, this does not have any effect on increasing the total organic carbon content after the mix bed during the filtration time of 480min, meaning that during this filtration time, the specific organic carbon that was removed in the WBA, can be removed within the SBA, MB resins.

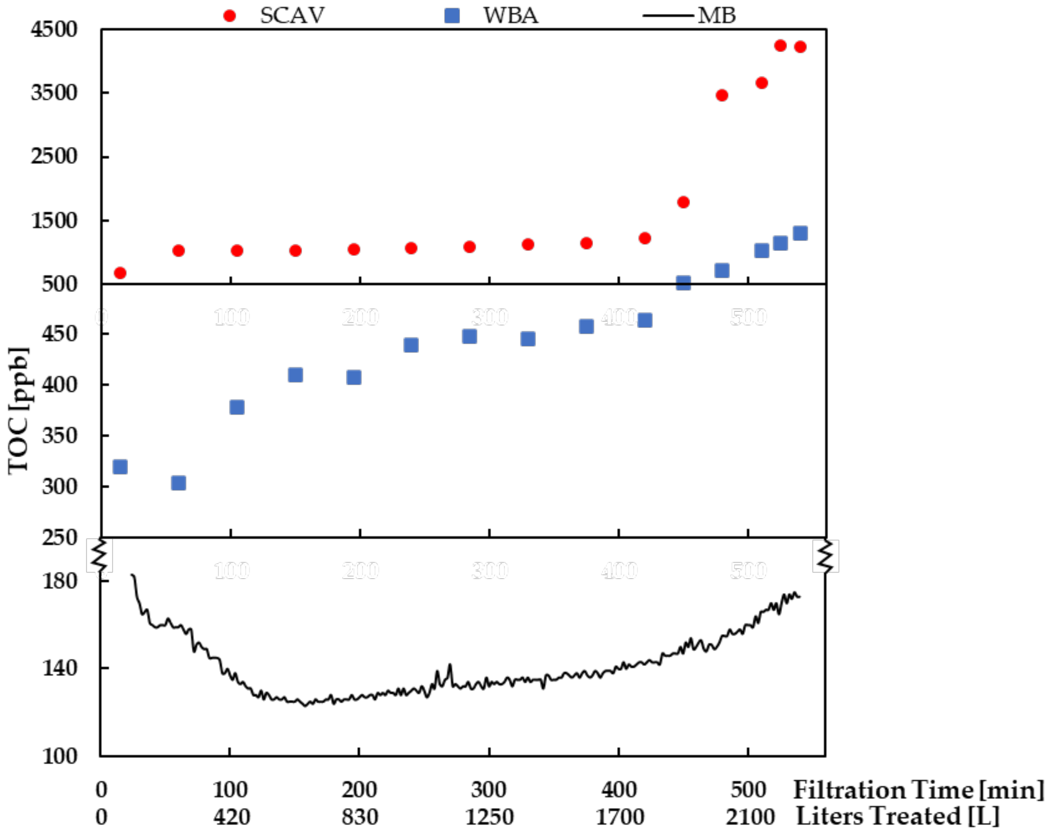


Figure 4.6. Evolution of the TOC during 540min of FT with a configuration of SCAV+SAC+WBA+SBA+MB on th 22/07/2022

As can be observed, the SCAV resins have similar behavior as the followed on 03/06 in Figure 4.4, in this case, the TOC growth occurs around 420min of filtration time. This effect carries over to the WBA and as a difference with Figure 4.5, in this case these organics are not able to exchange with the available ions of the SBA and MB resins, confirming that these specific organic compounds have affinity only for the organic scavenger resins. The increase that occurred on the MB is again over 50 ppb as during the 03/06 evaluation in Figure 4.4.

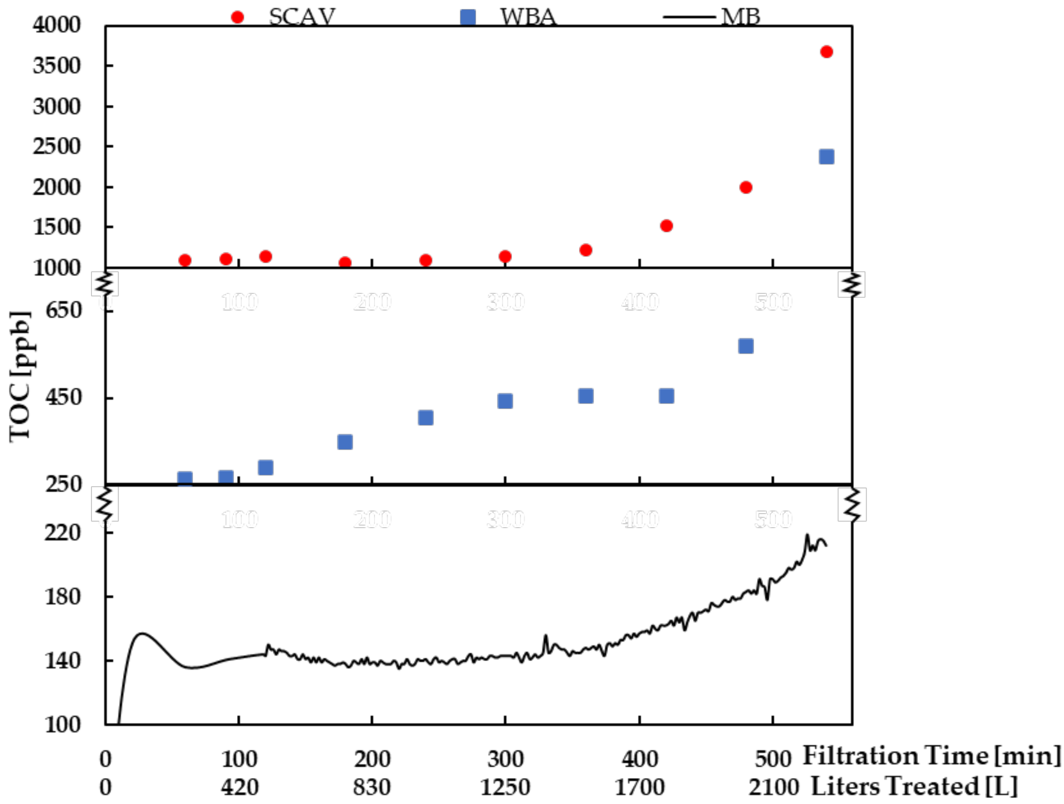


Figure 4.7. Evolution of the TOC during 540min of FT with a configuration of SCAV+SAC+WBA+SBA+MB on th 26/07/2022

During the 3rd monitoring of the SCAV, the TOC of the WBA increased faster to bigger values than in previous experiments also a higher content of organics (3600 ppb). This increase represented a 80ppb increase of TOC on the MB outlet.

On the second period of experiments with this train of technologies, similar total organic carbon feed water was used, being more valid the comparison between options:

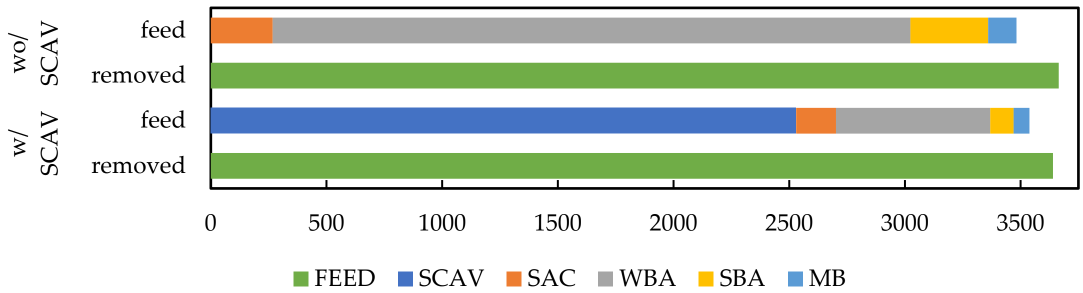


Figure 4.8. Summary of the daily results for TOC removal in absolute value from 19/07/2022 to 26/07/2022

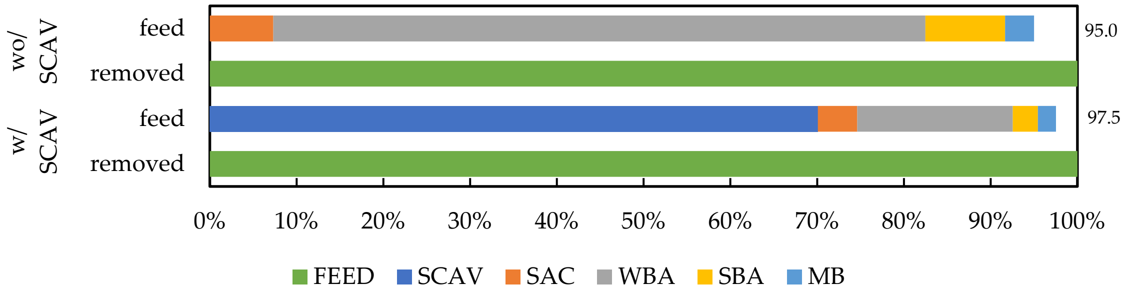


Figure 4.9. Summary of the daily results for TOC removal in relative value from 19/07/2022 to 26/07/2022, total removal for each period represented numerically in % in the chart

4.1.1 DOC Fractionation

During the 26th of July 2022 scavenger experiment, the DOC Fractionation was done for three sample points: the VER Water, after SCAV and after MB. The selection of the sample points where on the VER Water and MB to compare with the previous DOC Fractionations done on 2021. And on after the Organic Scavenger in order to check which type of dissolved organic carbon was especially removed.

Table 4.1. DOC Fractionation Reports from the last 3 samples on 15/06/2021, 21/10/2021 and 26/07/2022, results from the current process hidden due to confidentiality

Sample Date:	15/06/2021		21/10/2021		26/07/2022		
Parameter in ppb	**VER**	**After Demin Plant**	**VER**	**After Demin Plant**	**VER**	**SCAV**	**After AquaSPICE**
DOC (total)	**0000**	**000**	**0000**	**000**	**3140**	**1104**	**164**
HOC	000	00	000	00	256	280	10
Biopolymers	000	00	000	00	196	87	41
HS	0000	0	0000	0	1564	1	1
Building Blocks	000	00	000	00	696	272	33
LMW Acids	0	0	0	00	1	172	7
LMW Neutrals	000	00	000	00	248	292	73

As can be observed, within this DOC Fractionation, the lowest value of HOC is achieved, having a similar composition of VER water in HOC comparing it with 15/06/2021. This can be explained with the adsorption behavior of hydrophobic compounds expected from the fabricant [37]. About biopolymers, the highest input value is found for the 3 samples on the 26/07/2022, due to organic scavenger affinity for the adsorption of biopolymers, a bigger removal is found on this date in comparison the other periods of sampling. About building blocks, similar results are achieved as the 21st of October 2021 but within a higher input. LMW Acids are increased on the Scavenger by possible exchange of ions, this is mainly removed on the following resins but not removed totally as in previous samples. About LMW Neutrals, a higher value is obtained at the outlet of the trains with a lower feed value than in previous samples.

4.2. Alternative 2: VER+RO+(MB)

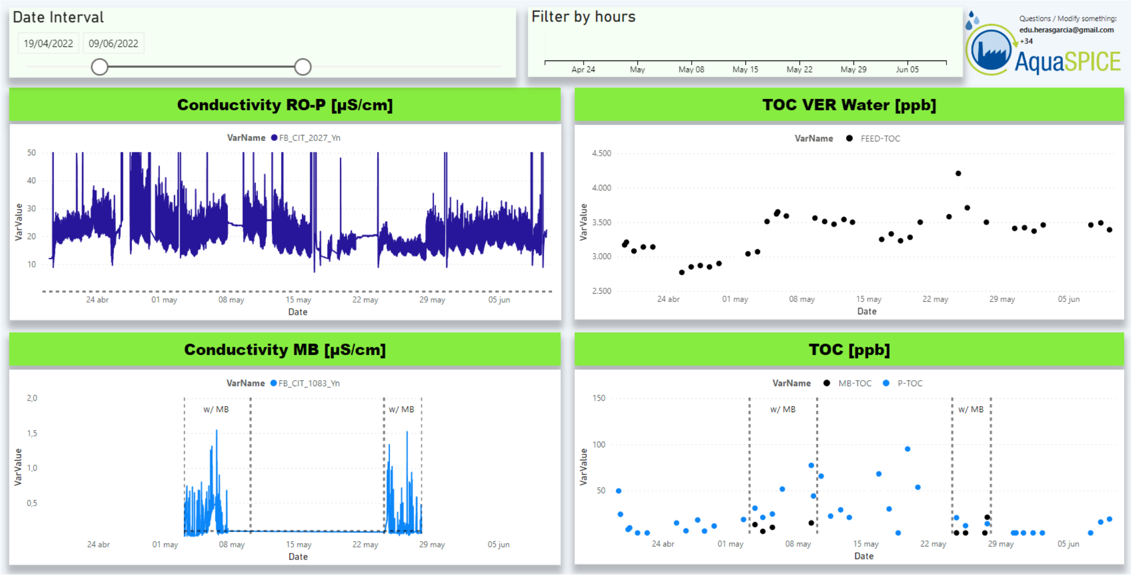


Figure 4.10. Daily data obtained through the reverse osmosis and reverse osmosis' MB from 19/04 to 09/06

During the two months of operation within the VER water, the MB was applied in the periods compressed with the vertical black lines, the first interval was from the 3rd of May till the 9th of May and the second period from the 23th of May till the 27th of May.

The application of a semipermeable membrane of reverse osmosis to the pre-treated water reduces the TOC from 3500 to less than 100 ppb. Talking about the conductivity, this oscillates between 15 to 30 µS/cm. The addition of MB resins after the reverse osmosis allows to reduce the conductivity under 0.5 µS/cm on average.

4.3. Alternative 3: BACF+(UF)+(SCAV)+Current IEX

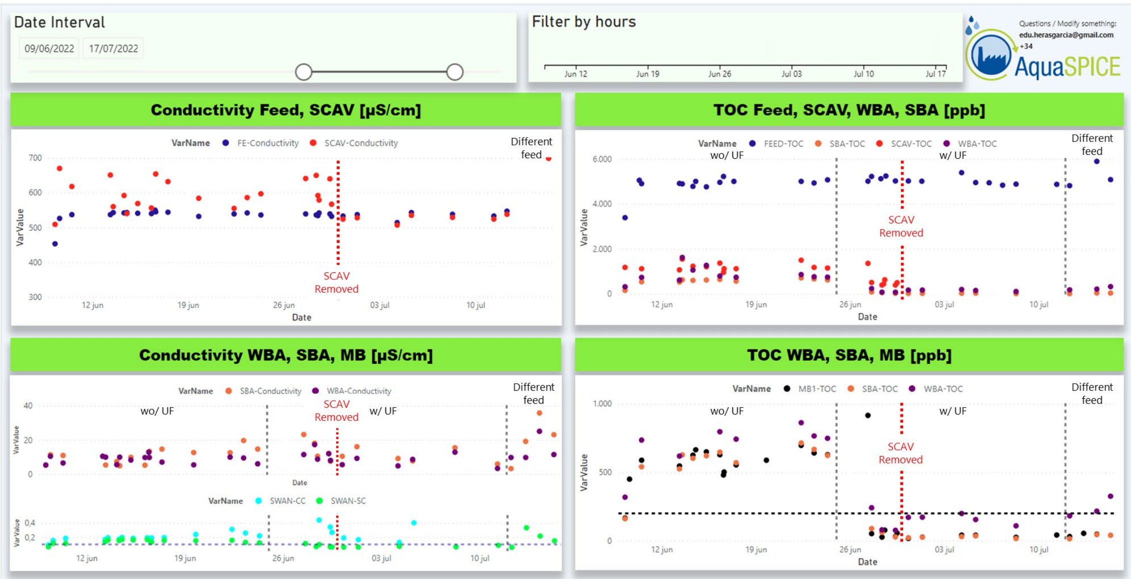


Figure 4.11. Daily data obtained through the ion exchange train from 09/06 to 17/07

During the trials of the Witznitz water, several trials of the pre-treatment were done. The 1st period, limited with the first black vertical line on the 24th of June, represents the operation of the BACF with the ion exchange resins of SCAV+SAC+WBA+SBA+MB. After the 24th of June, Ultrafiltration was added after the BACF till the end of the trials. A third period is defined with the red vertical line on the 29th of June with the removal of the SCAV Resins. A fourth period is started with the last vertical line on the 13th of July with different composition water, mixing lake with river water.

BACF as pre-treatment allows a lower load of organic carbon to the rest of the technologies but as can be observed in the 1st period of the chart, the overall value after the MB is much higher (more than 300ppb) than with the coagulation/flocculation + RSF used at Dow. BACF adsorbs most of the TOC that had an affinity with the ion exchange resins while Dow process can remove TOC species that do not have an affinity with the ion exchange resins used.

Within the addition of the Ultrafiltration membrane, most of the TOC species that did not have an affinity within the BACF pre-treatment were removed always getting a final value after the WBA under 200ppb.

The removal of the SCAV resins on the 29th of June, did not affect the TOC Removal, meaning that the specific organic compounds that had affinity within the SCAV resins were mostly removed within the BACF and UF pre-treatment.

4.4. Alternative 4: BACF+(UF)+RO+(MB)

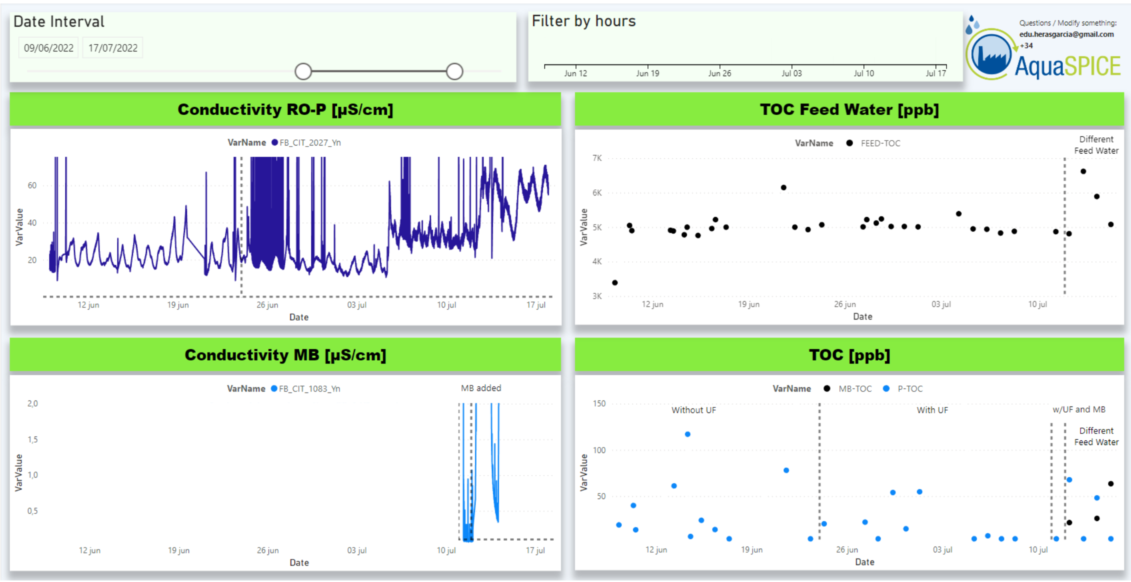


Figure 4.12. Daily data obtained through the mix bed train from 09/06 to 17/07

As in the previous alternative, on the 24th of June Ultrafiltration was added after the BACF till the end of the trials. In the case of reverse osmosis, the application of an ultrafiltration membrane does not affect significantly in the reduction of conductivity or the removal of total organic matter.

5. SCALING-UP OF THE SELECTED TECHNOLOGIES TRAIN

5.1. Process Description

Within the use of ion exchange resins, the production of Demin water is a discontinuous process. Due to the exhaustion of the available ions in the resins, the regeneration step is needed to be able to exchange the different ions present in the water.

The Demin Water demand in the industrial site is taken from the Demin Water Tank continuously in different amounts depending on the current demand of the Industrial processes. To transform this cyclical/discontinuous production into continuous production, the water treatment in the Demin Plant is divided in 4 different parallel streets with different volumes and flows**, the presented values are not the ones used at the existing demin plant but are used as a reference for calculations and design**:

(1) Small streets (A, B, C): 3 parallel streets with a flow of 30-60 m^3/h each

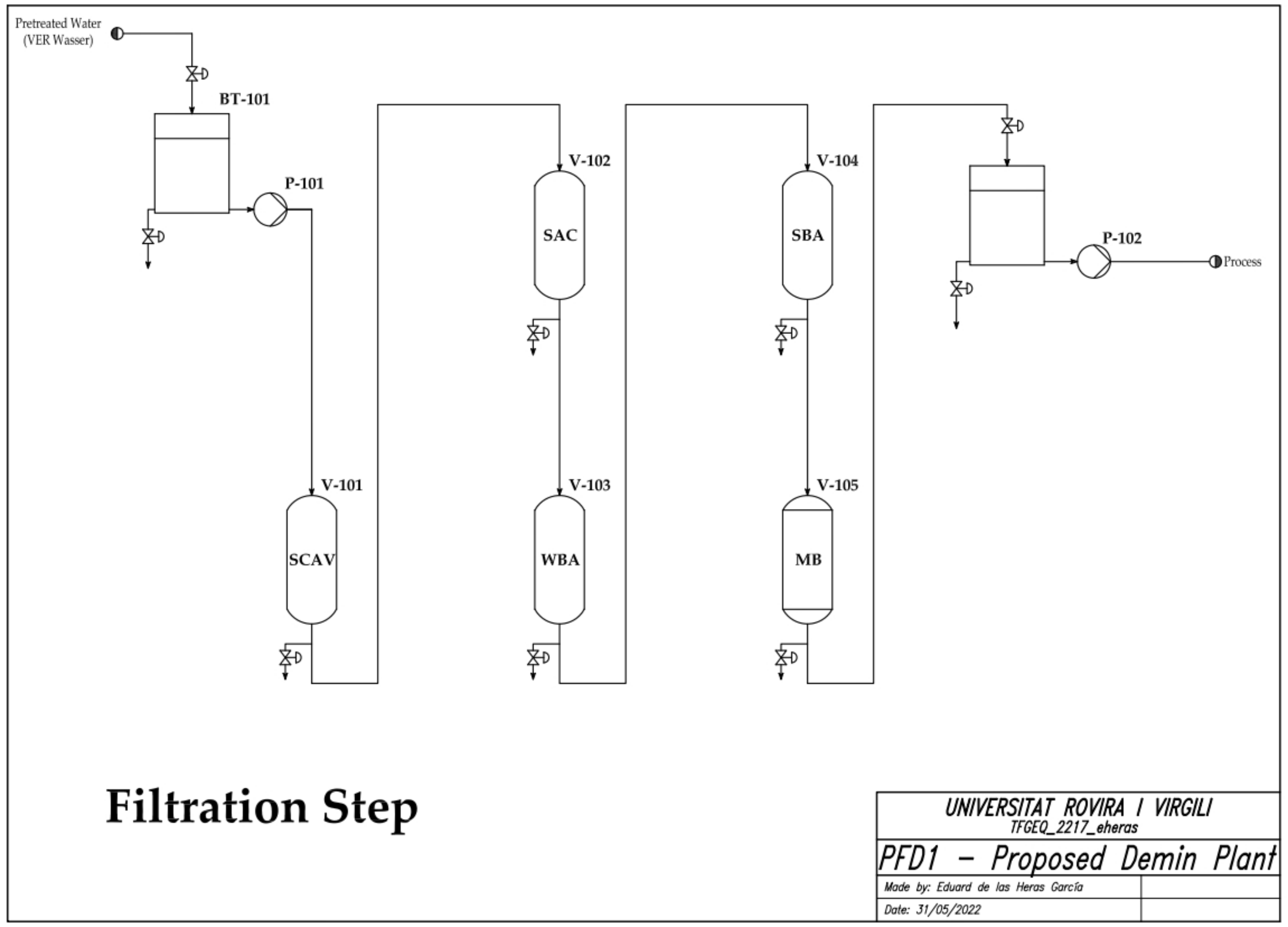
(2) Big street (D): a street with a flow of 120-150 m^3/h

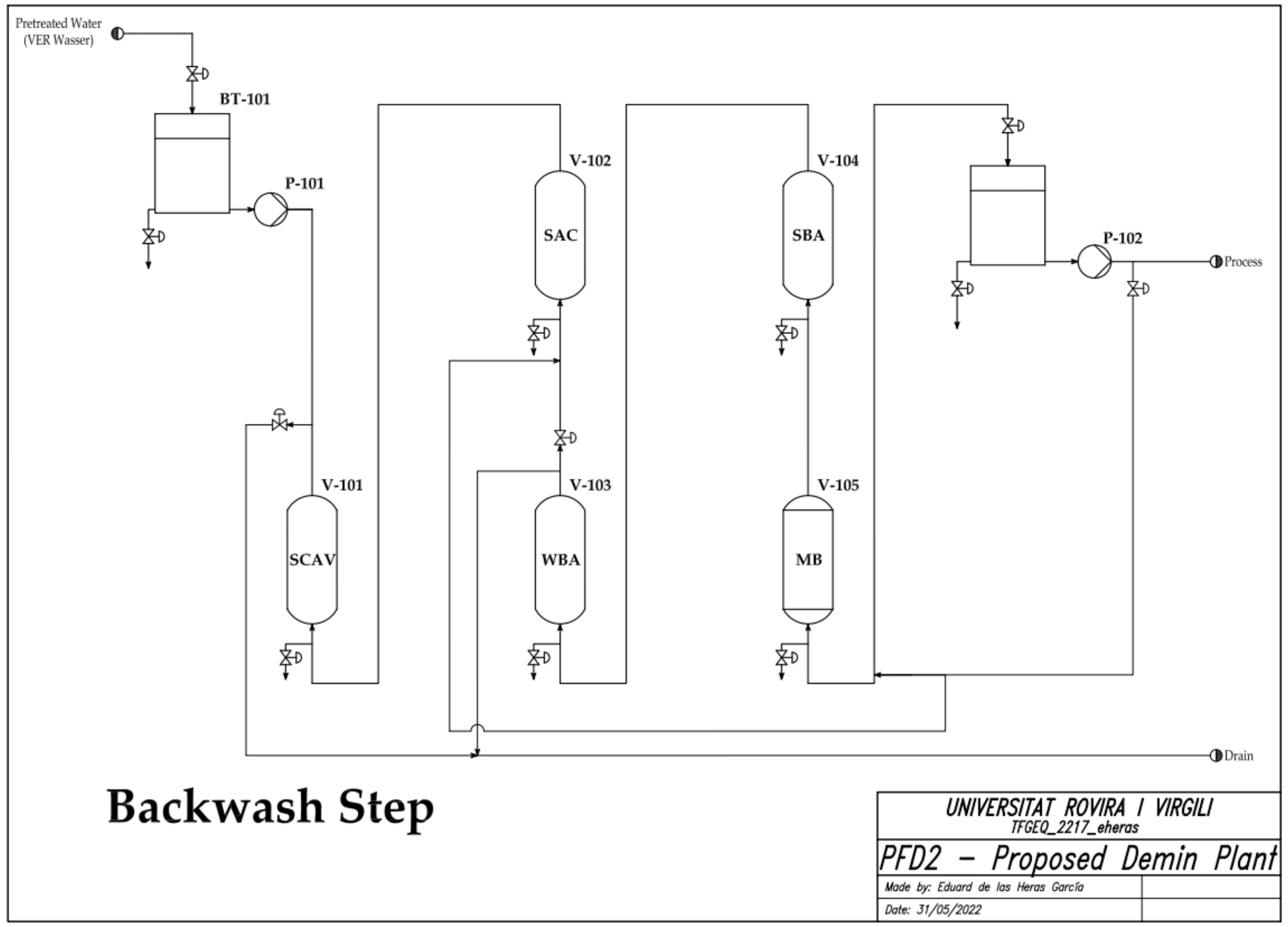
These different streets are designed and controlled in the same way. The **duration of the filtration cycle has been defined for this estimation as 60 hours**, this duration in a real-case scenario is limited by the outlet quality, depending on internal operational limits of conductivity or silica at the end of each production street.

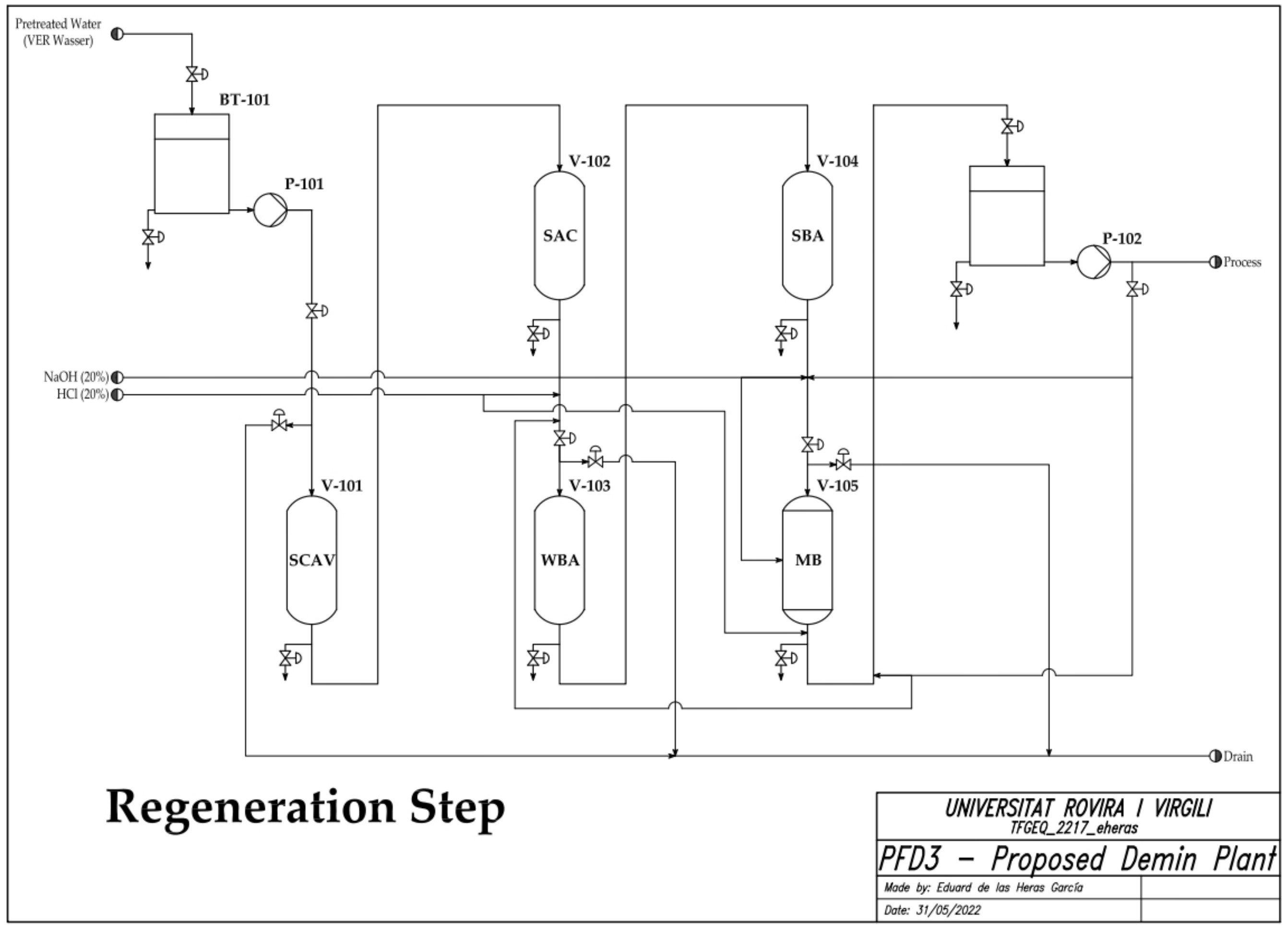
The regeneration of the different streets is done at different times to avoid producing much less water that the current demand of the process water used. Street D is always operated, and the small streets are used to cover the water demand on the site or during the regeneration of the big street.

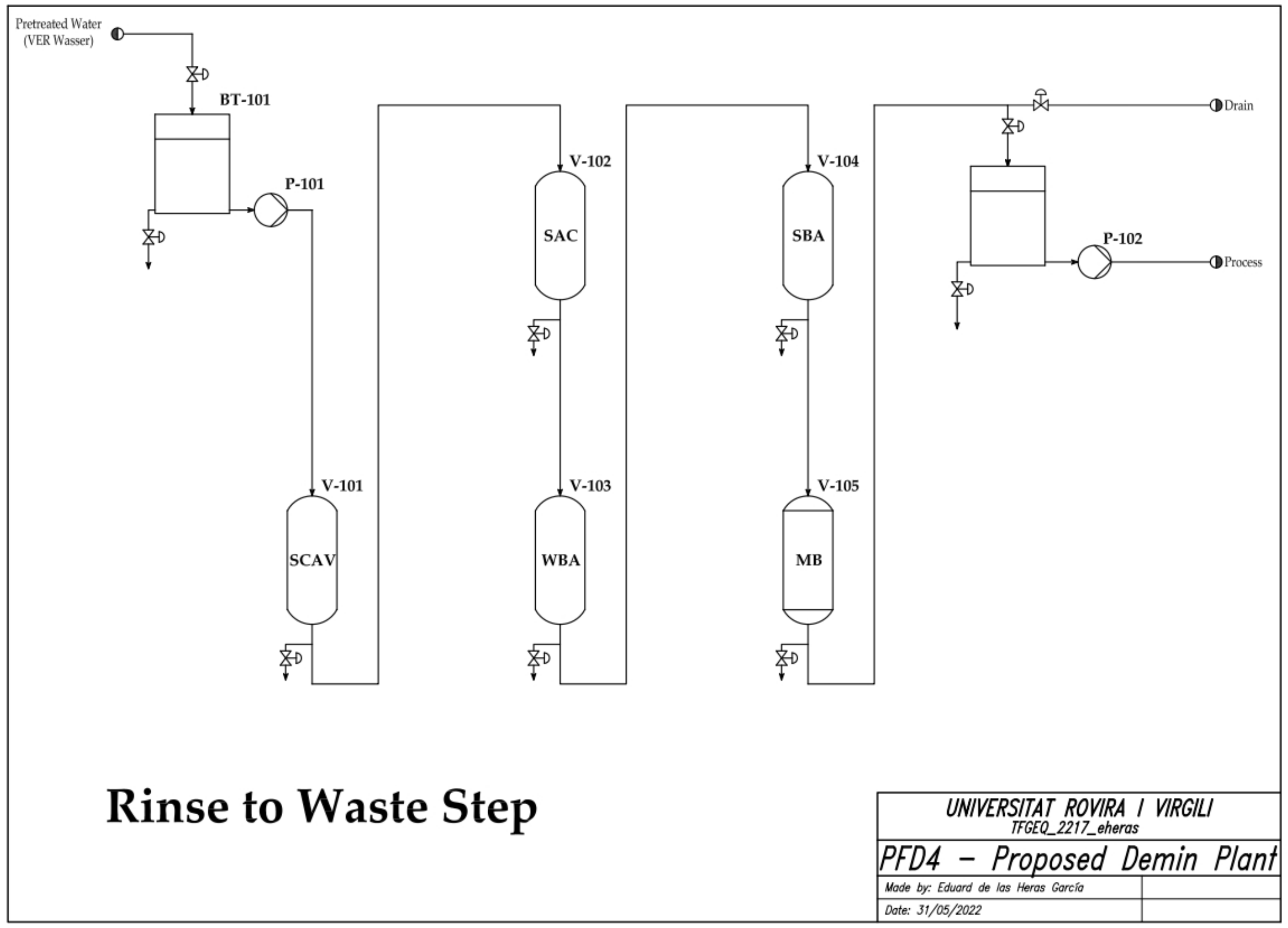
The addition of the AmberLite SCAV4 Cl Resins will represent the addition of an extra column to the current system before the SAC column and a resizing of the current pumping system due to the increased pressure drop. The basic PFD represents one of the streets of the Demin Plant in the different process steps.

The Process Flow Diagram for the modified part and the proper control system is presented below in the following Chapter 5.2 and 5.3 respectively.

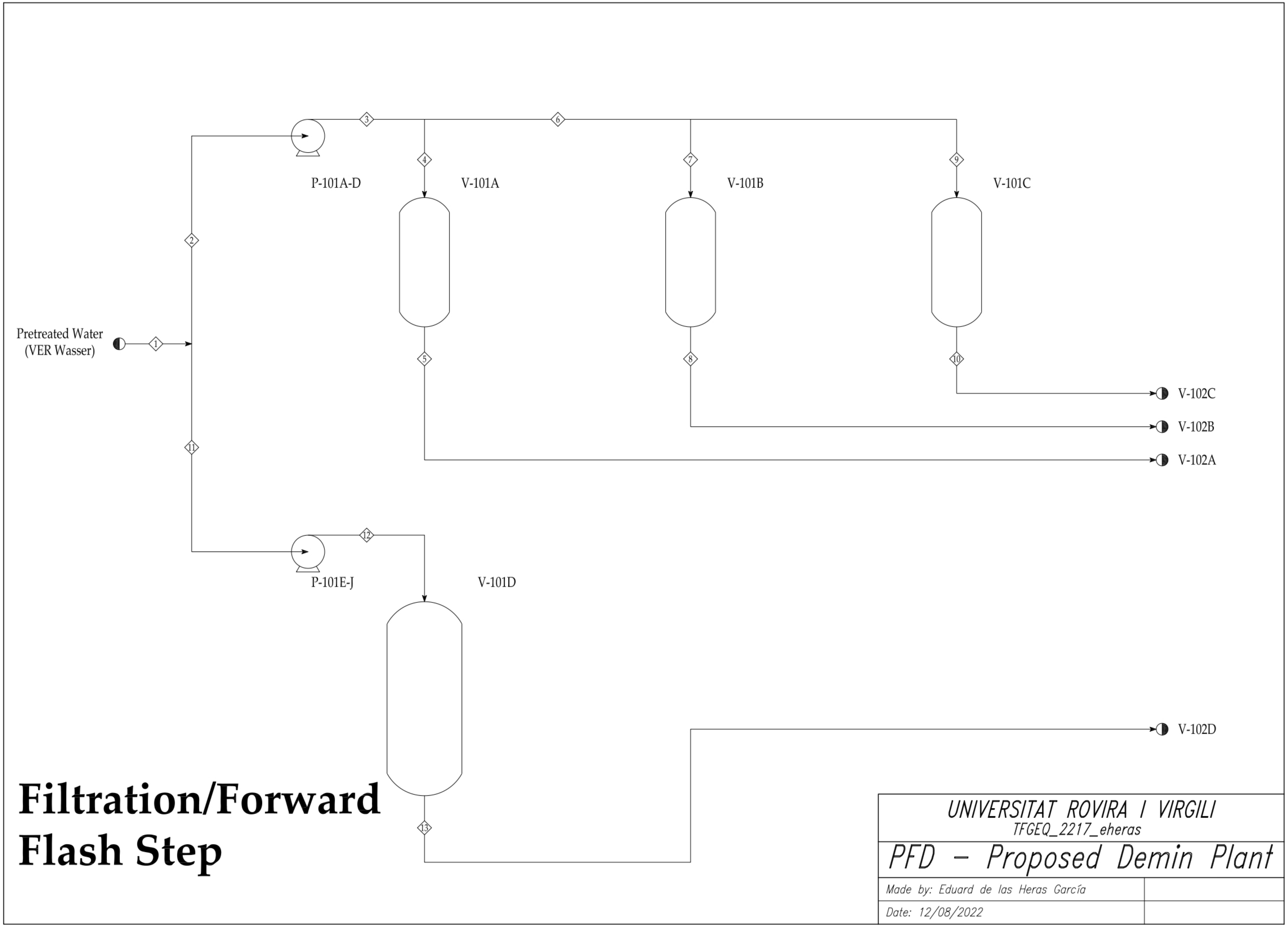

Pretreated Water (VER Wasser)
BT-101
P-101
V-102
SAC
V-104
SBA
P-102
Process
V-101
SCAV
V-103
WBA
V-105
MB
Filtration Step
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
PFD1 – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 31/05/2022

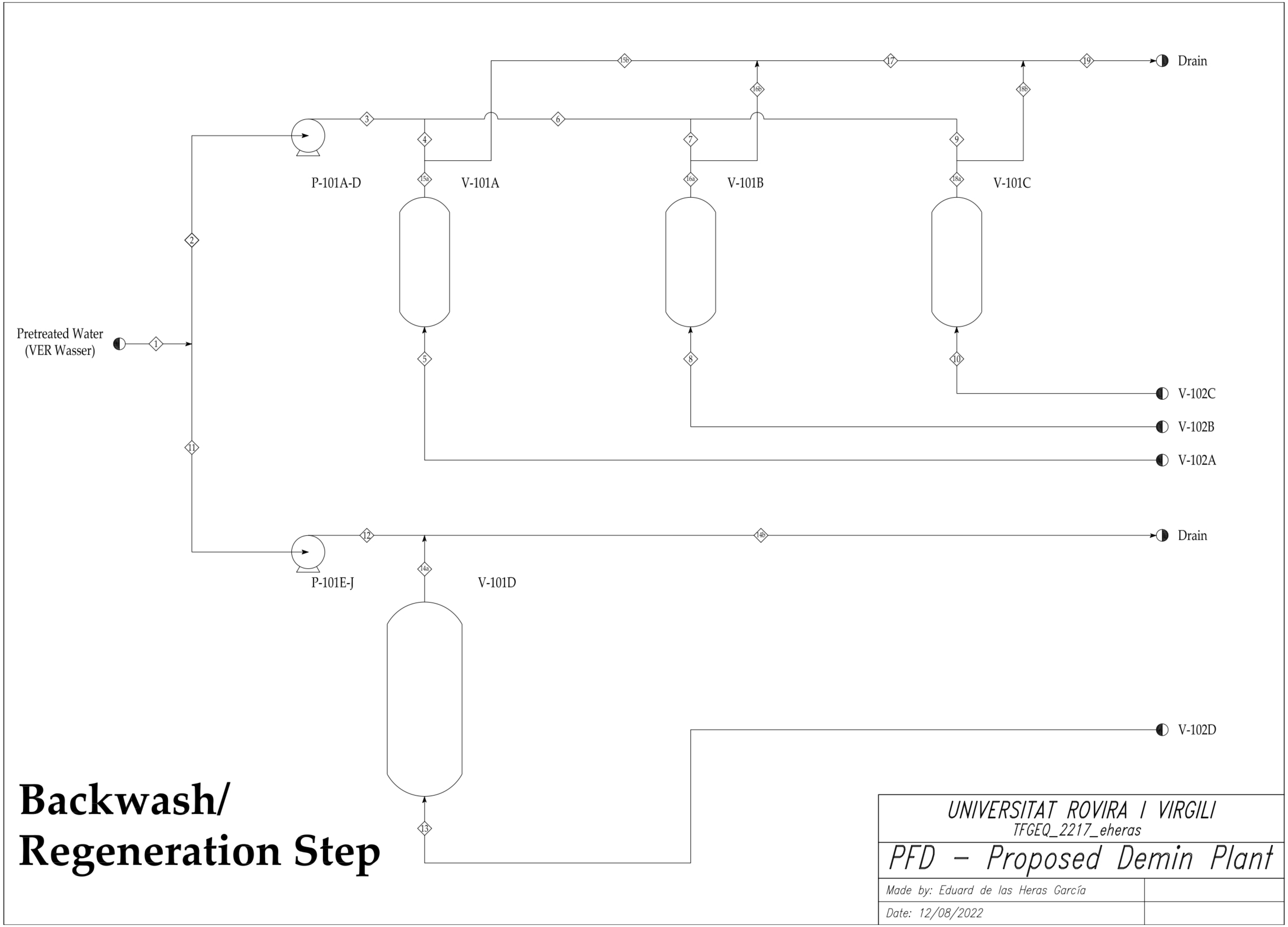

Pretreated Water (VER Wasser)
BT-101
P-101
V-102
SAC
V-104
SBA
P-102
Process
V-101
SCAV
V-103
WBA
V-105
MB
Drain
Backwash Step
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
PFD2 – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 31/05/2022


Pretreated Water (VER Wasser)
BT-101
P-101
V-102
SAC
V-104
SBA
P-102
Process
NaOH (20%)
HCl (20%)
V-101
SCAV
V-103
WBA
V-105
MB
Drain
Regeneration Step
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
PFD3 – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 31/05/2022


Pretreated Water (VER Wasser)
BT-101
Drain
P-101
V-102
SAC
V-104
SBA
P-102
Process
V-101
SCAV
V-103
WBA
V-105
MB
Rinse to Waste Step
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
PFD4 – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 31/05/2022

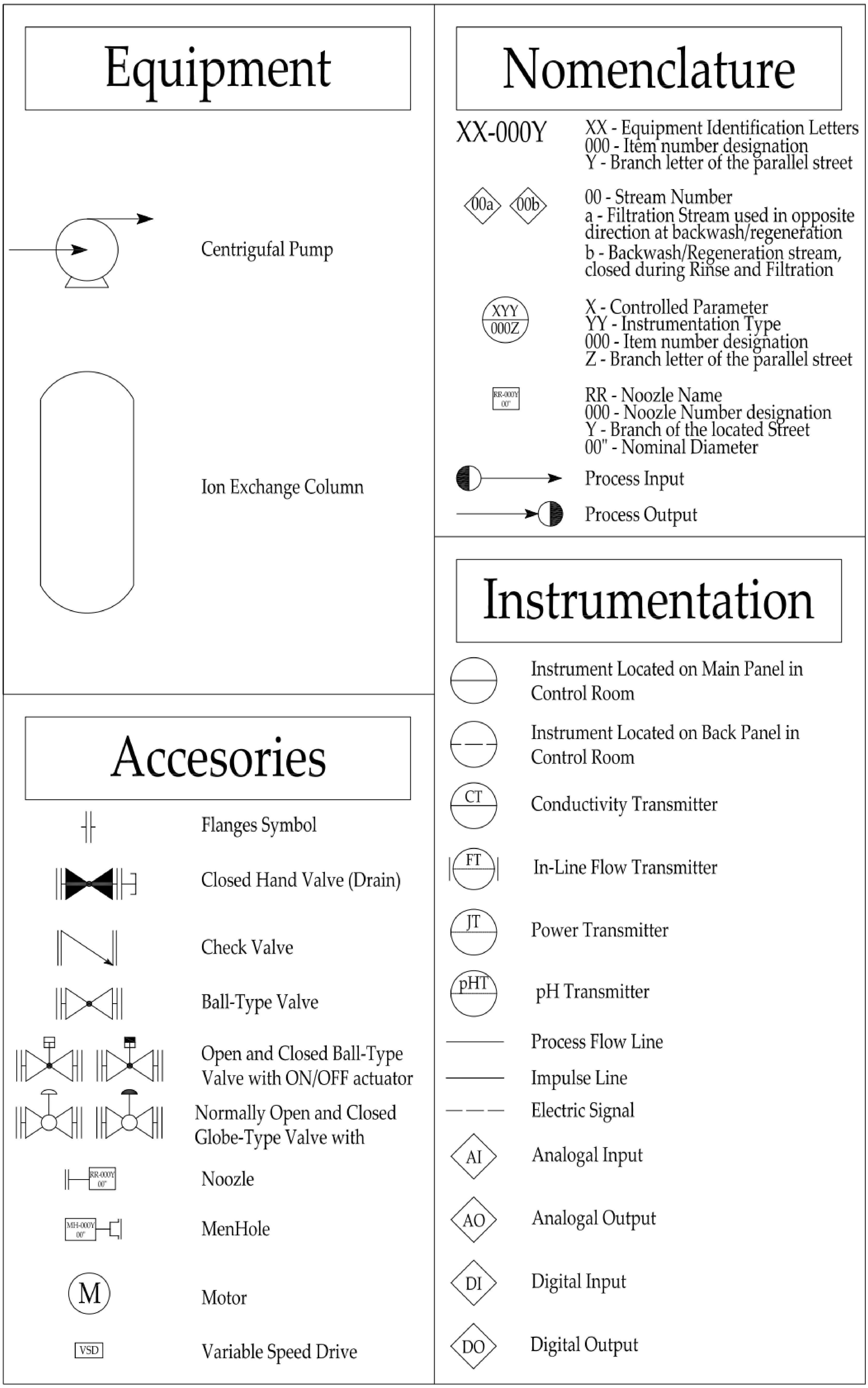
5.2. PFD


P-101A-D
V-101A
V-101B
V-101C
Pretreated Water
(VER Wasser)
V-102C
V-102B
V-102A
P-101E-J
V-101D
V-102D
Filtration/Forward
Flash Step
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
PFD – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 12/08/2022

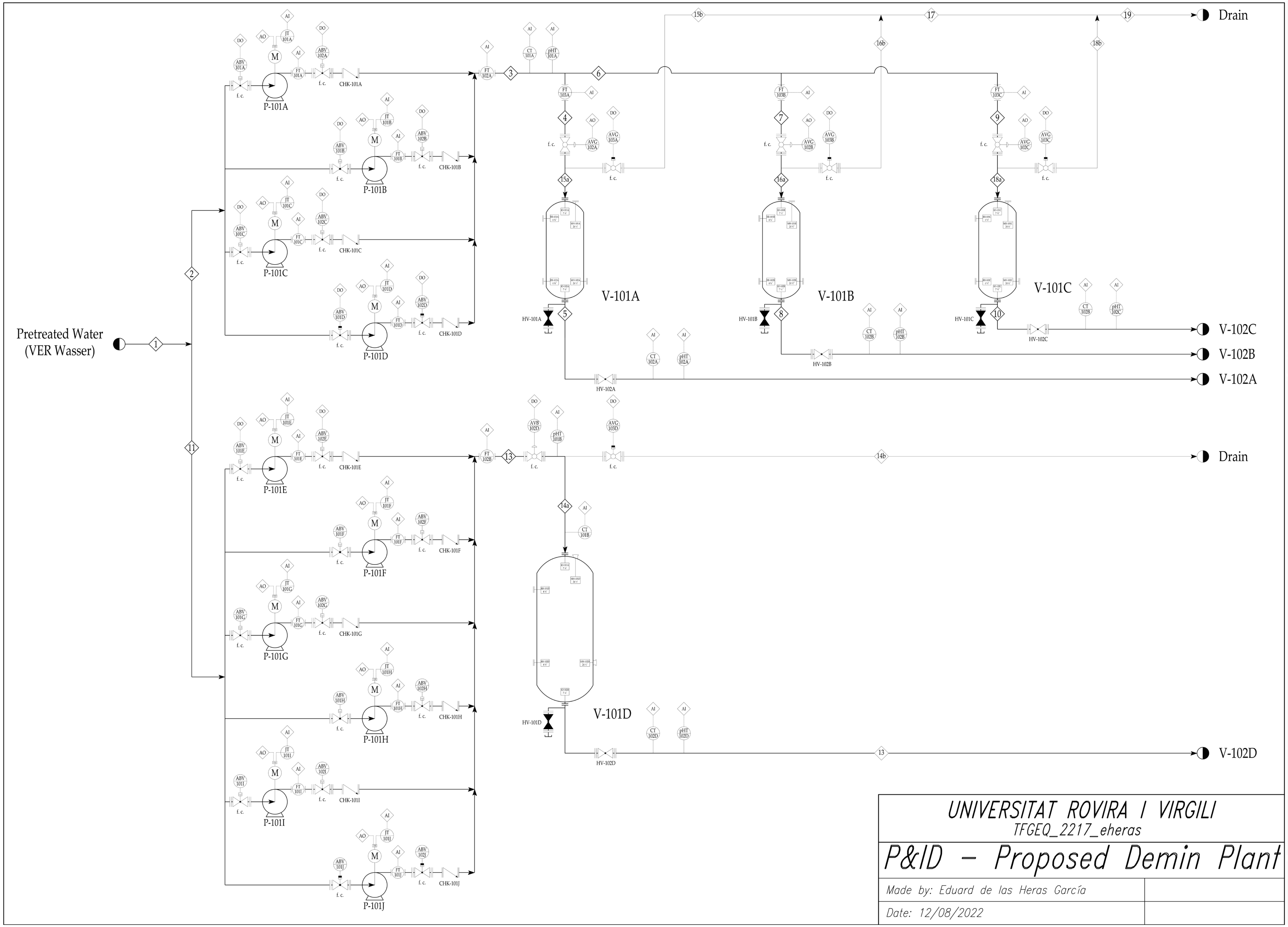

Drain
P-101A-D
V-101A
V-101B
V-101C
Pretreated Water
(VER Wasser)
V-102C
V-102B
V-102A
Drain
P-101E-J
V-101D
V-102D
Backwash/
Regeneration Step
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
PFD – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 12/08/2022

5.3. P&ID

5.3.1 Simbology



5.3.2 Diagram


Pretreated Water
(VER Wasser)
P-101A
P-101B
P-101C
P-101D
P-101E
P-101F
P-101G
P-101H
P-101I
P-101J
V-101A
V-101B
V-101C
V-101D
Drain
V-102C
V-102B
V-102A
Drain
V-102D
UNIVERSITAT ROVIRA I VIRGILI
TFGEQ_2217_eheras
P&ID – Proposed Demin Plant
Made by: Eduard de las Heras García
Date: 12/08/2022

5.4. Control System in the different Operational Steps

5.4.1 Pumping Station

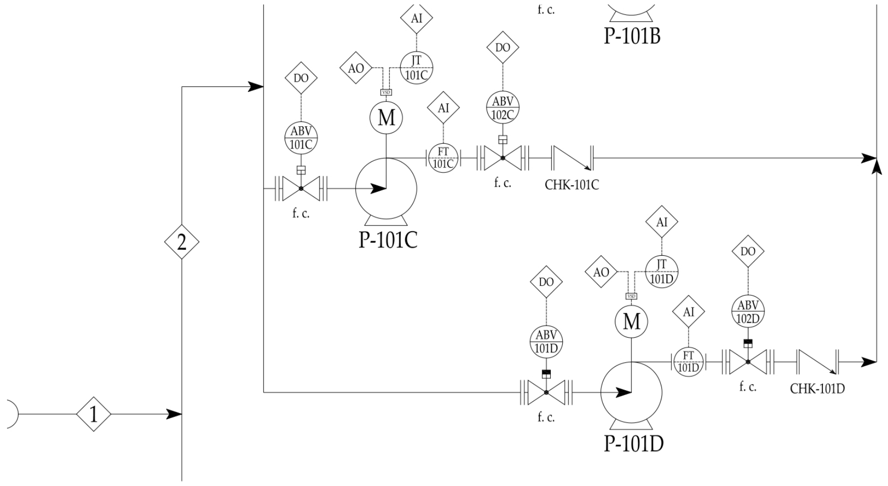


Figure 5.1. P&ID of the pumping station on the small street

There are two pumping systems that are independent for the big and small streets. The small streets consist of four pumps disposed in parallel, the fourth pump (P-101D) is marked with a black cap in the automatic blocking valves (ABV-101D and ABV-102D) symbolling that is normally disconnected, acting as a backup pump. This ABV is presented within a small blackball symbolizing a ball-type valve. These automatic blocking valves will also take place when a replacement of the pump or flow transmitter is needed, their digital output sends a binary signal to totally open or close the valve when required.

A flow transmitter (FT-101) is disposed in-line after the pump and before the ABV-102 to get the most accurate measure of flow. This measure is sent to the system and plotted at the back panel in Control Room (marked with a discontinuous line inside the tag). This measure allows to verify the required flow for the specific pump and give a reaction if the flow does not match with the pump setpoint.

The pump's flow or pressure is adjusted by a Variable Speed Drive (VSD) with an electrical analogical signal to pump the required flow to cover the water demand. This can also shut down/start the pump. The power applied is transmitted within the JT-101 transmitter to evaluate the proper Analogical output to be sent to the pump.

At the end of each branch, an anti-return valve, check valve (CHK-101) is located to avoid having reverse flow due to power differences between the pumps or when a branch is off due to low demand.

In the case of the big street D, the same structure is presented with a six-pump system, one of them acting as a backup pump (P-101J).

5.4.2 Control Strategy for the Organic Scavenger Columns V-101A-D

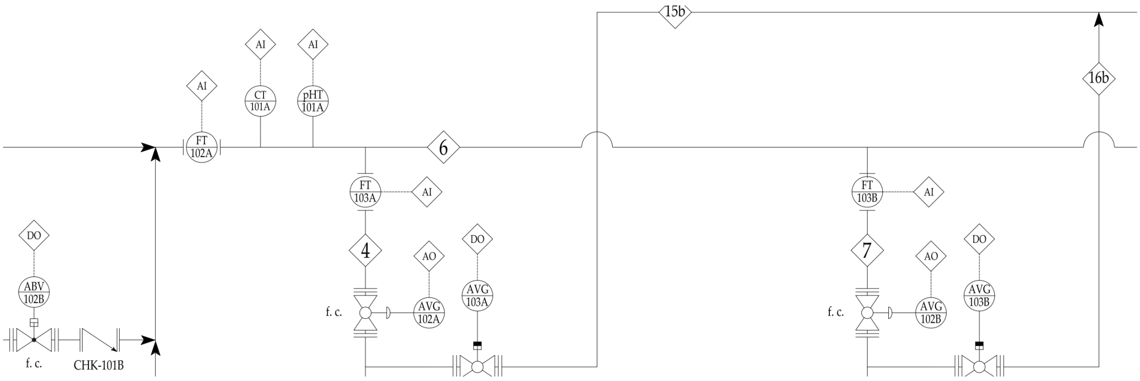


Figure 5.2. P&ID part of the brunching of parallel disposition of the small streets

The small streets have to operate independently. All the small streets require the possibility of being operated while other small streets are being regenerated or not used. This is obtained within a parallel distribution from the pumping station for the small streets. The total flow is measured to make sure that the required demand to treat is reached. After each branch, the flow is measured in the different FT103 again to adjust properly within the different small streets, adjusting the opening degree of the Automatic Globe-Type Valve AVG102. The signal is sent with an analogical signal to the main panel of the control room.

The AVB-103 are presented normally closed (black painted hat) due to their only implication during the backwash and regeneration steps. Within the starting of this cycle, the AVB-103 is totally opened (for the columns required to be regenerated) and the AVB-102 is closed simultaneously. Then the flow comes to the column in regeneration from bottom to top.

The control strategy for the big street column (V-101D) acts in the same way as the small streets.

5.4.3 Determination of the exhaustion of the columns

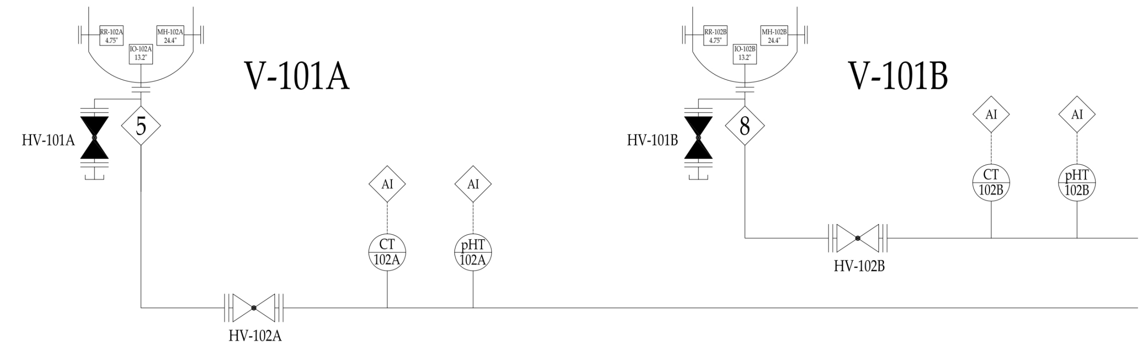


Figure 5.3. P&ID part of the filtration outlet of the columns

As a clear dependence on the conductivity and the pH have been observed in the experiments done for the SCAV Resins. The C-101/C-102 and the pH-101/pH-102 will provide information at the inlet and the outlet of every SCAV column to determine the exhaustion level and identify the proper moment to finish the filtration and start the regeneration cycle. Also a drain/sample point (HV-101) and a hand valve (HV-102) is connected at the outlet of every column to be able to act in case of needed repair or emptying the tank and prepare grab sample tanking.

5.5. Design of the pumps P-001 (A, B, C & D)

For the determination of the required pumps, an estimation of the maximal expected pressure drop has to be done.

In this calculation, the effect from two different sources has been considered:

- Resistance applied by flowing water through the resins, this has been done following the different bibliographic charts of the resin fabricant[37]. The worse possible scenario has been applied to the calculation of this pressure drop. As the resins apply more resistance at lower temperatures[37], 5ºC temperature has been used in the calculation.
- Estimation of the major and minor losses for a constant flow velocity through the piping system. This has been done within the calculation process and different hypotheses found in "Fluid Mechanics –Fundamentals and Applications" – YUNUS ÇENGEL"[39]. The different approximations can be found in Appendix A.4

The pressure drop generated within the different Filter Nozzles supported in the Nozzle Plate and its available surface reduction due to the small sieves (see Detail 2 in Chapter 5.6.2) has been included in the safety factor applied at this calculation, being a 100% safety factor due to calculation differences and the effect explained before. The calculation process can be followed in Appendix A.4.

The effect of oversizing in this specific case does not significantly impact the construction due to the insignificant increase in the cost nor in the operational pressure definition. A bigger volume of resins will increase the available ions to exchange, and the pressure drop. This volume can be adjusted by removing resins to get the resin exhausted at the same time as the other columns.

The pump required for the system is determined through the Affinity Pump Selection Tool from Flowserve[36]. This software allows the client to find several possibilities for the pumping needs. The input parameters required by the software are:

- Pump head: required pressure in (m) to be achieved by the pump
- Volumetric Flow (m^3/h): maximum expected volumetric flow to be pumped.
- NPSHa (m): net positive suction available as a difference between the height of the highest point of the vessel and the pump input and a difference between the tank pressure and the vapor pressure of the fluid at operational conditions.

Once these parameters are entered into the system the software performs a search and proposes different pumps classified by power and height. All these options comply with the NPSHa restriction and follow the indicated design standards. The detailed selection process for the pumps can be followed in Appendix A.5. The main parameters are summarized below:

Table 5.1. Summary of the Hydraulic Data Sheet for the process pumps selected within Affinity Pump Selection Tool

Parameter	**P-101A-C (30-60 m³/h)**	**P-101D (24-30 m³/h)**
Commercial Pump Name	WDX Ring Section 3WDXE D	WD Ring Section WDE32
$\dot{V}_{max}$ [m³/h]	66	45
h_{max} [m]	148	150
BEP [m³/h]	42.5	36.0
NPSHr [m]	1.4	0.6
Driver Power [kW]	17-24	13.3-18.6

5.6. Design of the Organic Scavenger Columns (R-001A, B, C & D)

The design of the ion exchange column filled with AmberLite SCAV4 Cl Resins[37] has been done for two different capacities due to the different sizes of the streets. The followed design method has been the ASME Boiler and Pressure Vessel Code, Section VIII, Division I[40]. This method is based on the maximum stress theory. Defining the elastic failure of the vessel when the maximum tensile stress becomes equal to the yield strength of the material.

The addition of the AmberLite SCAV4 Cl Resins[37] in the current train will reduce the load charged into the WBA, SBA, and MB. Due to this effect, the duration of the filtration will be extended being the SCAV resins the limiting resin. Due to this effect and the **possible scaling up difference**, a **safety factor of 20%** has been added.

The detailed calculation process of the design is described in Appendix A.5.2, the main results are summarized in the following Specification Sheets for the big and small streets:

5.6.1 Specification Sheet for Streets A, B and C

PROJECT	AquaSPICE	SPECIFICATION	Nº	
	SCAV Column		Sheet Nº	1 de 2
COMPANY	Dow Chemical	Pressure Vessel	Date	10/08/2022
DEPARTMENT	Demin Plant		Prepared	
SITE	Dow Böhlen	TFGEQ_2217_edelasheras	Reviewed	
			Aproved	
ITEM	V-101A-C		Units	3
SERVICE				

OPERATION	Description	Ion Exchange Column with AmberLite SCAV4 Cl Resins for the small streets A, B and C.	
	Product		
	Temperature	35.00 ºC	
	Pressure	4.90 barg	
	Density	995.65 kg/m3	

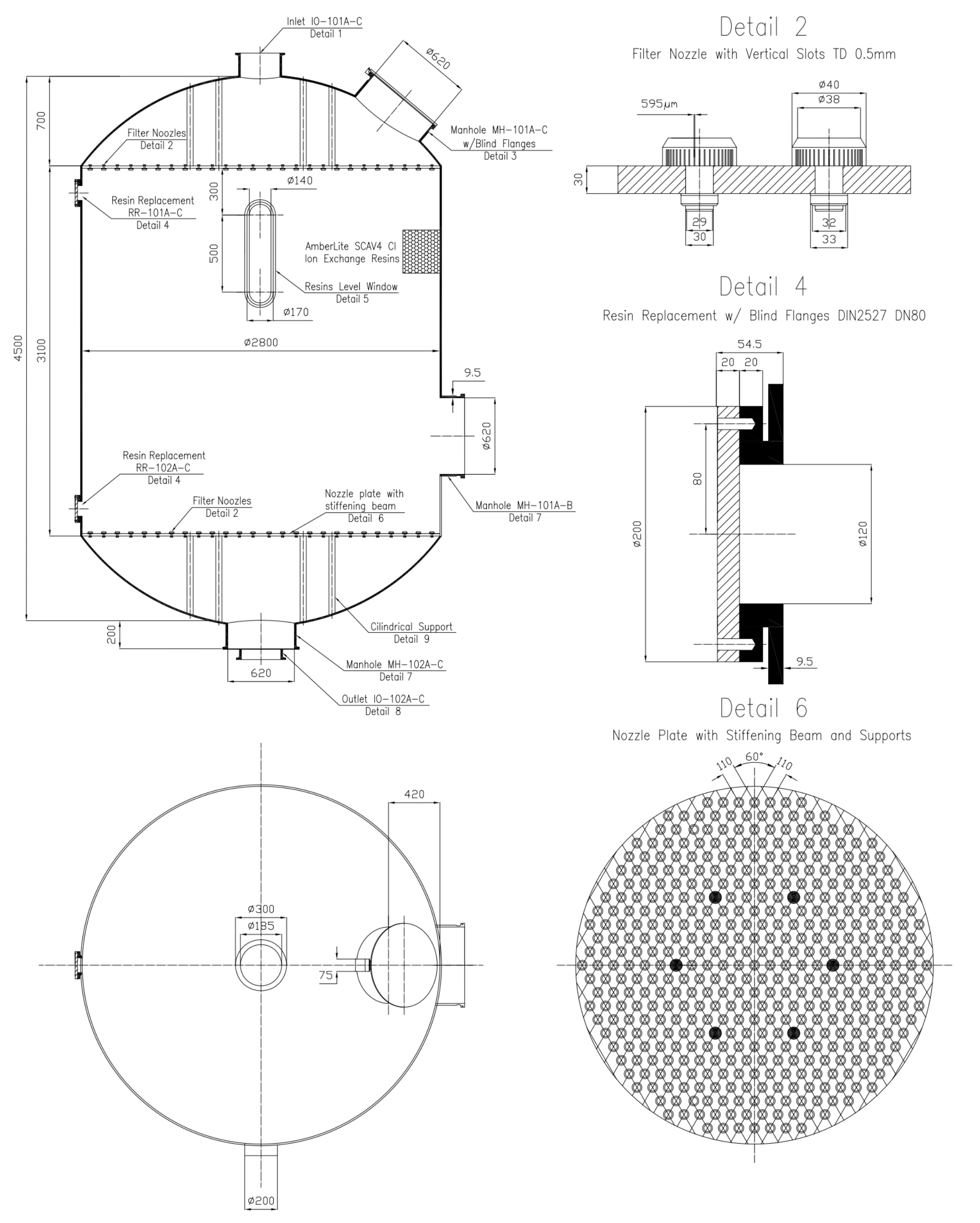
STRUCTURE	Size	Diamenter	2.80 m	DESIGN AND TEST	CODE	ASME Code for Pressure Vessels, Section VIII, Division I	
		Height	3.10 m				
		Thickness	9.50 mm		DESSIGN CONDITIONS	Temp.	55 ºC
	Head	Upper	2:1 Ellipsoidal			Pressure	9.4 kg/cm2 g
		Lower	2:1 Ellipsoidal			Density	985.7 kg/m3
	Volume / Weight	Util Volume	15.31 m3		TEST PRESSURE	Hydraulic	12.2 barg
		Total Volume	24.84 m3			Pneumatic	-
		Weight	21,043 kg		CORROSSION THICKNESS		3.175 mm
	Instalation				WELDING EFFICENCY		0.85
	Isolation				STRESS RELEASE		-
	Painting				RADIOGRAPHIC EXAM.		PARTIAL

	ITEM	DESCRIPTION	REMARKS
MATERIALS	HEAD/BOTTOM		
	BODY FLANGES	P265GH	
	PRESSED FLANGES	P265GH	
	TUBULAR FLANGES	P265GH	
	NOZZLE	P265GH	
	INTERNAL SUPPORTS	P265GH	
	INTERNAL SCREWS/NUTS	P265GH	
	EXTERNAL SCREWS/NUTS	P265GH	
	INTERNAL JOINTS	P265GH	
	EXTERNAL JOINTS	P265GH	
	EXTERNAL SUPPORTS	P265GH	
	BOTTOM NOZZLES	P265GH	
	FILTER NOZZLES WITH VERTICAL SLOT	PPFV	Slot Widht of 0.5mm < 0.65mm (Resin Diam)

	TAG	AMOUNT	SERVICE	N.D.	RATING
NOZZLES	Detail 1 - IO-101A-C	1	Inlet of water during Filtration & Rinse	185mm	150 #
	Detail 3 - MH-101A-C	1	Man Hole with Window	620mm	150 #
	Detail 4 RR-101A-C	1	Upper Resins Discharge/Replacement Hole	120mm	150 #
	Detail 4 RR-102A-C	1	Lower Resins Discharge/Replacement Hole	120mm	150 #
	Detail 7 - MH-102A-C	1	Man Hole	620mm	150 #
	Detail 8 IO-102A-C	1	Outlet of water during Filtration & Rinse with an adaptado plate to be used as Man Hole to reach the bottom section	185mm	150 #

REMARKS	Tags are expressed as XX-000Y-Z, defining XX the type of equipment or element, 000 the identification number, Y-Z the street located, as the process is divided in parallel streets, each of them is defined with a letter. A, B, C for the Small street and D for the Big Street.
	Bottom Nozzles are supported to the ellipsoidal heads by cilindrical supports in hexagonal distribution due to the estimated. deflexion by the pressure drop and resins
	Column with an 80% of the cilinder filled with AmberLite SCAV4 Cl Ion Exchange Resins.
	Detail 2 has to be selected in order to fit within the resins dimensions and minimize the pressure drop.
	Detail 4 is prepared with Blind Flanges to be used in case of removal/replacement of Resins.
	Detail 5 is dispossed in the resins high to identify the exhaustion of the resins by the resins tank level.

PROJECT	AquaSPICE	**SPECIFICATION**	**Nº**	
	SCAV Column		**Sheet Nº**	2 de 2
COMPANY	Dow Chemical	**Pressure Vessel**	**Date**	10/08/2022
DEPARTMENT	Demin Plant		**Prepared**	
SITE	Dow Böhlen	**TFGEQ_2217_edelasheras**	**Reviewed**	
			Aproved	
ITEM	**V-101A-C**		**Units**	3



5.6.2 Specification Sheet for Street D

PROJECT	AquaSPICE	**SPECIFICATION**	**Nº**	
	SCAV Column		**Sheet Nº**	1 de 2
COMPANY	Dow Chemical	**Pressure Vessel**	**Date**	10/08/2022
DEPARTMENT	Demin Plant		**Prepared**	
SITE	Dow Böhlen	**TFGEQ_2217_edelasheras**	**Reviewed**	
			Aproved	
ITEM	**V-101D**		**Units**	1
SERVICE				

OPERATION	**Description**	Ion Exchange Column with AmberLite SCAV4 Cl Resins for the Street D
	Product	
	Temperature	35.00 ºC
	Pressure	10.30 barg
	Density	995.65 kg/m3

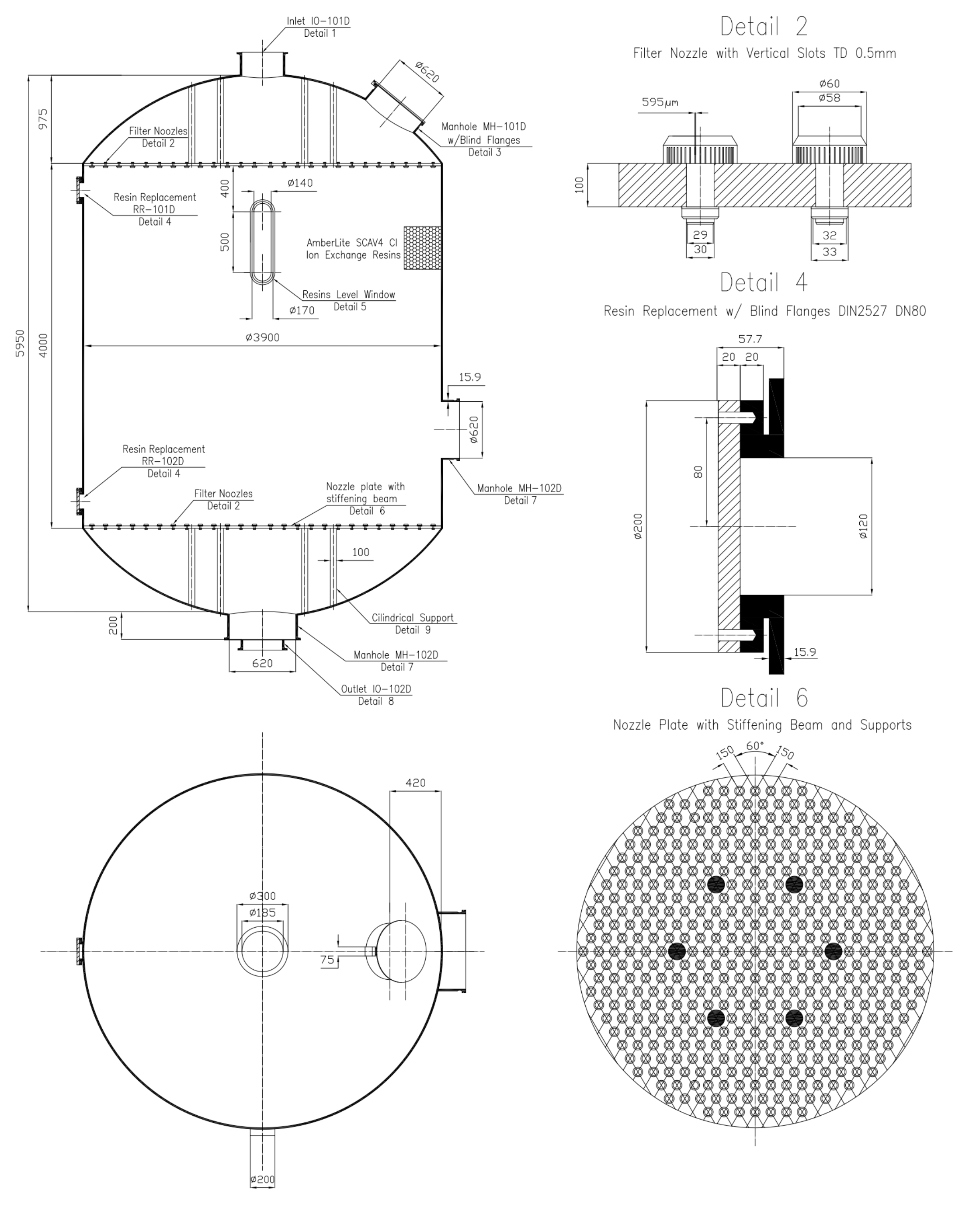
STRUCTURE	**Size**	**Diamenter**	3.90 m	**DESIGN AND TEST**	**CODE**		ASME Code for Pressure Vessels, Section VIII, Division I
		Height	4.00 m				
		Thickness	15.90 mm		**DESSIGN CONDITIONS**	**Temp.**	55 ºC
	Head	**Upper**	2:1 Ellipsoidal			**Pressure**	13.6 kg/cm2 g
		Lower	2:1 Ellipsoidal			**Density**	985.7 kg/m3
	Volume / Weight	**Util Volume**	38.26 m3		**TEST PRESSURE**	**Hydraulic**	17.7 barg
		Total Volume	63.31 m3			**Pneumatic**	-
		Weight	54,109 kg		**CORROSSION THICKNESS**		3.175 mm
	Instalation				**WELDING EFFICENCY**		0.85
	Isolation				**STRESS RELEASE**		-
	Painting				**RADIOGRAPHIC EXAM.**		PARTIAL

	ITEM	DESCRIPTION	REMARKS
MATERIALS	**HEAD/BOTTOM**		
	BODY FLANGES	P265GH	
	PRESSED FLANGES	P265GH	
	TUBULAR FLANGES	P265GH	
	NOZZLE	P265GH	
	INTERNAL SUPPORTS	P265GH	
	INTERNAL SCREWS/NUTS	P265GH	
	EXTERNAL SCREWS/NUTS	P265GH	
	INTERNAL JOINTS	P265GH	
	EXTERNAL JOINTS	P265GH	
	EXTERNAL SUPPORTS	P265GH	
	BOTTOM NOZZLES	P265GH	
	FILTER NOZZLES WITH VERTICAL SLOT	PPFV	Slot Widht of 0.5mm < 0.65mm (Resin Diam)

	TAG	AMOUNT	SERVICE	N.D.	RATING
NOZZLES	Detail 1 - IO-101D	1	Inlet of water during Filtration & Rinse	185mm	150#
	Detail 3 - MH-101D	1	Man Hole with Window	620mm	150#
	Detail 4 RR-101D	1	Upper Resins Discharge/Replacement Hole	120mm	150#
	Detail 4 RR-102D	1	Lower Resins Discharge/Replacement Hole	120mm	150#
	Detail 7 - MH-102D	1	Man Hole	620mm	150#
	Detail 8 IO-102D	1	Outlet of water during Filtration & Rinse with an adaptad plate to be used as Man Hole to reach the bottom section	620mm	150#

REMARKS	Tags are expressed as XX-000Y-Z, defining XX the type of equipment or element, 000 the identification number, Y-Z the street located, as the process is divided in parallel streets, each of them is defined with a letter. A, B, C for the Small street and D for the Big Street.
	Bottom Nozzles are supported to the ellipsoidal heads by cilindrical supports in hexagonal distribution due to the estimated. deflexion by the pressure drop and resins
	Column with an 80% of the cilinder filled with AmberLite SCAV4 Cl Ion Exchange Resins.
	Detail 2 has to be selected in order to fit within the resins dimensions and minimize the pressure drop.
	Detail 4 is prepared with Blind Flanges to be used in case of removal/replacement of Resins.
	Detail 5 is dispossed in the resins high to identify the exhaustion of the resins by the resins tank level.

PROJECT	AquaSPICE	**SPECIFICATION**	**Nº**	
	SCAV Column		**Sheet Nº**	2 de 2
COMPANY	Dow Chemical	**Pressure Vessel**	**Date**	10/08/2022
DEPARTMENT	Demin Plant		**Prepared**	
SITE	Dow Böhlen	**TFGEQ_2217_edelasheras**	**Reviewed**	
			Aproved	
ITEM	**V-101D**		**Units**	1



5.7. Monitoring of the Specifications

In order to improve the current process control and be able to evaluate continuously the exhaustion of the street and the content of Total Organic Carbon, an online analyzer for the expected operating range at the end of every street should be required. A possible suggestion would be the Sievers M500 Online TOC Analysers Series from Suez[38], a TOC analyser for ultrapurewater applications with an operating range of 0.03 ppb to 2.5ppm and high accuracy of ±5% or 0.1ppb and a precision of 1% or 0.3 ppb, fitting on the system with a continuous measurement frequency of 3 minutes. [38]

Figure 5.4. Sievers M500 Online TOC Analyzers Series from Suez[38]

6. ECONOMIC ESTIMATION

A first economic estimation of the proposed modification on the current Demin Plant has been carried out using Turton Methodology[41]. The Organic Scavenger resins column has been estimated within the values of the vertical pressure vessel. Also, the material factor has been approximated for the behavior of the P265GH to the Carbon Steel. The addition of the different manholes, connections, nozzle plats, and nozzle filters are considered with a safety factor of 20%.

For the estimation of the pump station, Carbon Steel has been defined as the construction material and the required power has been taken from the FlowServe Data Sheet presented in Chapter 5.5.

Defining the cost estimation as a class 4 (Conceptual Study), the expected accuracy associated with the calculation is 40% lower than the given value to 60% higher.

Table 6.1. Summary of the different cost estimations in American Dollars for the different equipments.

Equipment	Description	Item	$C^0_{p_T}(2001)$	$C^0_{p_T}(2022)$	C_{BM_T}
C-101A-C	Vertical Pressure Vessel	3	7.74E+04	1.57E+05	1.28E+06
C-101D	Vertical Pressure Vessel	1	5.41E+04	1.09E+05	1.42E+06
P-101A-D	Centrifugal Pump	4	2.31E+04	4.67E+04	1.56E+05
P-101E-J	Centrifugal Pump	6	2.93E+04	5.92E+04	3.45E+05

The installation cost, piping, and other elements required for the operation of the units are estimated by applying a factor of 30% to the Bare Module Cost[41]. To this estimation, the estimated purchase cost of the required 53.6 m^3 of AmberLite SCAV4 Cl calculated at Appendix A.3 is added with the available online prices[42]. This price will change with the commercial agreements but estimation is presented.

With , 56 m^3 (8 packs of 7 m^3) will be taken into the calculation.

$$C_T = 1.3 \cdot \sum C_{BM_{T_i}} + C_{SCAV4\ Resins} \quad (6.1)$$

Giving a total cost of 3.74 M€ within the current conversion of 25th August 2022. The detailed calculation can be followed in the Appendix

7. EVALUATION OF THE WATER CYCLE AT DOW BÖHLEN

Within AquaSPICE objectives of a near-zero water footprint with a minimum freshwater consumption[5] and Dow global goals to reduce the water in-take in a 20% for 2025[4] different water management improvements can be taken in to account. One is proposed in this thesis, optimizing the quality of the deminwater plant to significantly reduce the risk of corrosion and improve the water cycle through minimizing condensate losses.

Looking at the river discharge at Dow Böhlen, one of the biggest water discharges is due to the Cooling Towers BlowDown (CTBD), being a possibility as water management improvement.

Cooling water is used to control the temperature at critical parts of any plant process. This water is heated up within the heat exchangers in the process and needs to be cooled down before recirculating again into the process.[43]

Cooling towers carry out this heat extraction from the cooling water by evaporation and latent heat transfer between the hot water and the fresh atmospheric air. As evaporation occurs, the available water decreases up to 1-2%[45] and as the impurities and dissolved hydrocarbons are not evaporated, their concentration increases in the cooling water.

This water within the cycles of concentration (CoC) is getting saturated with oxygen from being cooled with air, increasing the possible corrosion and Total Dissolved Solids content. This is usually avoided within a chemical treatment or by adding a protective film o the metal surfaces. [43] Being a water rich in Total Dissolved Solids and organic chemicals[44]

To avoid getting this high concentration, part of this cooling tower is discharged as Cooling Tower BlowDown (CTBD), to cover this discharge and the water evaporation more fresh water (Make-up water, CTMU) is added to the cooling system.

By improving the water quality in the cycle, the content of impurities in the water will be lower, meaning the possibility of increasing the cycles of concentration[45]. Using the same water for a longer time would mean a reduction of the water intake and the discharge to the river.

The reuse of CTBD, requires a pre-treated that allow the removal of organic chemical in order to protect the following physico-chemical treatment for desalination. This could be interesting studies to be tested in further projects. Some possible alternatives to evaluate with this water would be Alternative 4 presented in this thesis (BACF+UF+RO), due to the effectiveness of the granular activated carbon in the adsorption of this organic chemicals and the UF+RO capacity of desalination. Another possibility would the use of constructed wetlands[46] instead of the current pretreatment of BACF used in Alternative 4.

8. CONCLUSIONS

The results presented on this thesis are based on the continuous experiments done with the IMPROVED Research facility in Dow Böhlen using Witznitz Lake water as raw water for the production of demin water quality water. These containers provide a variety of water treatment technologies that allow to prove its efficiency within different feed waters. During the experimental time, several alternative technology trains to improve the existing Demin Water quality have been tested. . These different alternatives differ from the implementation of the smallest modifications, trying to reuse the actual treatment (pretreatment composed by Coagulation/Flocculation followed with a Rapid Sand Filtration), to changing completely the current water treatment of the site. Results shown that with the addition of an organic scavenger resin (AmberLite SCAV4 Cl) between the VER pretreatment and the ion exchange resins of the Demin Plant it is possible to achieved the desired quality to avoid corrosion formation downstream.

The organic scavenger resins used, presented a clear effect in the organic carbon removal, being able to remove contaminants hardly removed with the current technologies, resulting on on an average of 50 ppb additional Total Organic Carbon removal in Demin Water. The organics compounds removed are Hydrophobic Organic Compounds and Biopolymers, this can be explained by the adsorption effect of the hydrophilic constituents by the scavenger resins at low pH[35].

Once the experimental phase is completed and the optimum technology train chosen, a design of the pumping station and organic scavenger columns is done to implement the proposed modification on the current demin plant. The design of the column has been done following the ASME Boiler and Pressure Vessel Code, Section VIII, Division I[40] for the estimated resin volume calculated to work at similar conditions as the actual treatment. The pumping station selection has been done with the Affinity Pump Selection Tool from Flowserve Software, giving a list of possible commercial pumps in the operating specifications selected.

In addition, a first cost estimation for the implementation of the proposed solution has been carried out following TURTON's methology[41] resulting in an estimated capital cost of 3.7 million euros.

In order to improve the process control at the Demin Plant, the addition a Online Analyzer of TOC is suggested at the end of each production street for better management of the product quality sent to the demin tank and better decision-making during the duration of the filtration cycle.

Further research after this thesis results are open to be studied. Due to the observed adsorption effect of the SCAV4 Cl Resins for Hydrophobic Organic Compounds and biopolymers at acidic mediums, the following possibilities would be an object of study:

- Addition of acid dosing before the proposed demin plant Ion Exchange resins to study the adsorption behavior at different pH.
- Changing the order of the SCAV resin after the SAC column in order to use the acidic medium after the strong acid cation resins (SAC).

9. REFERENCES

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APPENDIX

A.1. RESIN TYPES BY FUNCTIONALITY

A.1.1. Weak Acid Cation Resins (WAC)

In this type of resins, the ionizable group is the carboxylic acid (COOH), the resins behave similarly to weak organic acids that are weakly dissociated, in this case, the degree of dissociation is strongly dependent on the pH solution, having a lower capacity over 6 pH. [28]

A.1.2. Strong Acidic Cation Resins (SAC)

These resins receive their name because their chemical behavior is similar to a strong acid. These resins are highly ionized in the acid and salt form of the sulfonic acid groups ($R\text{-}SO_3H$).

The hydrogen and sodium forms of the SAC are highly dissociated and available for the exchange with Na^+ and H^+ protons, being independent of the pH of the solution. These resins can be used in their hydrogen form (to have complete deionization) or in their sodium form (for the removal of calcium and magnesium at water softening).

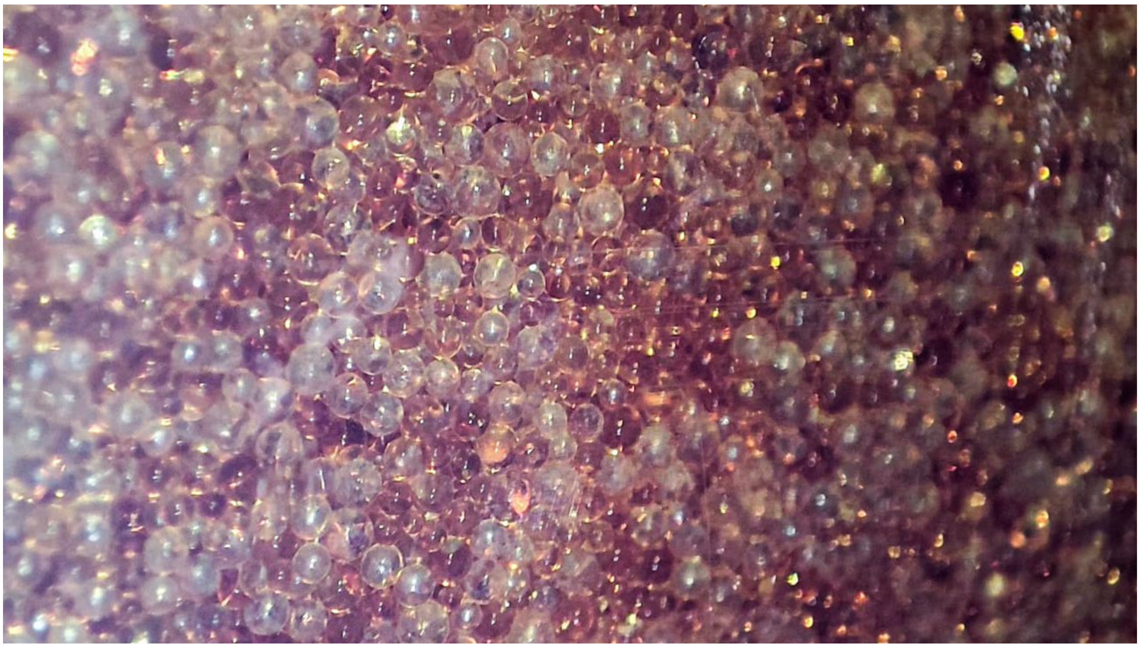


Figure A.1. DOWEX Marathon 1200H

A.1.3. Degasser

After the cation exchange resins, bicarbonate and carbonate ions are transformed into carbonic acid or carbon dioxide. In water demineralization, degasser is used to stimulate the extraction of carbon dioxide and carbonic acid from the air, reducing the ionic load on the basic anion resins. [28]

A.1.4. Weak Base Anion Resins (WBA)

At the WBA, the behavior is similar to the WAC due to the influence of the water pH in its degree of ionization, needing a pH over 7. Instead of using the hydroxide ion form as the SBA, it uses amine functional groups. The resins adsorb free mineral acidity (Cl and SO_4). [28]

Figure A.2. DOWEX Marathon 9000

A.1.5. Strong Base Anion Resins (SBA)

As the SAC, these resins are highly ionized and can be used independently of the pH. These, are used in the hydroxide form (OH) for water deionization, being capable of converting an acid solution into pure water[28]. The regeneration of these resins when they are exhausted is used to be done by sodium hydroxide (NaOH).

Figure A.3. AmberJet 9000OH SBA Resin

A.1.6. Mix Bed Resins (MB)

MB resins are a combination of strong acid cation and basic anion resins added as the last treatment step in the water purification industry to achieve demineralized water quality or after a reverse osmosis treatment. [28]

Figure A.4. DuPont AmberLite MB20 H/OH

A.1.7. Organic Scavenger (SCAV)

The Organic Scavenger is a non-known new type of resins that is not been investigated thoroughly in the literature. This resin is produced by copolymerization of styrene and divinylbenzene with subsequent chloromethylation and amidation. This kind of resin is a specific type of SBA resins that can be operated in Cl- form and OH-form, also they can **adsorpt a high load of undesired NOM species** that can be easily released with the proper regeneration conditions, for the case of the Cl- operational form, it just requires HCl to be regenerated.[47]

Figure A.5. DuPont AmberLite SCAV4 Cl

A.2. CONTINUOUS MONITORING OF THE ORGANIC SCAVENGER BEHAVIOUR IN A FILTRATION CYCLE

Further information on the organic scavenger resins AmberLite SCAV4 Cl behavior can be found in this chapter.

A.2.1. 03/06 Daily Experiment – SCAV Behaviour

To understand the behavior of the organic scavenger resins in the current water treatment at Dow Böhlen during the experimentation, electroconductivity was measured continuously by the online sensors and the total organic carbon was analyzed with continuously at the end of the train (MB outlet) and with the highest frequency possible after the SCAV (every 20-25 during the first 2 hours and every 45min till the end of the cycle). The feed water at the mix bed (VER Water) was also analyzed every 60 min to see the differences at the feed quality during the cycle.

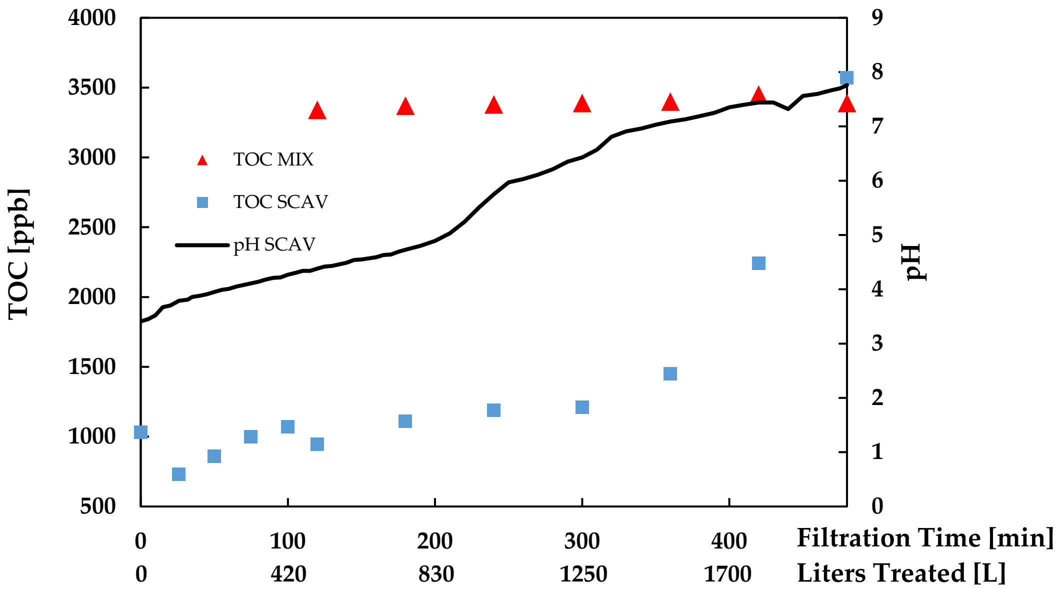


Figure A.6. TOC (main axis) and pH (secondary axis) behaviour in front of the filtration time/liters treated of the IEX technologies

A clear dependence of the organic scavenger removal of organics can be observed within the pH, the acidic the medium is the highest removal is present. This can be explained by the adsorption effect of the hydrophilic constituents by the scavenger resins at low pH[35]. At the point where pH is between 6-7, the TOC after the SCAV resins increases exponentially.

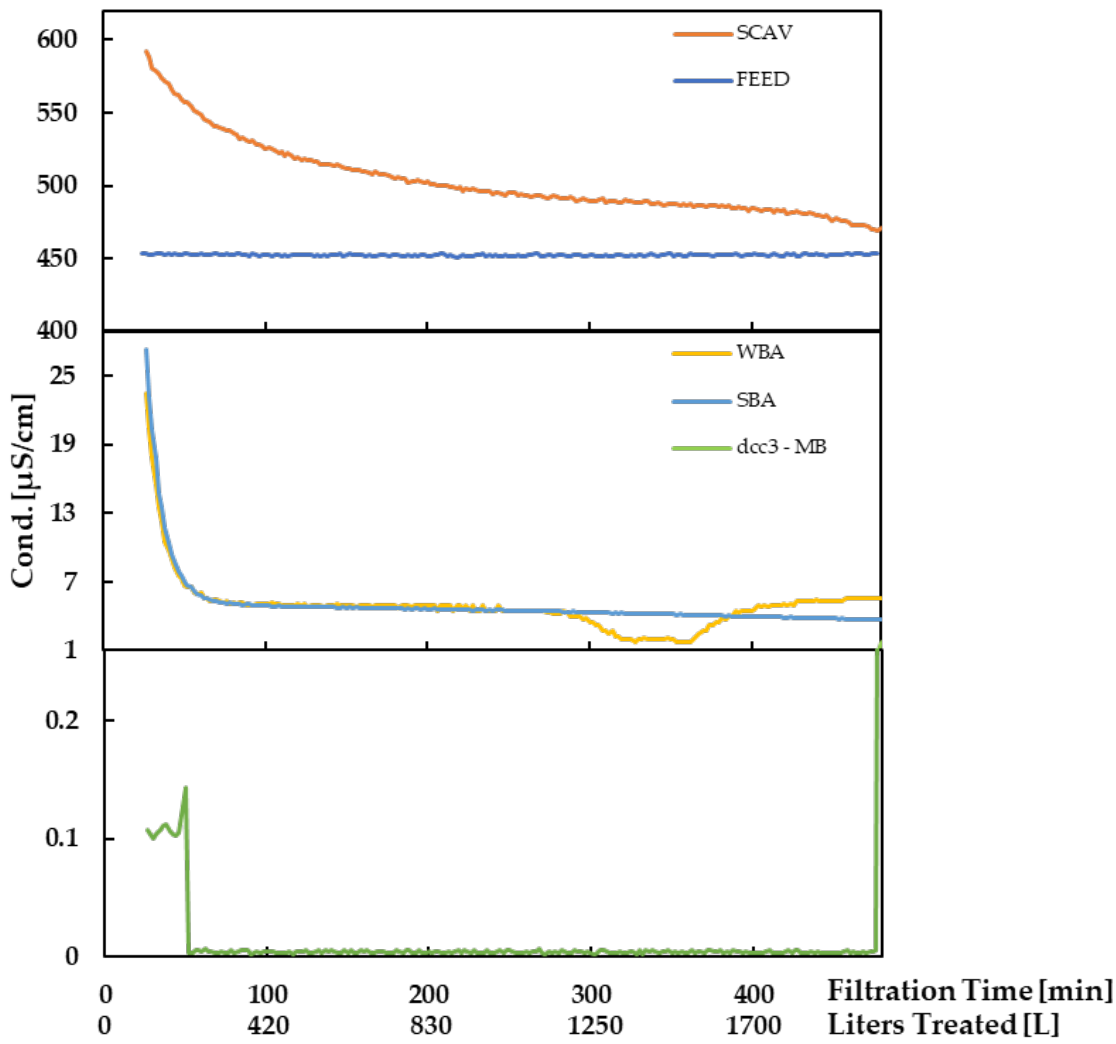


Figure A.7. Conductivity in front of the filtration time/liters treated of the IEX technologies

As can be observed, the electroconductivity of the SCAV is increased due to the exchange of ions available in the VER Water to Cl-. In the WBA conductivity a non-expected trend is observed at the same moment where the SCAV TOC content started to increase in the previous Figure A.7.

A.2.2. 20/07 Daily Experiment – SAC+WBA+SBA+MB Behaviour (current treatment)

In order to compare the current treatment and the addition of a SCAV resins to it. The evolution of the conductivity and pH of the resins during a filtration cycle has been done for the current water treatment.

A pH/conductivity sample taking every 30min has been done. Also, a grab TOC sample every 45 min at the SCAV and WBA has been taken to observe the evolution of the total organic carbon in the filtration cycle, for further comparison with the WBA behavior at the SCAV experiments.

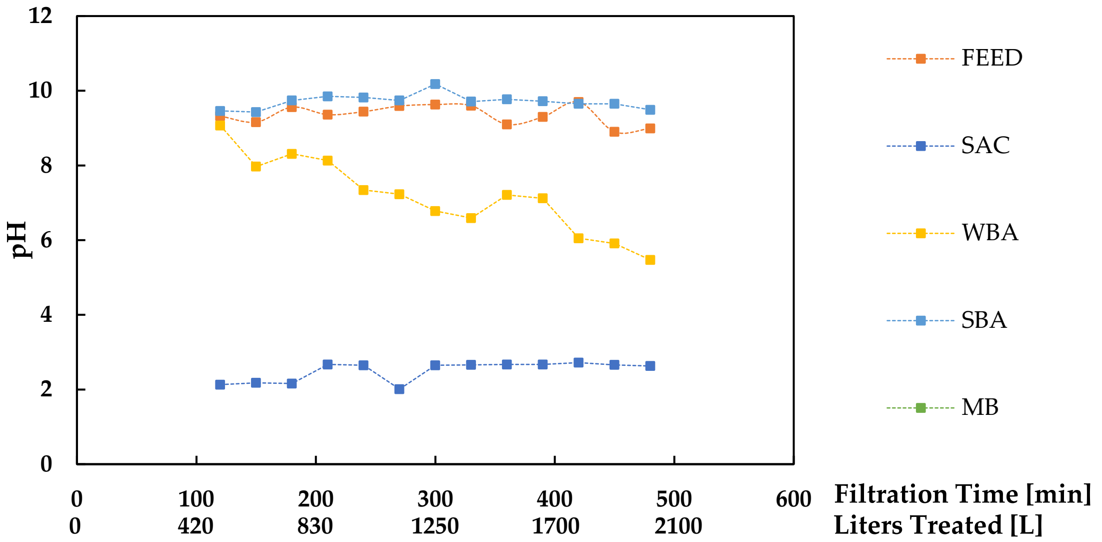


Figure A.8. pH in front of the filtration time/liters treated for the complete train of SAC+WBA +SBA+MB resins

At this experiment, it can be observed that the WBA had a similar pH like the previous SBA resin, within the filtration cycle it has been reduced to a pH of 5.9.

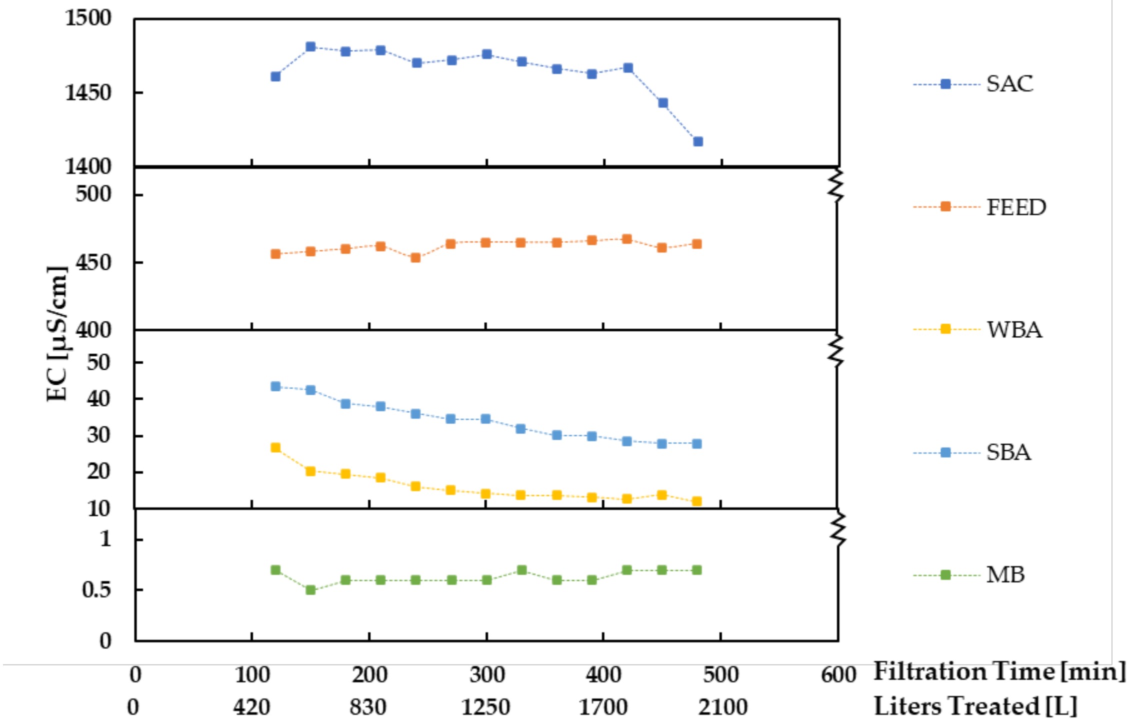


Figure A.9. Conductivity in front of the filtration time/liters treated of the IEX technologies

During these trials, the duration of the rinse with demin water step before the filtration step was increased in order to start the cycle in more similar conditions as a real demin plant. Due to this reason, the rapid decrease of conductivity at the beginning of the analysis is not produced as in Figure A.8.

A.2.3. 22/07 Daily Experiment – SCAV+SAC+WBA+SBA+MB Behaviour (Day 1)

To understand the evolution of the conductivity and pH of the resins during a filtration cycle, a sample taking every 15-30min has been done. Also a continuous analysis of TOC at the MB has been done with a grab TOC sample every 45 min at the SCAV and WBA. To see the different WBA behaviour with a SCAV resin in front, comparing it to the 20/07 Daily experiment.

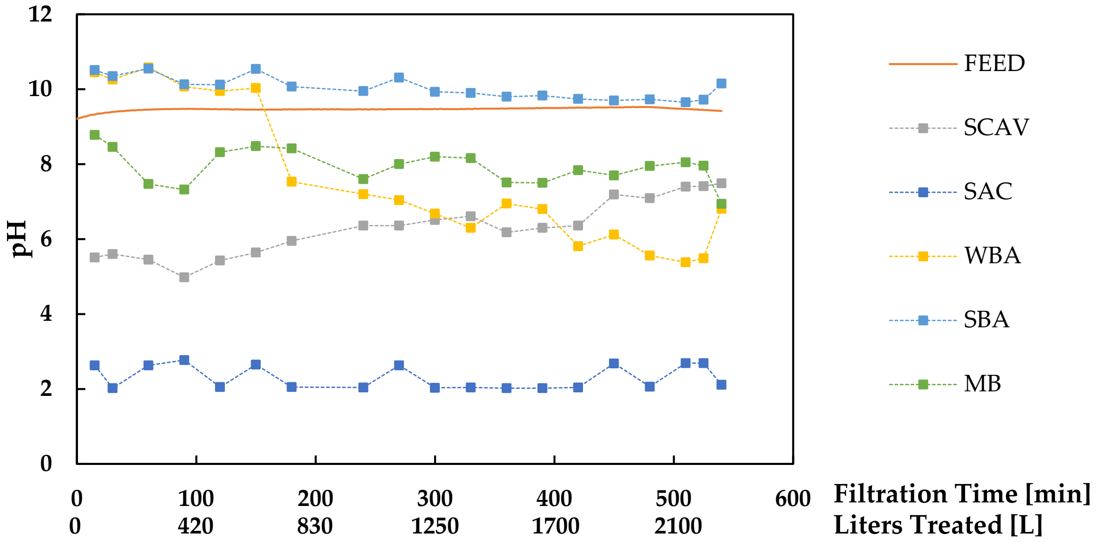


Figure A.10. pH in front of the filtration time/liters treated for the complete train of SCAV+SAC+WBA +SBA+MB resins

As observed in the previous SCAV experiments, a clear increase is observed in the SCAV pH in front of the filtration time. With the WBA data, as weak resin a decrease of pH is observed but instead, the strong resins (SBA and SAC) present a constant pH value for the whole filtration time. The small differences are given by the sensibility of the pH meter used during the experimentation. For the pH on the SCAV, the same behavior as in previous Figure A.6 has been observed. The TOC of the organic scavenger increases exponentially when a pH between 6-7 is achieved.

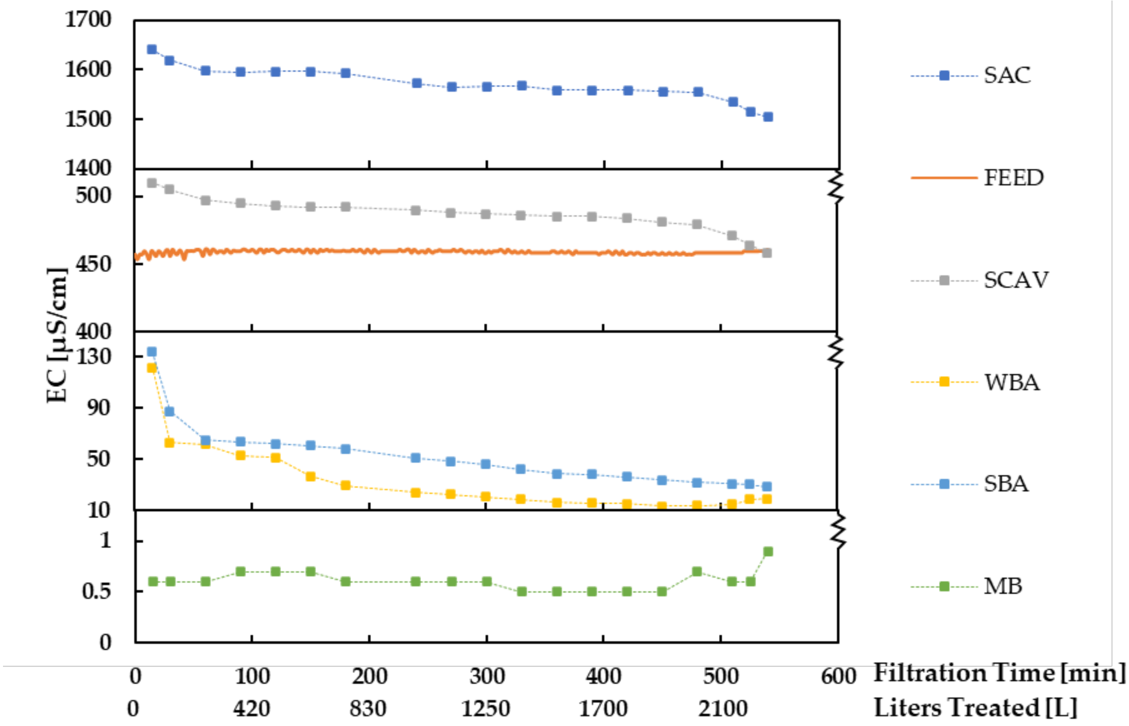


Figure A.11. Conductivity in front of the filtration time/liters treated for the completed IEX Train of SCAV+SAC+WBA +SBA+MB resins

In terms of conductivity, similar behavior is observed within the previous experiment of Chapter A.2.1. The SAC presents the same conductivity pattern as the SCAV resins with the exchange of cations. The SCAV conductivity decreases within the filtration time as in previous Figure A.7. At the beginning of the chart is observed the main difference with both experiments is that the previous step before the filtration (Rinse) was set longer for these experiments, flowing a bigger amount of Demin water through the resins.

A.2.4. 26/07 Daily Experiment – SCAV+SAC+WBA+SBA+MB Behaviour (Day 2)

The same experiment as the 22/07 was repeated in order to doblecheck the behaviour. At this time, the frequency of pH/conductivity sample taking was 60 minutes.

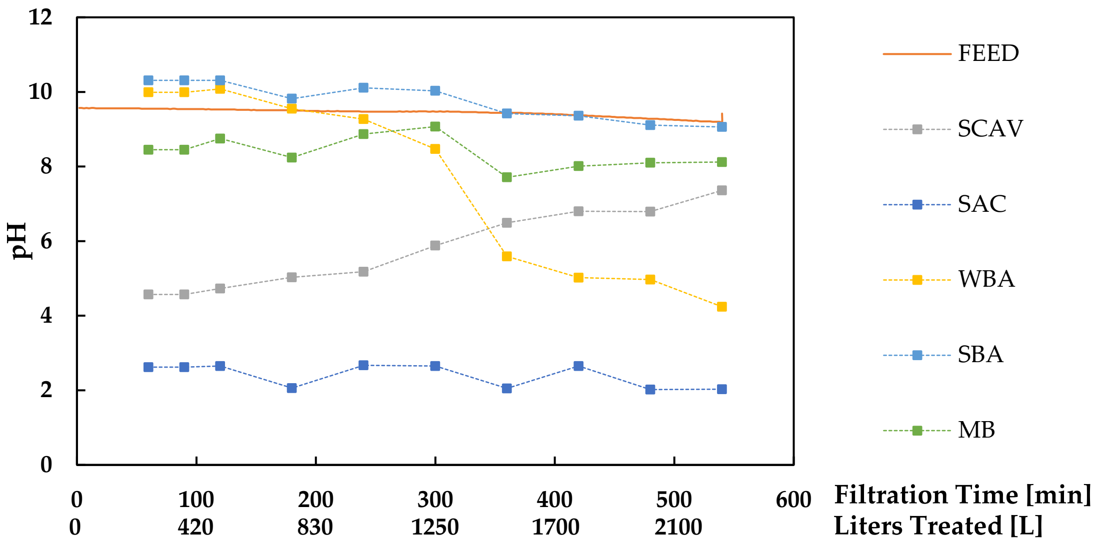


Figure A.12. pH in front of the filtration time/liters treated for the complete train of SCAV+SAC+WBA +SBA+MB resins

Similar behavior is presented from the experiment presented the Chapter A.2.3, the main difference is that the pH of the WBA decreased till 4 during the filtration cycle, while in the previous experiment stayed in 5.5 pH and went higher due to possible sample contamination.

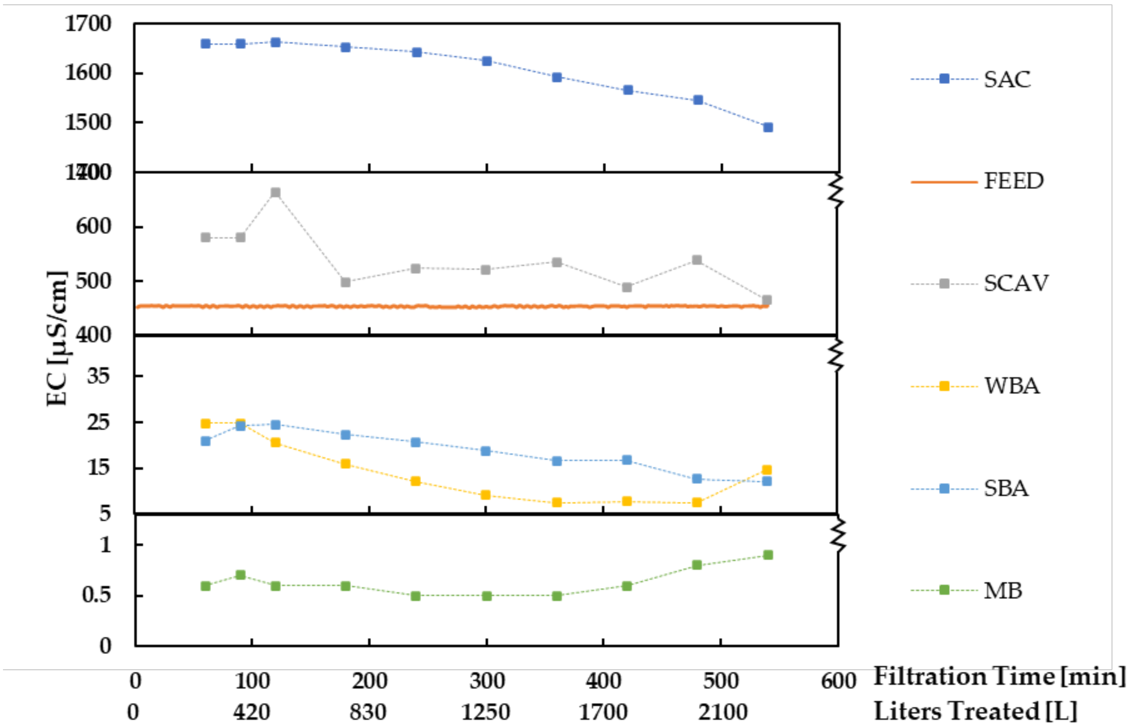


Figure A.13. Conductivity in front of the filtration time/liters treated for the completed IEX Train of SCAV+SAC+WBA +SBA+MB resins

During this experiment, in comparison with the other SCAV experiments, lower values of conductivity are achieved after the WBA and SBA.

A.3. ESTIMATION OF THE REQUIRED ORGANIC SCAVENGER RESINS VOLUME

Regarding the volume difference between the SCAV and the other ion exchange resins in the IMPROVED Containers [26] the Bed Volume per hour is 65% higher for the SCAV than the other resins. This factor represents a smaller resins volume, having less amount of available ions to exchange achieving faster the exhaustion. Limiting the duration of the filtration cycle.

As is observed in the study of the organic scavenger during the filtration cycle at Chapter 4.1, the exhaustion time of the organic scavenger resins is around 420min of filtration time. With a flow of 250 L/h, this represents that with the available volume its possible to treat a total amount of 1750 L of VER water, being a ratio of 280 L of water for 1 L of AmberLite Organic Scavenger SCAV4 Cl resins.

Within this ratio, the calculation is extrapolated to actual duration of the filtration time and the water flows at the current demin plant:

$$V_{SCAV_i} = \frac{\dot{V}_i \cdot t_{filt\ time_{Dow}}}{(\dot{V}_{AS} \cdot t_{filt\ time_{AS}})/V_{SCAV_{AS}}} \qquad \text{A.14.}$$

The addition of the scavenger resins, as observed in the experimental results of the Chapter 4.1 in the TOC removal charts as in Figure 4.2, reduces the organic load on later treatment stages, delaying the exhaustion of the WBA, SBA and MB resins. A design safety factor of 20% has been added on the estimation to prevent the SCAV4 resins to be exhausted before the current demin plant.

Table A.15. Estimation results of the Required Organic Scavenger Resins Volume for the different streets

Parameter	**Small Streets (A, B and C)**	**Big Street (D)**
AquaSPICE SCAV4 Cl Volume ($V_{SCAV_{AS}}$) [L]	6.2	6.2
AquaSPICE Filtration Time ($t_{filt\ time_{AS}}$) [h]	7	7
AquaSPICE Volumetric Flow ($\dot{V}_{AS}$) [L/h]	250	250
Dow Filtration Time ($t_{filt\ time_{Dow}}$) [h]	60	60
Dow Volumetric Flow ($\dot{V}_i$) [L/h]	60 000	150 000
Required SCAV4 Cl Volume (V_{SCAV_i}) [L]	15 300	38 300
Required SCAV4 Cl Volume (V_{SCAV_i}) [m^3]	15.3	38.3

A.4. ESTIMATION OF THE SYSTEM PRESSURE DROP

To determinate the different pressure drops of the resins, the worse operational scenario has been considered. The calculation has been done checking the different pressure drop curves for the used resins according to their column characteristics.

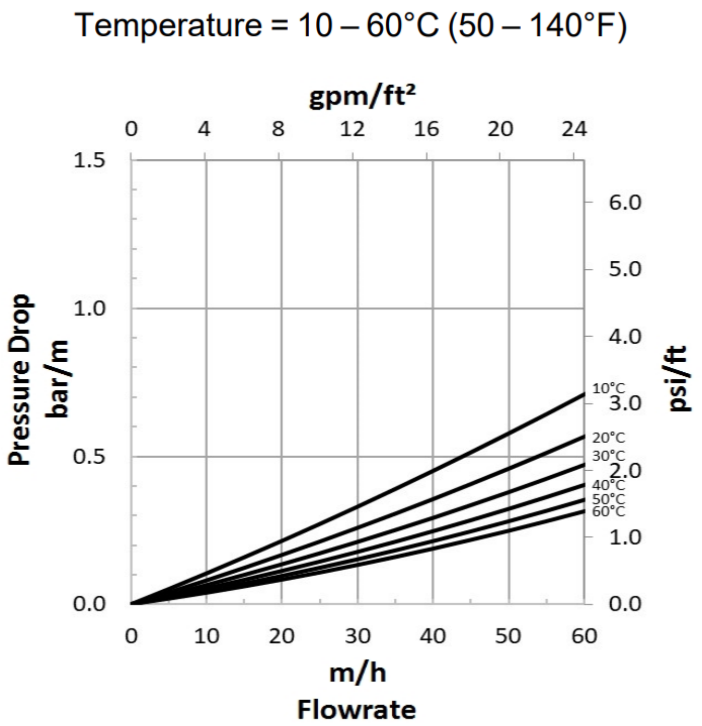


Figure A.16. Pressure drop per meter of column depending on the linear velocity of the flow through the Amberlite SCAV4 Cl Resins at different isothermal lines between 10-60 ºC [37]

As observed in the previous Figure A.16. the worst-case scenario where the pressure drop is highest is when the maximal flow rate and the lowest temperature is achieved. Reproducing the calculation for the main production street (Street D), the maximal expected flow is 180 m^3/h and the lowest temperature is 5 ºC.

Defining $\dot{V}$ as the volumetric flow in m^3/h and D as the internal diameter of the column in m. The flowrate can be described as:

$$v = \frac{\dot{V}}{A} = \frac{\dot{V}}{\pi \cdot \left(\frac{D}{2}\right)^2} \quad \left[\frac{m}{h}\right] \tag{A.17.}$$

$$P_T = \frac{P_{20ºC}}{0.026 \cdot T_{ºC} + 0.48} \quad \left[\frac{bar}{m}\right] \tag{A.18}$$

Defining T as the temperature in Celsius degrees and $P_{20ºC}$ as the pressure drop at 20ºC for the flowrate obtained within the expression A.17, the pressure drop per meter of column can be extrapolated to 5ºC within the expression A.18[39]

The result of the calculation of the different pressure for other columns can be found in the following table:

Table A.19. Pressure drop for the different columns in the big production Street (Street D)

Parameter	SCAV[37]	SAC[48]	WBA[49]	SBA[50]	MB[51][52]
dP/L (20ºC)	0.28	0.22	0.28	0.22	0.28
dP/L (5ºC)	0.37	0.30	0.37	0.30	0.38
Pressure Drop	0.43	1.00	0.95	0.67	0.85

Table A.20. Pressure drop for the different columns in the small production Streets (Street A,B and C)

Parameter	SCAV[37]	SAC[48]	WBA[49]	SBA[50]	MB[51][52]
dP/L (20ºC)	0.09	0.11	0.13	0.11	0.25
dP/L (5ºC)	0.12	0.16	0.18	0.14	0.31
Pressure Drop	0.30	0.50	0.46	0.33	0.70

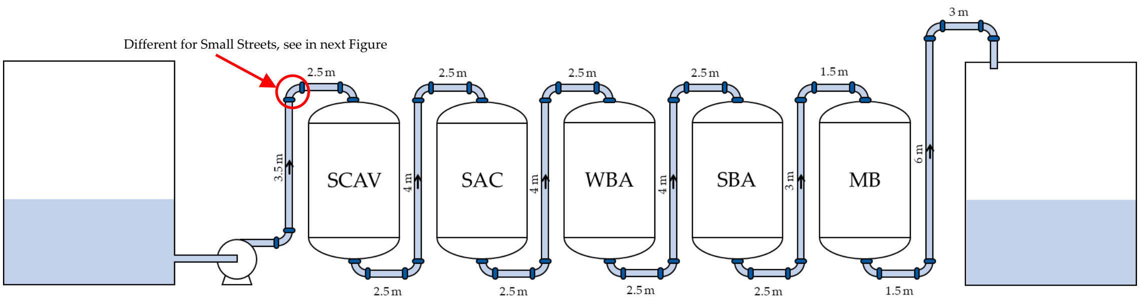


Figure A.21. Front view of the proposed system for the pressure drop estimation for small and big streets

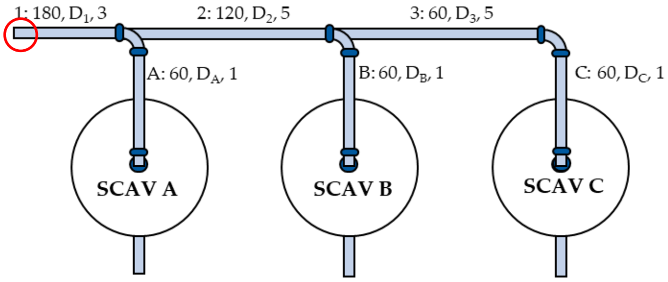


Figure A.22. Upper view to complete the representation for the small streets (located at red circle), the different parameters presented are volumetric flow in m³/h, Nominal Pipe Diameter, and Pipe's length in m

The determination of the pump head has been determined within Bernoulli's expression assuming an incompressible and turbulent flow[39]:

$$\frac{p_1}{\rho g} + z_1 + \frac{v_1^2}{2g} + h_b = \frac{p_2}{\rho g} + z_2 + \frac{v_2^2}{2g} + h_L \quad \text{A.23.}$$

Rearranging the terms, we find that the height of the pump is:

$$h_b = \frac{P_2 - P_1}{\rho g} + \frac{v_2^2 - v_1^2}{2g} + (z_2 - z_1) + h_L \quad \text{A.24.}$$

In the first place, the head loss has been calculated, this is divided into minor and major losses. Minor losses are calculated using the following expression:

$$h_{L,m} = \sum_i K_{L,i} \frac{v_i^2}{2g} \quad \text{A.25.}$$

Where $K_{L,m}$ is a constant that depends on the type of element (elbow, valve, flare). The K values are tabulated constants obtained from ÇENGEL[39] and the fluid linear velocity has been determined from the following expression where an attempt has been made to choose a pipe diameter that ensures that the linear velocity is less or around 2 m/s for metallic pipes[39]:

$$Q = \frac{\pi}{4} D^2 \cdot v \quad \text{A.26.}$$

According the previous Figure A.21 the proposed piping system consist approximately in:

Table A.27. Number of accessories for the 3 small production streets with the K constant tabulated depending on the type of accessory

Type of Accessory	K [39]	Street 1	Street 2	Street 3	Street A or B	Street C
Elbow	0.3	2	0	1	21	22
Widening	0.5	0	0	0	5	5
Narrowing	1	0	1	1	5	5
Globe Valve	10	0	0	0	1	1
Ball Valve	0.05	0	0	0	5	5
T Joint	1	1	1	0	0	0
h_L (m)		0.35	0.42	12.45	12.45	12.50

Table A.28. Number of accessories per street D with the K constant tabulated depending on the type of accessory

Type of Accessory	K [39]	Number of accessories per street
Elbow	0.3	23
Widening	0.5	5
Narrowing	1	5
Globe Valve	10	1
Ball Valve	0.05	5
h_L (m)		30.7

The major losses have been calculated with:

$$h_{L,M} = \sum_i f_i \frac{L_i}{D_i} \frac{v_i^2}{2g} \quad \text{A.29.}$$

Where the friction factor f_i has been calculated using the Colebrook equation, this expression is only valid for turbulent flow, this is determined when the Reynolds number of the following expression A.31 is higher than 3500. Using numerical methods, the solution of the non-linear equation has been determined. L_i refers to the length of the pipe in m, D_i the internal diameter in m, v_i the lineal velocity of the fluid in m/s and g gravity in m/s².

$$\frac{1}{\sqrt{f}} = -2.0 \log\left(\frac{\frac{\varepsilon}{D}}{3.7} + \frac{2.51}{Re\sqrt{f}}\right) \qquad \text{A.30.}$$

Where ε refers to the pipe roughness in mm and Re is the Reynolds number determined by:

$$Re = \frac{\rho v D}{\mu} \qquad \text{A.31.}$$

The summarized results of the calculations can be found below:

Table A.32. Results by section of the calculation described

	St. 1	**St. 2**	**St. 3**	**St. A, B and C**	**St. D**
Pipe Length (L) [m]	6.5	5	5	1	1
Pipe roughness (ε) [mm]	0.0455	0.0455	0.0455	0.0455	0.0455
Water density (ρ) [kg/m3]	1000	1000	1000	1000	1000
Dynamic viscosity (μ) [Pa·s]	0.001002	0.001002	0.001002	0.001002	0.001002
Fluid velocity (v) [m/s]	1.59	1.89	2.12	2.12	1.88
Diameter (D) [m]	0.20	0.15	0.10	0.10	0.2
Reynolds number (Re)	318 000	282 000	212 000	212 000	239 000
Friction factor (f)	0.016	0.017	0.018	0.018	0.018
Major loses ($h_{L,M}$) [m]	0.069	0.103	0.212	0.0423	0.87

To the total head loss of each line, the pressure drop generated with the resins has been added:

Table A.33. Results for the required pump head

Variable	**Street A,B,C**	**Street D**
P_2 [bar]	0	0
P_1 [bar]	0	0
ρ [kg/m³]	1000	1000
g [m/s²]	9.81	9.81
v_2 [m/s]	2.12	1.6
v_1 [m/s]	2.08	1.6
z_2 [m]	6	6
z_1 [m]	2	2
h_{L_T} [m]	67.7	102
h_{PUMP_T} [m]	72	106

A.4.1. Available NPSH (NPSHa)

An important parameter in pump selection is the NPSH. It is essential to choose a pump with a required NPSH lower than that available by the system. The NPSHa of the system is calculated using the expression:

$$NPSH_a = \left(\frac{P}{\rho g}\right)_{pump\ inlet} - \frac{P_v}{\rho g} + z \qquad \text{A.34.}$$

Where P is the pressure at the water surface of the tank in Pa, ρ is the density of the fluid (water) in kg/m^3, g is the gravity in m/s^2, P_v the vapor pressure of the fluid at the operational conditions in Pa. The different variables are also represented graphically in:

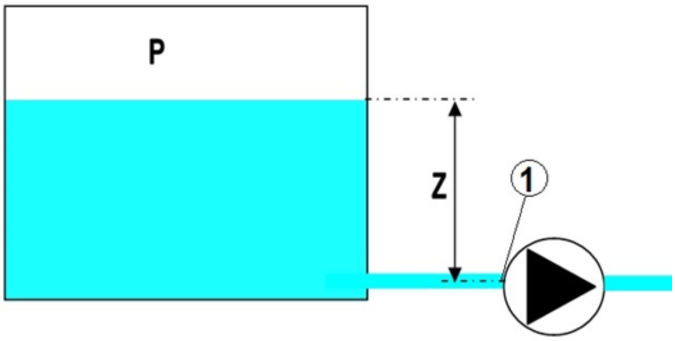


Figure A.35. Basic scheme of the pump inlet pipeline

Suposing that the tank level and the pump position is the same for both production lines, the results of the available NPSH are:

Table A.36. Summary of parameters needed for the estimation of the NPSHa

Variable	**Street A, B, C, D**
Temperature, T [ºC]	5
Tank Pressure, P[Pa]	1.20E05
Saturation Pressure at T, $P_v(T = 5ºC)$ [Pa]	0.09E05
Density, ρ [kg/m^3]	1000
Gravity, g [m/s^2]	9.81
Height Difference, Δz [m]	1.7
NPSH (available) [m]	13.3

A.5. PUMP SELECTION

The selection process is presented for the pump station for the small streets. This process has been repeated for the small streets train and the big street train with the conditions defined at the previous Table A.33. Once the data is introduced in the software, it gives several different commercial pumps within its hydraulic data sheet, including the pump curves.

The selection parameters considered have been:

- Maximal capacity available and maximum head: to be able to operate the pump at higher flow for possible increase of capacity on the plant future
- The operational point is located near the BEP (Best Efficiency Point) of the pump
- Driving Power used for the pump

For the case of the small street, three options were studied:

Table A.37. Selected pumps for the small street pumping station (30-60 m³/(h·pump), 4 pumps, 1 of back-up)

Option	Model	h_{max} [m]	$\dot{V}_{max}$[m³/h]	BEP [m³/h]	*P* [kW]
1	**WDX Ring Section 3WDXE D**	**148**	**66**	**42.5**	**17-24**
2	WDX Ring Section 4WDXE C	118	78	56.7	16-22
3	CPX Self Priming C/C 80-80CPX PM250	100.55	118	86.9	23-30

As can be observed, the 3rd option is capable to pump a bigger flow but their best efficiency point (where the pump works in a best performance in terms of energy efficiency and service life) is away from the current required flow (30-60 m³/h) per pump. Option 1 and 2 presents a value for the BEP inside the operational range. That means that inside the used operational range, the pum efficiency. Also as option 1 and 2 have a smaller maximum volumetric flow, give the possibility to do the same working with a lower electrical request. As the two firsts options have similar beviours and characteristics, Option 1 is chosen due to the possibility of be operated with a higher pump's head.

The most important limitation to consider with WDX Ring Section 3WDXE D is that the maximal pumping flow possible is only 6m³/h higher than the current maximal required flow, being susceptible to possible cavitation problems.

Table A.38. Selected pumps for the big street pumping station (24-30 m³/(h·pump), 6 pumps, 1 of back-up)

Option	Model	h_{max} [m]	$\dot{V}_{max}$[m³/h]	BEP [m³/h]	*P* [kW]
1	HPXM 1.5HPXM12A	145	37	28.3	21-22.6
2	**WD Ring Section WDE32**	**150**	**45**	**36.0**	**13.3-18.6**
3	HWMA In-Line 12HWMA	145	31	25.5	24.7-26.6

In the case of the big street, the option 1 and 3, present a BEP between the operation conditions, but the overall power used by the pump is higher than the power used for the option 2 due to its higher efficiency (more than 60% agains 30-40% of the other options). Also the 2nd option allow to be operating in a higher flow, reducing the amount of working pumps at the same time.

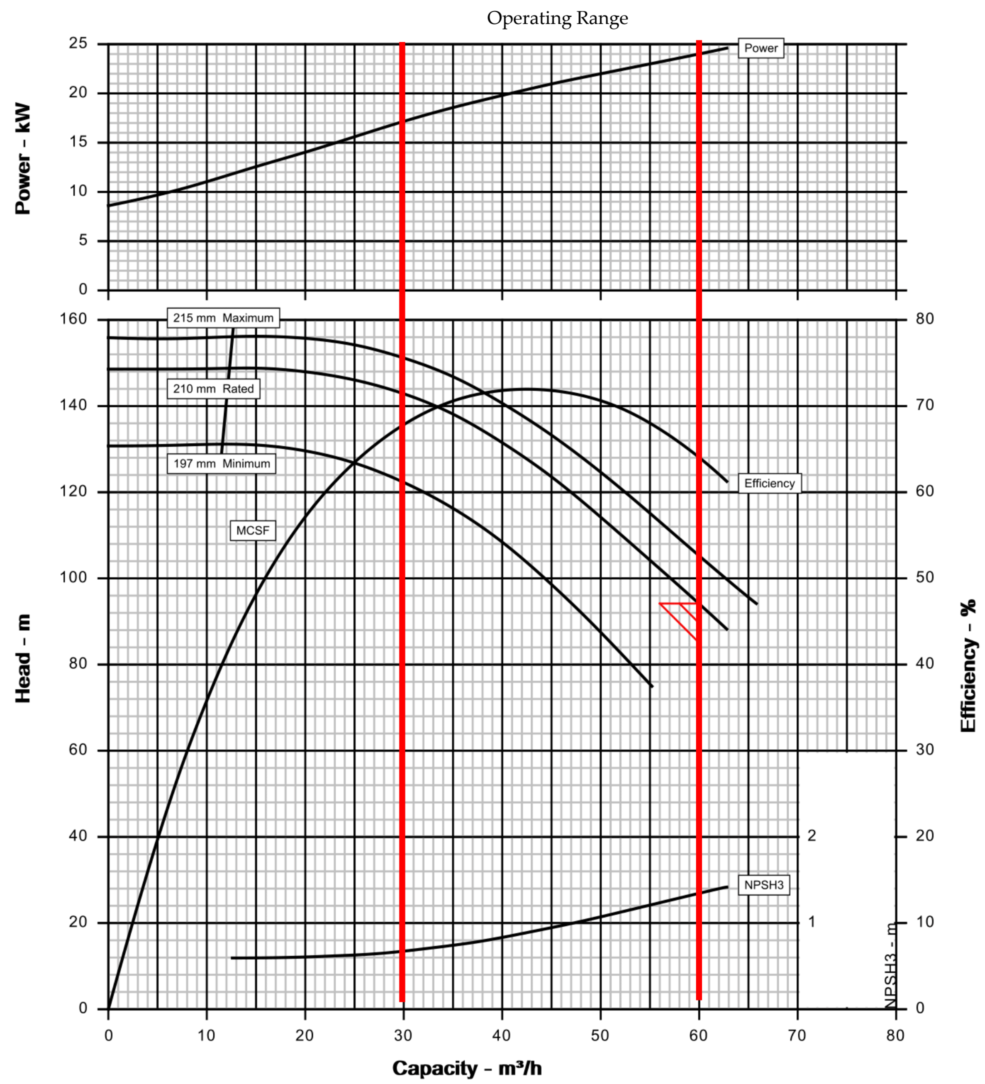
The specification data sheet for the selected pumps can be found below:

A.5.1. P101A-D

FLOWSERVE

		Pump size & type / Stages	: 3WDXE D / 6
		Based on curve no.	: 5991777B
		Impeller diameter	: 210 mm
Customer	: Eduard de las Heras	Capacity	: 60.0 m³/h
Item number	: Street ABC - 1	Head	: 94.00 m
Service	: -	Density / Specific gravity	: - / 1.000
Flowserve reference	: 4187695495	Pump speed	: 1,780 rpm
Date	: August 29, 2022	Ns / Nss (per eye)	: 19 / 209 (SI)
		Test tolerance	: ANSI/HI 14.6 Grade 1B

CURVES ARE APPROXIMATE, PUMP IS GUARANTEED FOR ONE SET OF CONDITIONS; CAPACITY, HEAD, AND EFFICIENCY.



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FLOWSERVE

Hydraulic Datasheet

Customer	: Eduard de las Heras	Pump / Stages	: 3WDXE D / 6
Customer reference	: -	Based on curve no.	: 5991777B
Item number	: Street ABC - 1	Flowserve reference	: 4187695495
Service	: -	Date	: August 29, 2022

Operating Conditions

Capacity (rated/normal)	: 60.0 m³/h / 60.0 m³/h
Water capacity (CQ=1.00)	: -
Total developed head	: 94.00 m
Water head (CH=1.00)	: -
NPSHa/NPSHa less margin	: 10.4 m / -
Maximum suction pressure	: 0.0 kPa.g

Liquid

Liquid type	: Other
Liquid description	: -
Temperature	: 16 °C
Density / Specific gravity	: - / 1.000
Solid Size - Actual / Limit	: - / -
Viscosity / Vapor pressure	: 1.00 cP / -

Materials / Specification

Material column code	: M2
Pump specification	: -

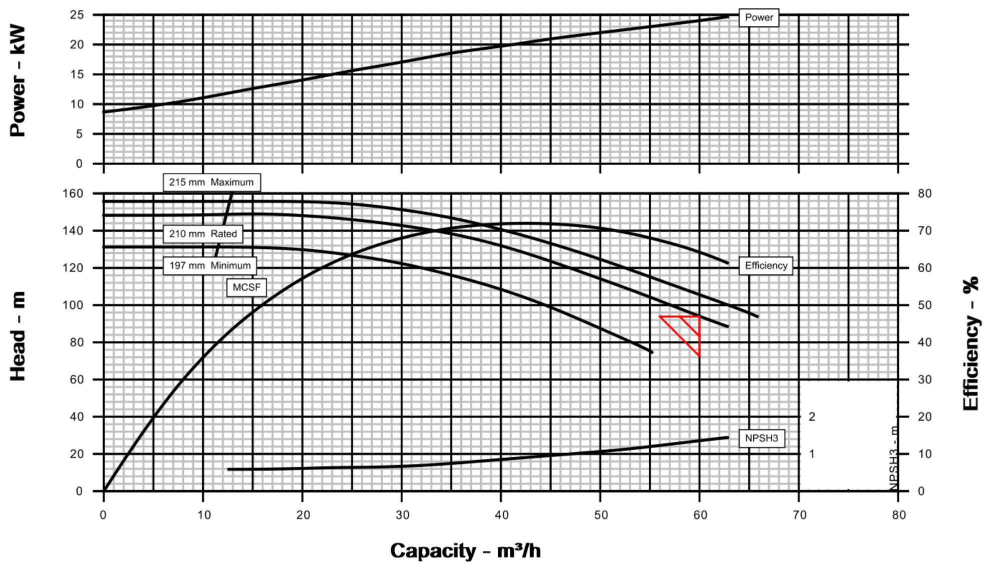
Other Requirements

Hydraulic selection : No specification
Construction : No specification
Test tolerance : ANSI/HI 14.6 Grade 1B
Driver Sizing : Max Power(MCSF to EOC) using SF

Performance

Hydraulic power	: 15.3 kW	Impeller diameter	
Pump speed	: 1,780 rpm	Rated	: 210 mm
Pump overall efficiency (CE=1.00)	: 64.3 %	Maximum	: 215 mm
NPSH required (NPSH3)	: 1.4 m	Minimum	: 197 mm
Rated brake power	: 23.9 kW	Ns / Nss (per eye)	: 19 / 209 (SI)
		Minimum continuous flow	: 12.3 m³/h
Maximum brake power	: 24.6 kW	Maximum head at rated diameter	: 148.51 m
Driver power rating	: 40.0 hp / 29.8 kW	Flow at BEP	: 42.5 m³/h
Casing working pressure	: 1,454.3 kPa.g	Flow as % of BEP	: 141.2 %
(based on shut off @ cut dia/rated SG)		Efficiency at normal flow	: -
Maximum allowable	: 6,400.0 kPa.g	Impeller diameter ratio (rated/max)	: 97.7 %
Hydrostatic test pressure	: 9,000.0 kPa.g	Head rise to shut off	: 58.0 %
Estimated rated seal chamber pressure	: -	Total head ratio (rated / max) / (max / rated)	: 89.5 % / 111.8 %

CURVES ARE APPROXIMATE, PUMP IS GUARANTEED FOR ONE SET OF CONDITIONS; CAPACITY, HEAD, AND EFFICIENCY.



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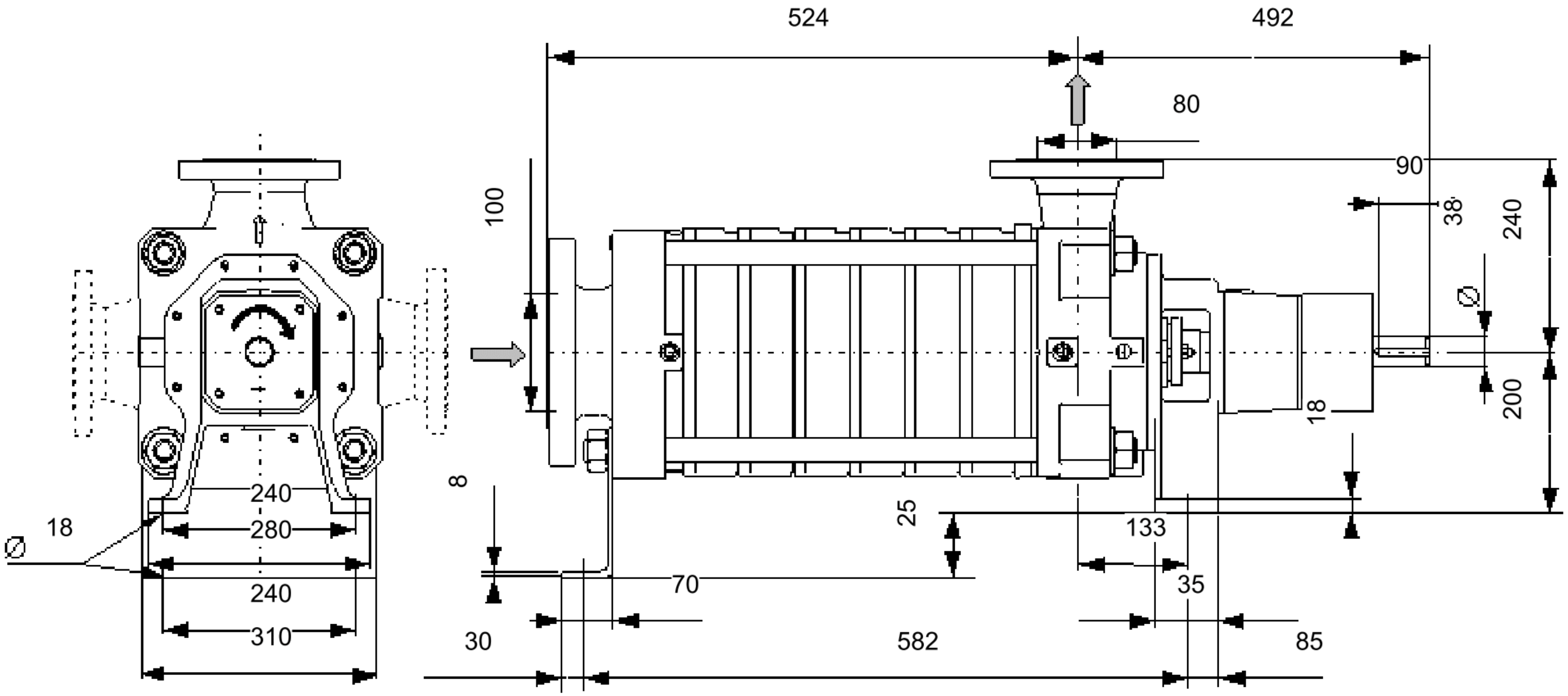
FLOWSERVE

Full Page GA Drawing

	Fy	Fz	Fx	ΣF	My	Mz	Mx	ΣM
Forces & Moments (daN & daN.m)								
SUC.	116	178	142	256	68	100	133	180
DIS.	89	133	107	193	47	72	95	128

PRELIMINARY DRAWING.
Certified drawing available after order.

All flange holes straddle centrelines.



-

Customer	: Eduard de las Heras	Pump size & type	: 3WDXE D	Drawing number	: -
Item number	: Street ABC - 1	Pump speed / Stages	: 1,780 rpm / 6	Date	: August 29, 2022
Service	: -	Flow / Head	: 60.0 m³/h / 94.00 m	Certified by / Date :	: -
Customer PO #	: -	Driver power / Frame	: 40.0 hp / 29.8 kW / -	Seal type	: N/A
Flowserve reference	: 4187695495	Volts / Phase / Hz	: 460 / 3 / 60 Hz	Seal flush plan	: -

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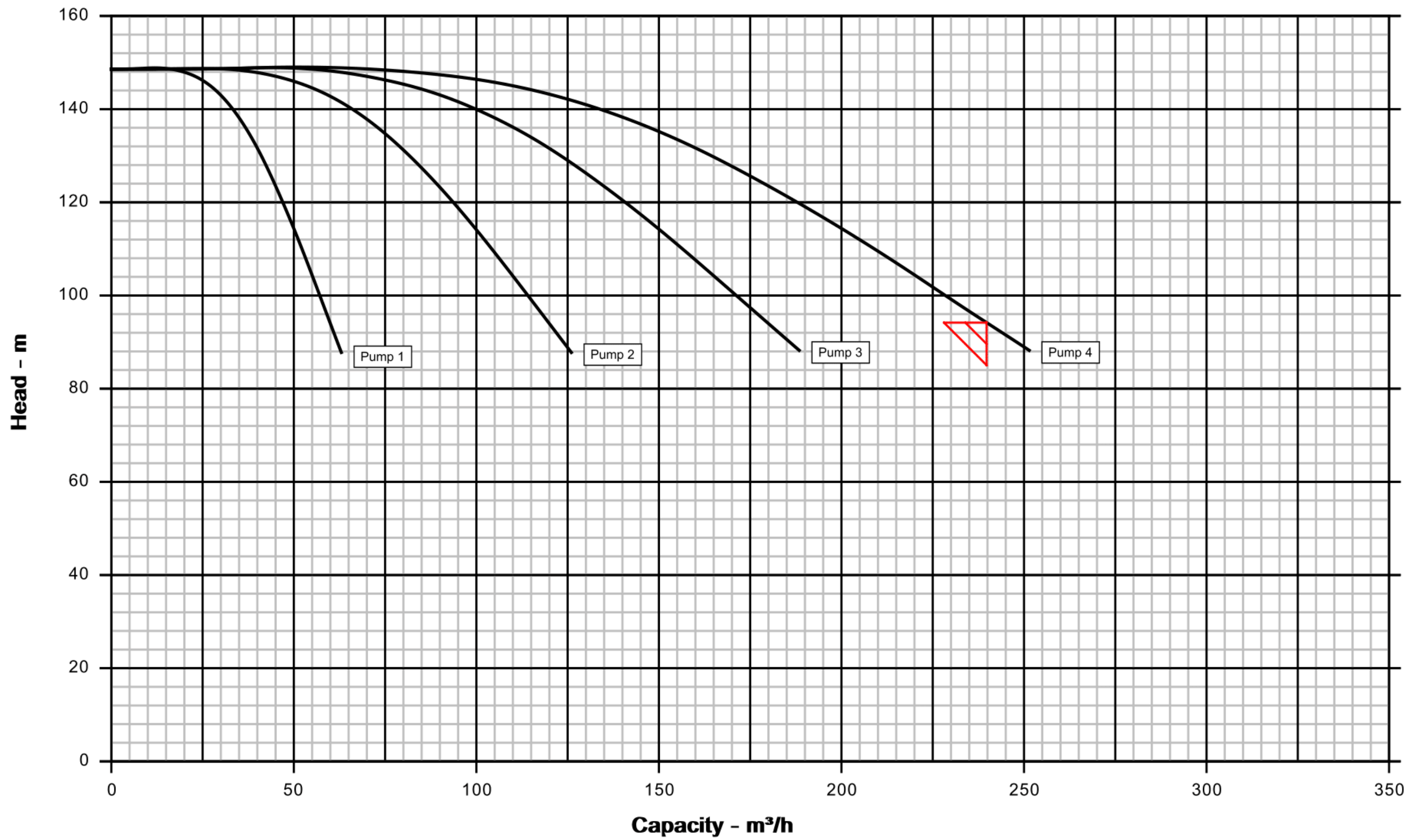
Customer	: Eduard de las Heras	Capacity	: 60.0 m³/h
Item number	: Street ABC - 1	Head	: 94.00 m
Service	: -	Density / Specific gravity	: - / 1.000
Flowserve reference	: 4187695495	Pump speed	: 1,780 rpm
Pump size & type / Stages	: 3WDXE D / 6	Ns / Nss (per eye)	: 19 / 209 (SI)
Based on curve no.	: 5991777B		
Impeller diameter	: 210 mm	Date	: August 29, 2022

CURVES ARE APPROXIMATE, PUMP IS GUARANTEED FOR ONE SET OF CONDITIONS; CAPACITY, HEAD, AND EFFICIENCY.



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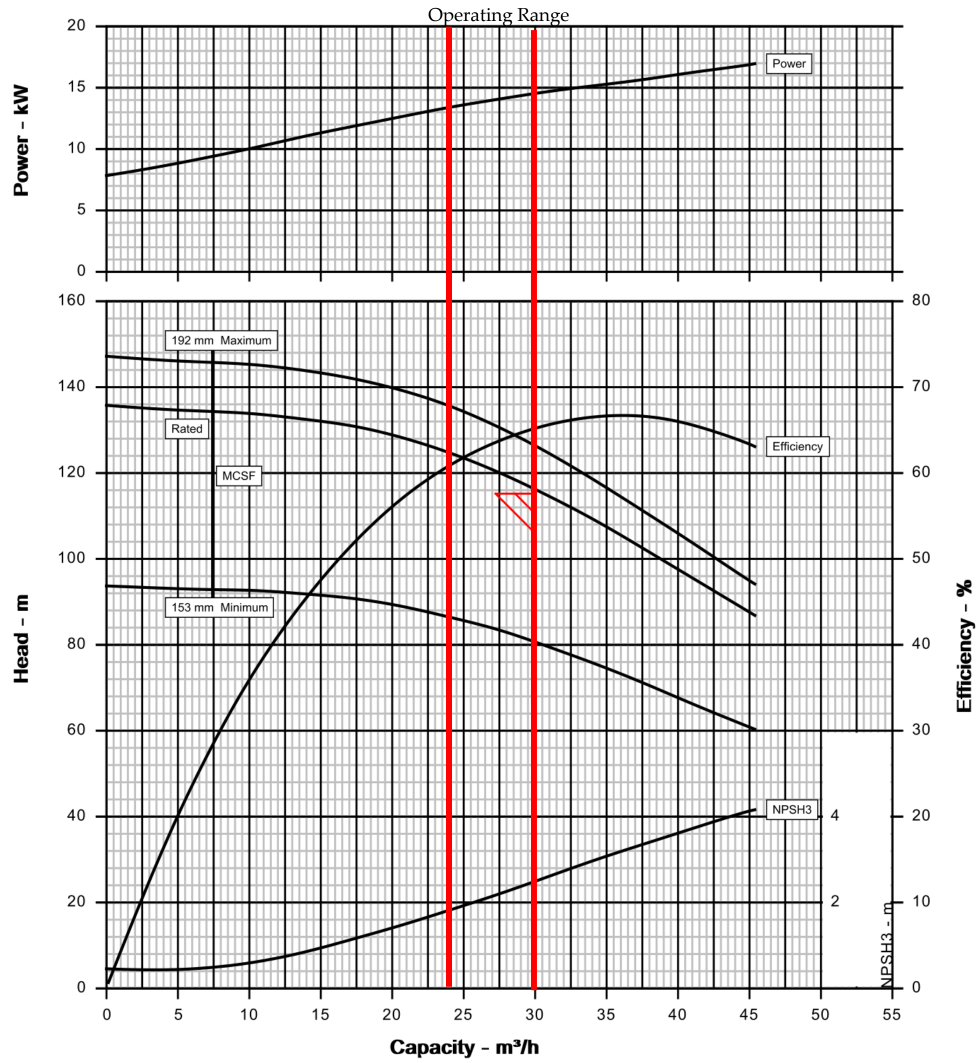
A.5.2. P101E-J

FLOWSERVE

Pump size & type / Stages	: WDE32 / 7
Based on curve no.	: A-15875R-5
Number of stages	: 5 / 1 / 1
Rated impeller diameter	: 192 mm / 173 mm / 153 mm

Customer	: Eduard de las Heras	Capacity	: 30.0 m³/h
Item number	: Street D - 2	Head	: 115.00 m
Service	: -	Density / Specific gravity	: - / 1.000
Flowserve reference	: 4210813100	Pump speed	: 1,775 rpm
Date	: August 10, 2022	Ns / Nss (per eye)	: 22 / 74 (SI)
		Test tolerance	: ANSI/HI 14.6 Grade 1B

CURVES ARE APPROXIMATE, PUMP IS GUARANTEED FOR ONE SET OF CONDITIONS; CAPACITY, HEAD, AND EFFICIENCY.



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FLOWSERVE

Hydraulic Datasheet

Customer	: Eduard de las Heras	Pump / Stages	: WDE32 / 7
Customer reference	: Street D - 2	Based on curve no.	: A-15875R-5
Item number	: -	Flowserve reference	: 4210813100
Service	: -	Date	: August 10, 2022

Operating Conditions	
Capacity	: 30.0 m³/h
Water capacity (CQ=1.00)	: -
Normal capacity	: -
Total developed head (requested / actual)	: 115.00 m / 115.00 m
Water head (CH=1.00)	: -
NPSH available (NPSHa)	: 13.3 m
NPSHa less NPSH margin	: -
Maximum suction pressure	: 0.0 kPa.g

Liquid	
Liquid type	: Other
Temperature / Specific gravity	: 16 °C / 1.000
Solid Size - Actual / Limit	: - / -
Viscosity / Vapor pressure	: 1.00 cP / -

Materials / Specification	
Material column code	: CI
Pump specification	: -

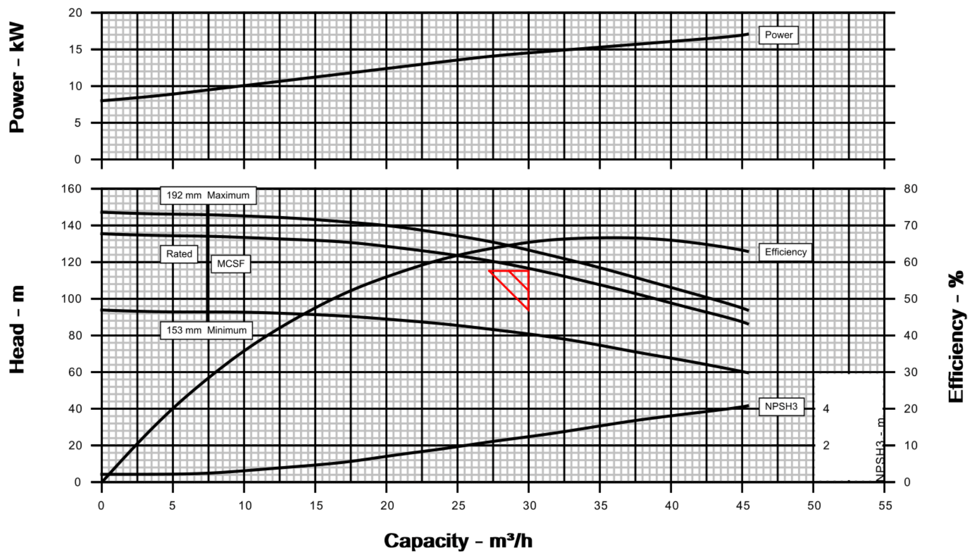
Other Requirements

Hydraulic selection : No specification
Construction : No specification
Test tolerance : ANSI/HI 14.6 Grade 1B
Driver Sizing : Max Power(MCSF to EOC) using SF

Performance

Hydraulic power	: 9.38 kW	Impeller diameter	
Pump speed	: 1,775 rpm	5 stage(s)	: 192 mm
Pump overall efficiency (CE=1.00)	: 65.4 %	1 stage(s)	: 173 mm
NPSH required (NPSH3)	: 2.5 m	1 stage(s)	: 153 mm
Rated brake power	: 14.5 kW	Ns / Nss (per eye)	: 22 / 74 (SI)
Maximum brake power	: 17.0 kW	Minimum continuous flow	: 7.4 m³/h
Driver power rating	: 25.0 hp / 18.6 kW	Maximum head at rated diameter	: 135.54 m
Casing working pressure	: 1,327.3 kPa.g	Flow at BEP	: 36.0 m³/h
(based on shut off @ cut dia/rated SG)		Flow as % of BEP	: 83.4 %
Maximum allowable	: 4,412.6 kPa.g	Efficiency at normal flow	: -
Hydrostatic test pressure	: 6,894.8 kPa.g	Impeller diameter ratio (rated/max)	: -
Estimated rated seal chamber pressure	: -	Head rise to shut off	: 17.9 %
		Total head ratio (rated / max) / (max / rated)	: 92.1 % / 108.6 %

CURVES ARE APPROXIMATE, PUMP IS GUARANTEED FOR ONE SET OF CONDITIONS; CAPACITY, HEAD, AND EFFICIENCY.



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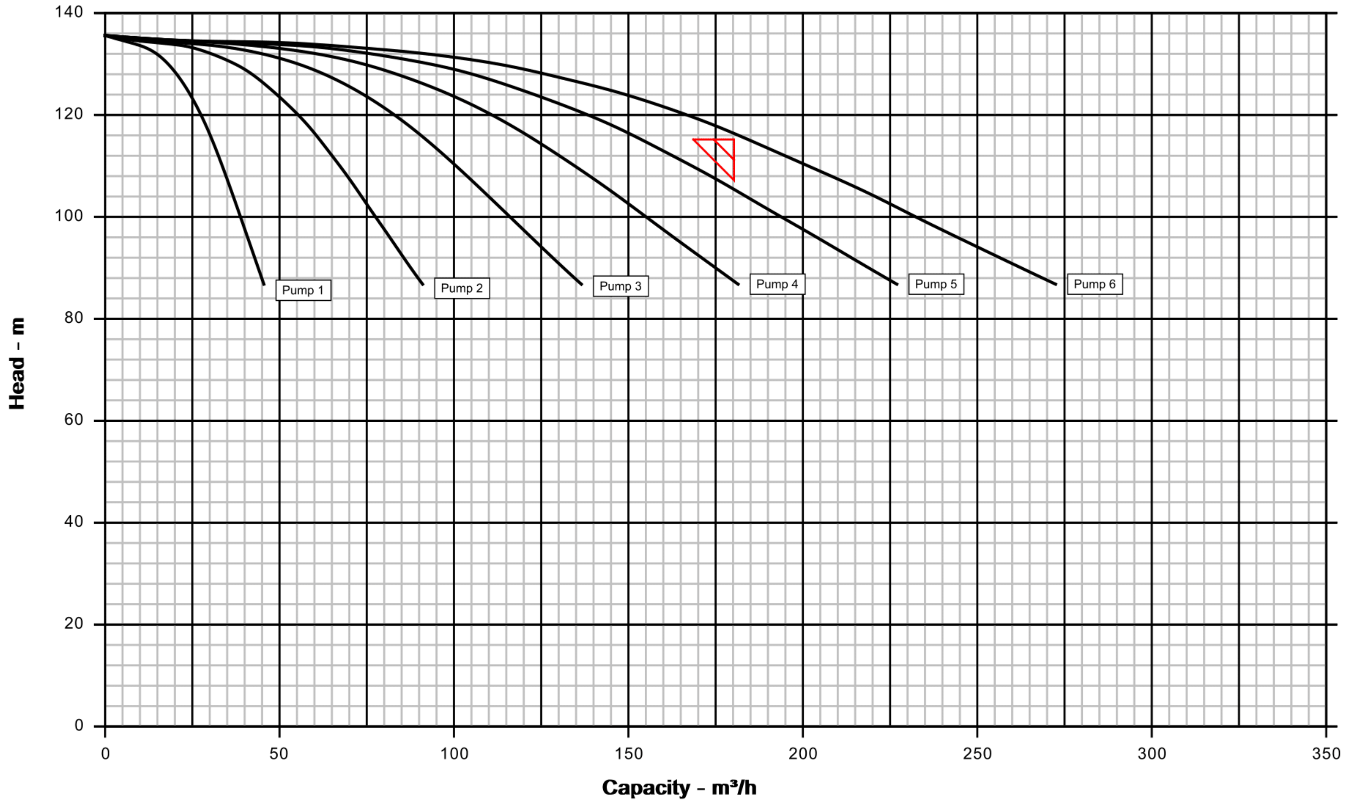
Customer	: Eduard de las Heras	Capacity	: 30.0 m³/h
Item number	: Street D - 2	Head	: 115.00 m
Service	: -	Density / Specific gravity	: - / 1.000
Flowserve reference	: 4210813100	Pump speed	: 1,775 rpm
Pump size & type / Stages	: WDE32 / 7	Ns / Nss (per eye)	: 22 / 74 (SI)
Based on curve no.	: A-15875R-5		
Number of stages	: 5 / 1 / 1		
Rated impeller diameter	: 192 mm / 173 mm / 153 mm	Date	: August 10, 2022

CURVES ARE APPROXIMATE, PUMP IS GUARANTEED FOR ONE SET OF CONDITIONS; CAPACITY, HEAD, AND EFFICIENCY.



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A.6. DESIGN OF THE ORGANIC SCAVENGER COLUMNS

A.6.1. Operational Conditions and Material Definition

In order to define the operational conditions for the design, the worse expected scenario has been taken into account. The worse physical properties of the metal are achieved in the highest temperatures. A water temperature of 35ºC can be expected as the highest value in this case, according to the ASME Code[40], a typical addition of 20 ºC is done

The selected material for the design of the vessel has been the carbon steel P265H, an ideal selection for boilers and pressure vessels operating at room temperature and temperatures under 300 ºC[53]. This metal provides excellent mechanical properties for such an economic price. [53]

A.6.2. Optimal Vessel Size Calculation

As described in the fourth chapter of Part II – Geometry and Layout of Pressure Vessels. The following ratio of height and diameter is used in the ASME code in order to minimize the use of the material according:

$$F = \frac{P}{C \cdot S \cdot E} \qquad \text{A.39.}$$

Defining F factor as a ratio of the design pressure P in psi, the corrosion allowance C in inches, the stress value of material S in psi and the joint efficiency E. The diameter of the vessel can be estimated with the vessel volume in ft^3 estimated in the previous Appendix 67 with the following chart:

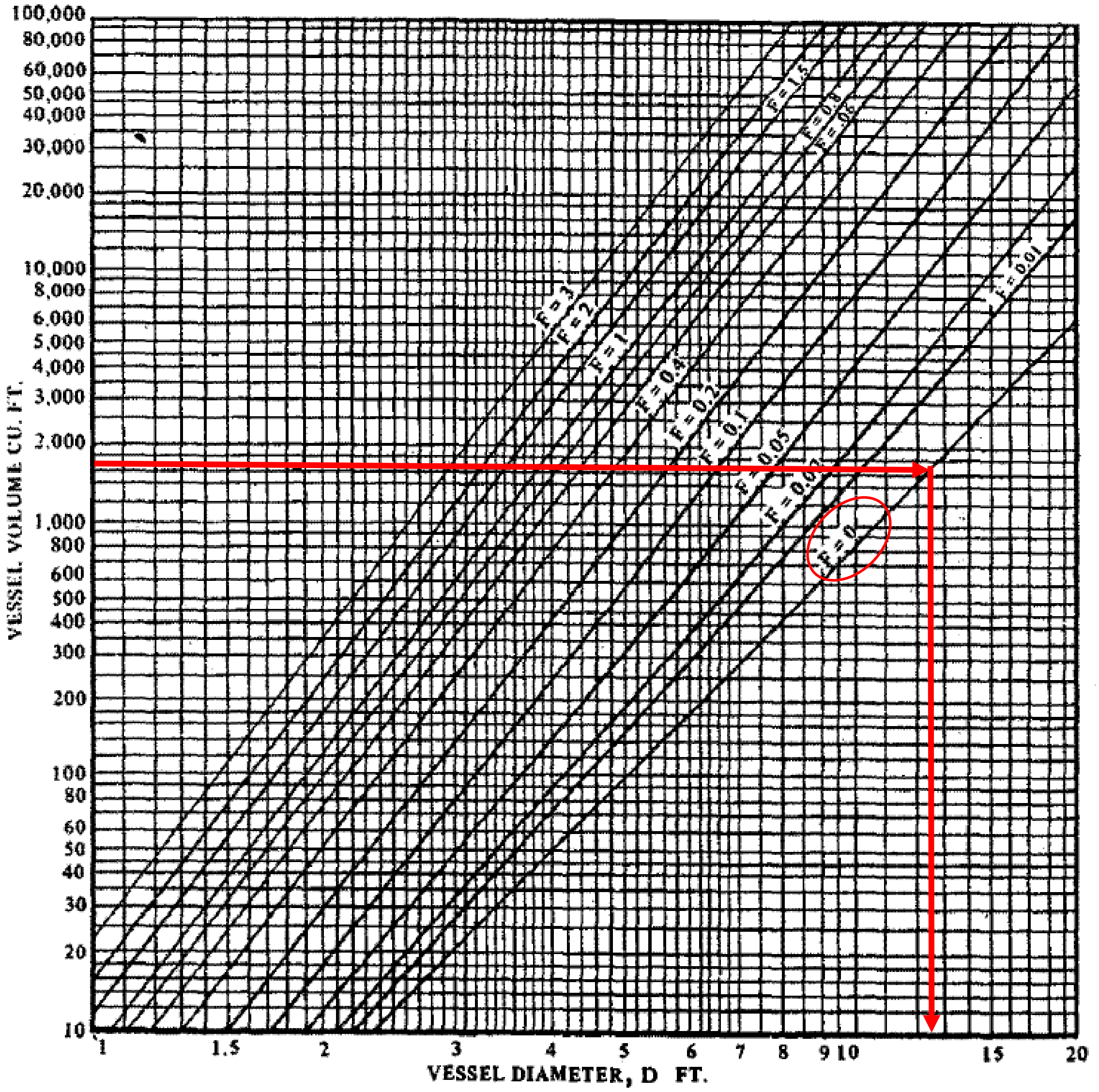

Figure A.40. Optimal ratio of the vessel volume and the diameter within *F* factor.

Once the diameter is determined, the height can be found within the following expression:

$$H = \frac{4 \cdot V}{\pi \cdot D^2} \qquad \text{A.41.}$$

Defining the volume of the vessel V in ft^3 and the inside diameter D in ft. The results obtained for the different designs are:

Figure A.42. Results obtained for an optimal design of a pressured vessel within the ASME Code Section VIII

Parameter	Small Streets (A, B and C)	Big Street (D)
Internal Diameter [m]	2.8	3.9
Height of the cylindrical part [m]	3.1	4

A.6.3. Minimum thickness calculation and commercial thickness selection

According to the minimal thickness calculation for pressure vessels under internal pressure described in the Handbook for Pressure Vessels [40] the thickness required to resist the designed pressure for the cylindrical shell can be found with:

$$t = \frac{P \cdot R}{S \cdot E - 0.6P} \qquad \text{A.43.}$$

Presenting the pressure P and the stress value of material S in the same units, and defining E as the joint efficiency and R the radius.

For the case of the heads of the vessel, the 2:1 ellipsoidal head has been selected for this particular design due to the diameter ratios[40].

$$t = \frac{P \cdot 2R}{2S \cdot E - 0.2P} \qquad \text{A.44.}$$

After obtaining the calculated values, a possible corrosion allowance is added to the calculation according to the ASME Code for Pressure Vessels [40]. As the corrosion effect is not expected, the minimal recommended value of 0.125 is added to the calculation.

Within the corrosion factor added to the thickness calculated, the immediately higher commercial thickness is selected to recalculate the design pressure.

A.6.4. Column Volume and Weight

The column is divided in 3 parts, a cilindrical body within 2 elipsoidal head of 2:1 relation. The volume of the cylinder and the ellipsoidal head with relation 2:1 are defined as:

$$V_{cil} = A_{circle} \cdot h = \pi \cdot \left(\frac{D}{2}\right)^2 \cdot h \qquad \text{A.45.}$$

$$V_{ellipsoidal\ head} = \pi \cdot \frac{D^3}{24} \qquad \text{A.46.}$$

$$V_T = V_{cil} + 2 \cdot V_{ellipsoidal\ head} \qquad \text{A.47.}$$

The volume corresponding to the external case is defined as the difference of volumnes within the external volume and internal volume, the difference between this dimensions is defined as t thickness determinated in the previous expression A.44. being:

$$V_{cil\ P265GH} = V_{cil_{out}} - V_{cil_{in}} = \pi \cdot \left(\frac{D_{out}}{2}\right)^2 - \pi \cdot \left(\frac{D_{in}}{2}\right)^2 = \pi \cdot \frac{1}{4} \cdot \left(D_{out}^2 - D_{in}^2\right) = \pi \cdot \frac{1}{4} \cdot \left(\left(D_{in} + t_{cil_{com}}\right)^2 - D_{in}^2\right) \qquad \text{A.48.}$$

$$V_{ellipsoidal\ head\ P265GH} = V_{ellip_{out}} - V_{elip_{in}} = \frac{\pi}{24} \cdot (D_{out})^3 - \frac{\pi}{24} \cdot (D_{in})^3 = \frac{\pi}{24} \cdot \left(D_{out}^3 - D_{in}^3\right) = \frac{\pi}{24} \cdot \left(\left(D_{in} + t_{cil_{com}}\right)^3 - D_{in}^3\right) \qquad \text{A.49.}$$

$$V_{T\ P265GH} = V_{cil} + 2 \cdot V_{ellipsoidal\ head} \qquad \text{A.50.}$$

By the P265GH[53] density, the total metallic weight can be found as:

$$W_{T\,i} = \rho_i \cdot V_{T\,i} \qquad \text{A.51.}$$

The resins volume and the water volume has been determinated with the expected filling of resins and the internal volume of the cylinder, determinated at previous expression A.45.

A summary of the volume and weight results are collected in the two tables presented below:

Table A.52. Summary of the different Volume Sizes of the designed SCAV columns

Parameter	V-101A-C	V-101D
V_{cil} [m³]	18.4	47.8
$V_{ellipsoidal\ head}$ [m³]	2.87	7.76
V_T [m³]	24.8	63.3
$V_{cil\ P265GH}$ [m³]	0.0419	0.0976
$V_{ellipsoidal\ head\ P265GH}$ [m³]	0.0294	0.0954
$V_{T\ P265GH}$ [m³]	0.101	0.288

Table A.53. Summary of the different Weights of the designed SCAV columns

Parameter	V-101A-C	V-101D
W_{SCAV4} [t]	10.7	26.8
W_{H_2O}[t]	9.56	25.1
W_{P265GH}[t]	0.789	2.23
W_T[t]	21.0	54.1

A.6.5. Bottom Plate Deflection

The bottom plate that supports the resins and the pressure applied is under a high load of stress. This stress generates a deflection into the plate reaching a possibility of generating a rupture in the plate.

This type of stress applied to the plate can be represented as a uniformly distributed load through the area.

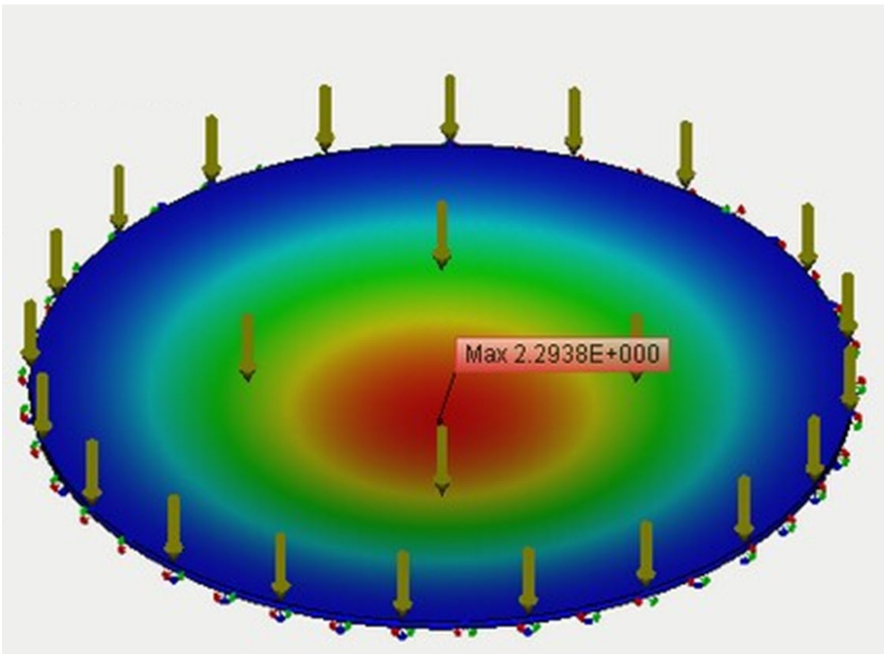

Figure A.54. Circular plate of a fixed thickness under a uniformly distributed load

The distributed load has been approximated to the pressure drop through the column and the total weight of the resins over divided per plate surface.

The maximal desviation at the center of the plate can be determinated within the approximated expression from AutoFEM Analysis Software[55]:

$$w_0 = \frac{q \cdot R^4}{64 \cdot Rig} \cdot \frac{1}{1 + 0.488 \cdot \frac{w_0^2}{h^2}} \quad \text{A.55.}$$

$$Rig = \frac{E \cdot h^3}{12 \cdot (1 - \nu^2)} \quad \text{A.56.}$$

$$w_0 = \frac{q \cdot R^4}{64 \cdot \frac{E \cdot h^3}{12 \cdot (1 - \nu^2)}} \cdot \frac{1}{1 + 0.488 \cdot \frac{w_0^2}{h^2}} = \frac{12 \cdot q \cdot R^4 \cdot (1 - \nu^2)}{64 \cdot E \cdot h^3} \cdot \frac{1}{1 + 0.488 \cdot \frac{w_0^2}{h^2}} \quad \text{A.57.}$$

Defining q has the distributed load in MPa, E as the Young's Module in MPa, w_0 as the maximal deformation in m, R as the radium of the internal area, and h as the thickness of the plate. Within solving the expression A.57. The following deformation is obtained:

Table A.58. Maximal deformation generated due to resins and pressure difference at the bottom plate.

Unit	**Small Streets (A, B and C)**	**Big Street (D)**
Thickness (t) [m]	0.03	0.1
Maximal deformation (w) [m]	0.220	0.231

Due to the significant deformation, the placement of rigid supports is needed, a configuration of 6 cilindrical supports in hexagonal disposition is proposed.

A.7. ECONOMIC ESTIMATION

As mentioned in the previous Chapter 6, the Turton methodology has been followed for this calculation. This cost estimation use to have a expected accuracy range depending the level of project definition/purpose of estimation. As the design presented in the thesis is defined as concept study or feasibility, the project has been defined as Class of Estimate 4. The other different classes are summarized in the table below:

Table A.59. Classification of Cost Estimates[41]

Class	Level of Project Definition [%]	Typical Purpose of Estimate	Expected Accuracy Range (Related to the best index of 1)
5	0 to 2	Screening or Feasibility	4 to 20
4	1 to 15	Concept Study or Feasibility	3 to 12
3	10 to 40	Budget, Authorization, or Control	2 to 6
2	30 to 70	Control or Bid/Tender	1 to 3
1	50 to 100	Check Estimate or Bid/Tender	1

To determinate the expected Desviation within the obtained result, every level is multiplied for a subjective factor between the range given in the last column of the Table A.59. and the accuracy for a Class 1 estimation. This is typically defined between a +6% and -4% accurate[41]. In the case of the project, in the Class of Estimate 4, the factor selected has been 10, so the price is expected to be compressed between a +60% higher or 40% lower.

A.7.1. Estimation of the Purchase Cost of the Equipments

As mentioned in the previous Chapter 6, the SCAV columns has been defined as a vertical pressure vessel build in carbon steel and the centrifugal pumps as a centrifugal pump build in carbon steel. Within this definition and the tabulated contants for 2001 in Turton's methodology[41], the Purchase Cost of the Equipments at 2001 is obtained with the following expression[41]:

$$\log C_p^0 = K_1 + K_2 \log(A) + K_3[\log(A)]^2 \qquad \text{A.60.}$$

Where A is the an specific parameter depending the design of the equipment and the diferent K_i the constant values inside the range of the design factor A. In the case of the Vertical Pressured Vessel this is the Volume of the Vessel in m^3 and for the centrifugal pump it is the Power in kW.

Table A.61. Equipment cost at 2001 for the Units added to the current process [41]

Unit	Description	Items	K1	K2	K3	A	Unit	C_p^0($)
V-101A-C	Vertical Vessel	3	3.4974	0.4485	0.1074	24.8	m^3	2.15E+04
V-101D	Vertical Vessel	1	3.4974	0.4485	0.1074	63.3	m^3	4.51E+04
P-101A-D	Centrifugal Pump	4	3.3892	0.0536	0.1538	24.6	kW	5.77E+03
P-101E-J	Centrifugal Pump	6	3.3892	0.0536	0.1538	17	kW	4.88E+03

For the equipment cost a safety factor of 20% is added due to considere the addition of the different manholes, connections, nozzle plats, and nozzle filters.

In order to take into account the changing economic conditions and update the equipment cost at 2001 to 2022, the Chemical Engineering Plant Cost Index (CEPCI)[56] is a cost index indicator related within the chemical engineering plants. The equipment cost at 2022 can be found with the following expression[41]:

$$C_{p_{2022}} = C_p^0 \cdot \left(\frac{CEPCI_{2022}}{CEPCI_{2001}}\right) \quad \text{A.62.}$$

Using the CEPCI values as 397 for 2001 [41] and 803.6 for 2022 [56] the equipment cost is equal to:

Table A.63. Total Equipment cost in € in 2022 by CEPCI[56] correlation

Unit	Items	C_p^0($)	$C_{p_T}^0$($)	$C_{p_T}^{2022}$($)	$C_{p_T}^{2022}$(€)
V-101A-C	3	2.15E+04	7.74E+04	1.57E+05	1.56E+05
V-101D	1	4.51E+04	5.41E+04	1.09E+05	1.09E+05
P-101A-D	4	5.77E+03	2.31E+04	4.67E+04	2.66E+04
P-101E-J	6	4.88E+03	2.93E+04	5.92E+04	5.90E+04

In the calculation of the total cost $C_{p_T}^0$, the safety factor of 20% has been added to the SCAV columns (V-101)

A.7.2. Estimation of the Cost Bare Module

The material and the pressure used in the design are also key parameters to take into account in this cost estimation, this is done within the material factor and pressure factor.

The material factor for each equipment is defined with a identification number depending the equipment type, description and construction. This is summarized in Table A.3, located at Appendix A. "Cost Equations and Curves for the CAPCOST Program" at TURTON[41] Analysis, Synthesis, and Design of Chemical Processes . This identification number is used to identify the Bare Module Factor in the chart bellow:

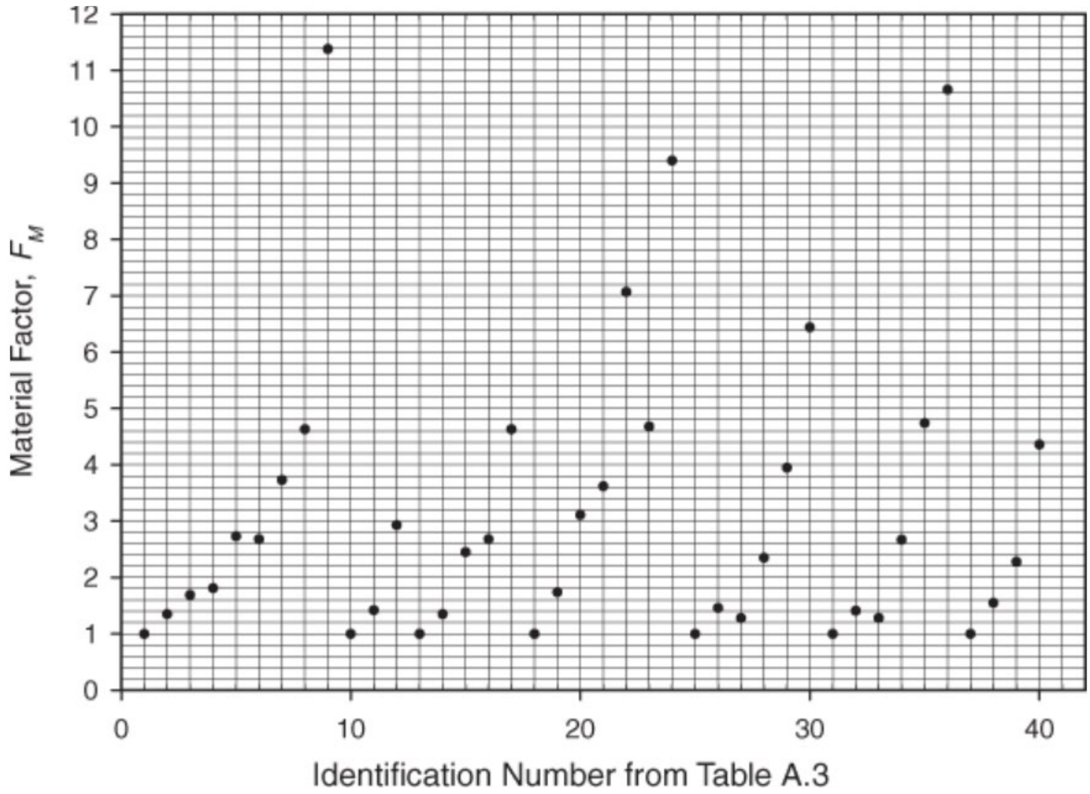

Figure A.64. Material Factors for Equipment in Table A.3 of TURTON [41]

Within the identification number and the relations represented at Figure A.64, the following Material Factors F_M are determinated:

Table A.65. Summary of the Material Factor for the different units

Unit	Description	Identification Number	F_M
V-101A-C	CS – Process Vertical Vessel	18	1
V-101D	CS – Process Vertical Vessel	18	1
P-101A-D	CS – Centrifugal Pump	38	1.6
P-101E-J	CS – Centrifugal Pump	38	1.6

The pressure factor is determinated by different correlations depending the equipment. In the case of the pressure vessels, the pressure factor is determined by the following expression[41]:

$$F_p = \frac{\frac{(P+1)D}{2[850-0.6(P+1)]}}{0.0063} + 0.003175 \quad \text{A.66.}$$

Table A.67. Summary of the Pressure Factor for the SCAV Columns

Unit	Diameter (m)	Pressure (bar)	F_p
V-101A-C	2.8	9.4	3.24
V-101D	3.9	13.6	5.88

While for centrifugal pump the following correlation is used[41]:

$$\log F_p = C_1 + C_2 \log P + C_3 (\log P)^2 \quad \text{A.68.}$$

The different constants C_i are defined from the Table A.2 in the Appendix 1 of TURTON[41] depending the type of pump used and its pressure range and the maximal available working pressure P defined in barg:

Table A.69. Summary of the Pressure Factor for the Centrifugal Pumps

Unit	P [barg]	C_1	C_2	C_3	F_p
P-101A-D	14.5	-0.3935	0.3957	-0.00226	1.16
P-101E-J	14.7	-0.3935	0.3957	-0.00226	1.16

Within the combination of the different Factors and tabulated constants, the Bare Module is calculalted following the expression:

$$C_{BM} = C_p^0(B_1 + B_2 F_M F_P) \quad \text{A.70.}$$

Table A.71. Summary of the Bare Mode for the different units

Unit	F_p	F_M	B_1	B_2	C_{BM}(€)
V-101A-C	3.24	1	2.25	1.82	1.28E+06
V-101D	5.88	1	2.25	1.82	1.42E+06
P-101A-D	1.30	1.6	1.89	1.35	2.05E+05
P-101E-J	1.72	1.6	1.89	1.35	2.61E+05