Modelling, Optimisation and Caustic Recovery for more Sustainable Bottle Washers

MSc Dissertation

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Executive Summary

In Europe, it has been a common practice to return used beer bottles to the breweries. To reuse these glass bottles, they need to be cleaned in the bottle washers with caustic soda. Currently, not much research has been carried out to study the compositions of the bottle washer wastewater or possible recovery techniques. Most of the practice is based on empirical industrial experience. Together with Heineken®, a preliminary study on beer bottle washers was carried out in this report, and real-life data was collected from a KRONES® bottle washer purchased by Quart de Poblet, located in Valencia, Spain.

To solve the caustic soda recovery problem step by step, four research questions were raised:

1. Can a model be built based on mass balance for a typical bottle washer to simulate caustic soda loss due to carry-over?

2. What is the typical composition of caustic effluent from the bottle washers?

3. Can the model of bottle washer be applied for different operational variables and structures?

4. What are the most suitable methods for bottle washers to reduce the total caustic soda consumption?

To better understand the water and caustic flows within the bottle washers, a base scenario (BS) Python model was built for analysis of the losses from the machines, and in the meanwhile, providing more insight on how to further improve the bottle washers to reduce water and caustic soda consumption. Another real-life model (Valencia) was established with real-life data from Quart de Poblet, and following scenarios were optimised towards certain individual criteria including water footprint and caustic soda consumption. A lab analysis of the compositions of three water samples from bottle washer caustic baths was carried out with three water samples obtained from Alken Maes, providing the possibility for discussion on caustic soda reclamation. A discussion between membrane techniques and electrodialysis was presented based on the composition.

As conclusions, it was possible to build basic Python models to study only the carry-over for a certain bottle washer. But it could be difficulty to validate the current model with real-life data or experiments. It should be easy to extend or adapt the BS model to other types of bottle washers with characterised working modes. The Valencia model was an example. The most effective and doable practices to reduce caustic soda consumption included reducing caustic concentrations in caustic baths and recirculating label extraction effluents. To recover caustic soda from wastewater, high pH tolerance materials for nanofiltration membranes and selectrodialysis are regarded as the possible solutions.

1

Introduction, Background and Research Objectives

Industrial water and material reusing and recycling have been a focus in the field of environmental engineering. One of the industries that require abundant chemicals and clean water is the food and beverage industry. In the European survey of CIAA, 2008, 8% to 15% of the total industrial water consumption is shared by the direct consumption in the food and beverage industry, which equals to 1% to 1.8% of the total water use. Under such conditions, one of the most common aspects of sustainability is reusing materials such as water and chemicals. In many places of the world, especially in Europe, reusing returned glass and plastic bottles has become a popular practice to promote sustainability. It can lengthen the life time and postpone the disposal of these bottles. The returned bottles are washed for reuse where caustic soda is commonly used to remove organic contaminants. As a consequence, the resulting wastewater usually requires neutralisation before discharge due to the high pH. Besides discharge, another way to deal with the wastewater is reuse in other fields such as agriculture. One of the popular means of wastewater reuse is the irrigation in agriculture. However, in addition to the high pH, the high sodium concentration in the bottle washer wastewater also limits the reuse in agriculture. Accordingly, the removal of sodium and hydroxyls from wastewater, which contains much caustic soda, becomes critical for agricultural reuse.

So far many researchers have been looking into water recycling in breweries, whereas chemical recovery from bottle washer wastewater has not been studied in detail. This research is focusing on the sustainable transformation of the bottle washing process by studying breweries of Heineken®. The aim is to simultaneously conserve and recovery both caustic soda and clean water from the bottle washers effluents. On the one hand, the overall consumption of caustic soda can be reduced in the brewery. On the other hand, the water after caustic soda reclamation will be more suitable for agriculture reuse purpose after the removal of sodium. Overall, the water footprint can be reduced and resource efficiency can be raised for the bottle washing process.

In this chapter, some background information about the bottle washing process and the Heineken® company will be provided, backing up the research topic with current industrial situations of bottle washers and available techniques for resource recovery. By identifying the knowledge gaps, the objectives of this research will be proposed with corresponding research methods.

1.1. INDUSTRIAL BACKGROUND

In food and beverage industries, there are two categories of water use: water with and without contact of the product. Almost 70% of the total water is used for sanitation operations in some specific sectors, where water has no contact with products (Henningsson et al., 2004). Therefore, washing and sanitation operations have become a major concern in reducing the total water consumption. The water use in beer bottle washers is the water which has no direct contact with the product, beer. The major impact from industries on water resources is the discharge of highly polluted wastewater rather than the enormous amount of water used (Tiwari et al., 2013). According to Maxime et al., 2006, the relative quantity of water use for washing, cleaning and disinfection is regarded as high in food and beverage industries.

The major problem in the industry in terms of water and chemical conservation is the lack of knowledge or data on the amount of water and chemical used and discharged at specific steps of the processing line (Tiwari et al., 2013). So it is imperative to obtain information from annual audit data and track the flows of water and chemicals in order to locate points of high water consumption or chemical loss.

1.1.1. THE HEINEKEN® COMPANY

The Heineken® Group, as one of the world biggest enterprises in brewery industry, has been devoted to reducing the water footprint of their beers over the years with the concept of sustainability embedded in their business strategy. Heineken® has many production sites all over the world, and those in water-stressed areas draw more attention. The ambition of the enterprise is to achieve fully balance in the water used in their products in water-stressed areas, including 30 sites in 12 countries, by 2030 (*Heineken® N.V. Annual Report 2020*, 2021). Heineken® breweries target at maximising reuse and recycling of water in water-stressed areas, and treating all the wastewater discharged from all breweries. A triangular approach has been used by Heineken® to achieve their 2030 target, involving "Water Stewardship" to fully balance the water used in its products, "Water Efficiency" to reduce water usage in production, and "Water Circularity" to ensure 100% of wastewater is treated whilst maximising opportunities to reuse and recycle water (Lumpur, 2021).

So far, Heineken® has achieved their commitment in 2020 in terms of protecting water resources. Currently, the average water consumption in water-stressed areas has been reduced from 5.0 hL/hL in 2008 to 3.1 hL/hL, and in all breweries from 3.8 hL/hL in 2014 to 3.4 hL/hL. The goal by 2030 is to lower the water consumption to 2.8 hL/hL in water-stressed areas and 3.2 hL/hL in all breweries (*Heineken® N.V. Annual Report 2020*, 2021).

Currently, chemical consumption has not drawn as much attention as water consumption in the industry. This research will focus on the last aspect of the triangular approach from Heineken® : circularity, not only for water, but also for chemicals.

1.1.2. BEER BOTTLE WASHERS

The bottle washing process involves the washing and cleaning of returned bottles with chemicals. There are also bottle washers for plastic bottles, but in this report, only glass beer bottle washers will be discussed.

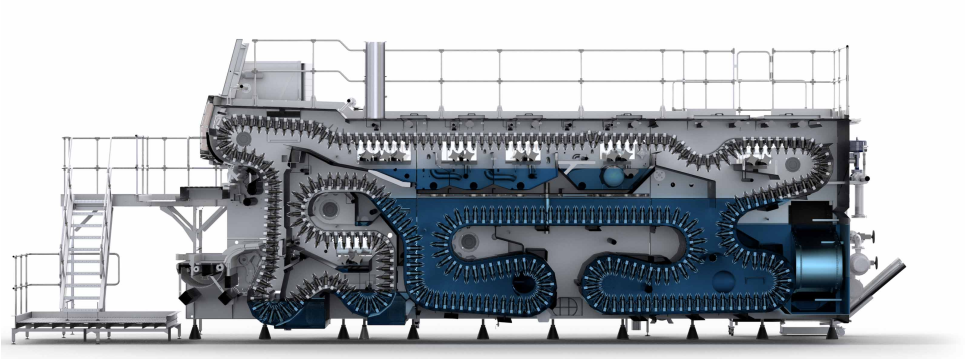


Figure 1.1: Sectional view into a bottle washer produced by KRONES®(KRONES®, n.d.)

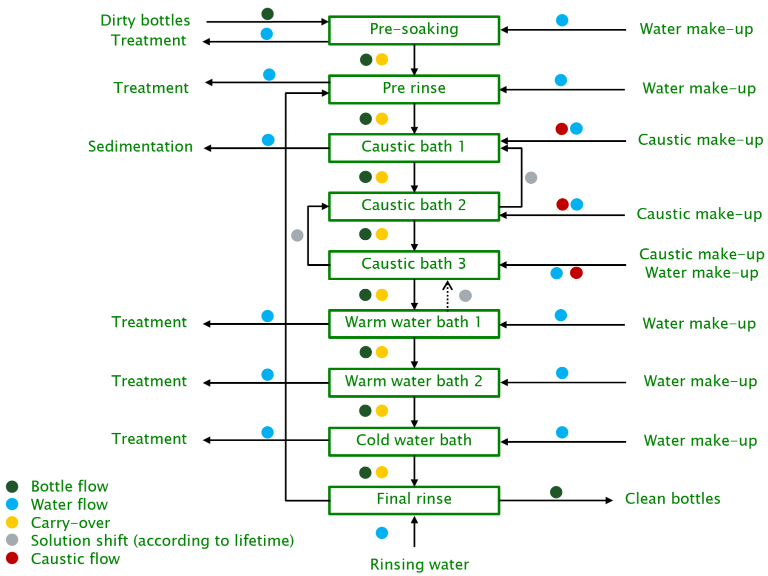


Figure 1.2: Conceptual process with water and caustic soda flows in a bottle washer

A sectional view of a typical bottle washer is presented in Fig.1.1, and the general process of beer bottle washers is included in Fig.1.2. To remove the pollutants from inside and outside of returned bottles, hot alkaline solutions consisting of caustic soda, i.e.

$NaOH$, are usually used in the form of hot baths. The concentration of the caustic solution is generally between 1.5% and 2%, and the temperature is usually between 65 $^{\circ}C$ and 70 $^{\circ}C$. According to empirical practices in breweries, the disposed caustic wastewater is usually first transferred to sedimentation tanks as the pre-treatment to remove solids before discharge from the breweries. Generally, the process consists of following major steps, sometimes with pre-soaking at the very beginning:

1. Pre-rinse
2. Caustic bath
3. Warm water bath and cold water bath
4. Final rinse

One of the most significant terms in this research was "carry-over". It refers to the thin layer of solution adhesive on the surface of beer bottles and conveying belt when bottles are rinsed or taken out from a bath of solution. The composition of the carry-over can be assumed to be identical as that in the rinsing effluent or the solution in the bath. Carry-over was the main variable to study in the modelling.

1.2. THEORETICAL BACKGROUND

In this section, some basic sustainability theories that used for this research will be introduced, including the concept of sustainability, water footprint, chemical footprint, and the 3 R's principle.

1.2.1. THE CONCEPT OF SUSTAINABILITY

The most widely accepted definition of "sustainable development" was originated from more than 30 years ago (Imperatives, 1987):

"Development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs."

The concept of sustainability can be related to different aspects in the human society, and it is vital to emphasise several dimensions from that. The three dimensions of sustainability can be included as economic, environmental, and social-cultural (Balkema et al., 2002). In this research, the environmental aspect will be the focus. Environmental sustainability is usually assessed by the ability of nature functions to sustain human life. The anthropological influences to the environment are mainly through obtaining natural resources and emitting pollution. Therefore, the environmental aspect of sustainability concerns mainly natural resource consumption and emission to the environment (Balkema et al., 2002).

As for the bottle washers in this research, the direct emission was identified as the highly caustic wastewater, composed of water, huge amount of caustic soda, and other impurities removed from the returned bottles. The direct resources consumed under concern were clean water, which is usually measured with water footprint, and caustic soda, within the scope of chemical footprint. It is not easy to really minimise the footprint of bottle washers, and there might be a long way to optimise bottle washers towards sustainability. This research started an initiative.

1.2.2. Water Footprint and Chemical Footprint

As one of the most significant indicators for sustainability assessment, the term "footprint" has been used to quantify the anthropological appropriation of natural resources during production (Hoekstra & Chapagain, 2006), and for describing the environmental burdens and impact on global sustainability generated from anthropological activities (Power, 2009). There are many types of footprint: water footprint, carbon footprint, chemical footprint, ecological footprint etc. Usually these footprint terms are used in life cycle assessment (LCA), integrated with environmental impacts (Sala & Goralczyk, 2013). In this research, LCA was not included in the scope, but chemical footprint and water footprint were assessed only for a certain bottle washer, where the caustic soda was the main focus.

Water footprint (WFP) can be defined as the volumes of water consumed by people, producing goods or services (Hoekstra & Chapagain, 2006). It has been defined as a significant indicator of direct and indirect water use by Hoekstra, 2008. The water audit work, which quantifies all the water flows for a certain system, gives decisive information for the redesign of sustainable bottle washers in terms of overall water management. There has been increasing need for water management and wastewater minimisation in industries, partially due to the increasing demand for fresh water. The development of methodology to minimise water and wastewater can effectively reduce overall fresh water demand and subsequently reduce the amount of effluent generated (Klemeš, 2012). But details and references on occupied space have not been given. With the discussion and calculation on the appropriate water reclaim techniques, space estimation will also be helpful to establish the treatment options in practice.

Similarly, chemical footprint (CFP) is the chemicals used in a certain production process. The potential risk from chemical consumption of a certain product, the anthropological and ecological hazard properties and the exposure potential of the ingredients can all be indicated with CFP (Panko & Hitchcock, 2011).

In this research, CFP and WFP were defined as the clean water and caustic soda consumed in a bottle washer, under certain conditions and within a certain period of operation. They were used as the parameters for analysing models and scenarios, and criteria for further model optimisation.

1.2.3. Reuse and Recycling of Water and Chemicals

Water reuse and recycling has drawn much attention from researchers, whereas chemical recovery has not. In food industry, around 70% of the total water use is not for the products but for other purposes such as cleaning and sanitising (Ölmez, 2013). This is regarded as one of the significant parts where water consumption can be reduced, without compromising product quality. Studies (Rögener et al., 2003) have been carried out looking into filtration technologies in terms of reusing bottle washers rinsing water. Besides, the anthracite/sand filtration as well as coarse and fine filters are proved to be the most successful options considering water quality and investment. With membrane processes treating the wasted alkaline solutions, COD elimination of up to 80% can be achieved and the required amounts of water, energy and chemicals will be reduced significantly (Götz et al., 2014). Super alkaline process water flows with a high product or co-product load have a negative effect on the filtration performance of low pressure membranes and should be eliminated or substituted before the filtration process. However, not much further investigations have been carried out in the scope, since the application of membrane separation in bottle washing alkaline solution treatment is considered as a state of art.

Effort has been devoted into eliminating polluting chemicals from industrial discharge, however, recovery and reuse should be the best approach to make products cleaner (Mawson, 1997). Membrane technologies have been regarded as good solutions for water and chemical recovery, and the cost is reducing dramatically (Hill, 2015), which is still a critical issue for other techniques. Nevertheless, there might be limitations on the feed water for some the membranes and pre or post treatment may be needed. Further systematic studies on effects of operational process variables need to be performed for the reclamation systems (Henck, 1995). Therefore, there is a demand to test the performance and cost of the design of treatment process with experiments.

Similar research focusing on industrial wastewater management has already been carried out several years ago in Heineken®, where cleaning-in-place (CIP) process was studied. According to a previous study by Holland, 2019, the major characteristics identified from the studied wastewater include COD, Na^+ and Total Nitrogen (TN). However, not all constituents were examined in the previous study, neither the designed networks of wastewater reuse and their feasibility, nor the economic benefits and drawbacks of the given solutions in the study. This guides future researchers to pay more attention to other components that may have an influence on sustainable designs.

1.3. OBJECTIVES AND RESEARCH QUESTIONS

To continue with the previous research on the chemical and water recovery, the objective of this thesis was formulated:

To build a mass balanced model of current bottle washers to better understand the loss of caustic soda due to physical processes, and to find suitable methods which can effectively recover caustic soda from the wastewater discharged from bottle washers.

Based on the limited knowledge in beer bottle washers and chemical reclamation, four research questions were raised to achieve the objective:

1. Can a model be built based on mass balance for a typical bottle washer to simulate caustic soda loss due to carry-over?
2. What is the typical composition of caustic effluent from the bottle washers?
3. Can the model of bottle washer be applied for different operational variables and structures as well as in industrial scale?
4. What are the most suitable methods for bottle washers to reduce the overall chemical consumption?

To solve the research questions, several research methods were used:

1. **Can a model be built based on mass balance for a typical bottle washer to simulate caustic soda loss due to carry-over?**
   Method: Use Python as the modelling tool, and mass balance methods to establish the relationship between operational variables in a bottle washing system, especially focusing on the caustic dosage, caustic loss and carry-over.
   Outcome: A conceptual Python model in which operational variables can be easily modified to adapt to other types of bottle washers.

2. **What is the typical composition of caustic effluent from the bottle washers?**
   Method: Literature reading and data collection from breweries. Necessary lab analysis on the composition of caustic bath solutions from a certain bottle washer.
   Outcome: A generic composition that can be used as the basis for the discussion over chemical reclamation and future research.

3. **Can the model of bottle washer be applied for different operational variables and structures?**
   Method: Trials with different values assigned to operational variables in scenarios and real-life operational data from breweries, analysis on how different variables influence the caustic soda loss.
   Outcome: Graphs of sodium concentrations in baths and rinsing effluents from models, and computation on caustic dose and loss.

4. **What are the most suitable methods for bottle washers to reduce the total caustic soda consumption?**
   Method: Simulating in different scenarios, literature review, analysing compositions of water samples from a real-life bottle washer, and discussion on existing technologies.
   Outcome: Suggestions on operational improvement after comparing optimisation scenarios based on current bottle washers regarding different criteria. Possible techniques according to the analysis on treatment and recovery process after the sedimentation of caustic effluent, which can be used for bottle washer wastewater.

2

METHODOLOGY

In this chapter, the methodologies that were used in this research will be introduced, including the calculation of electrical conductivity, mass balance model, Python modelling and details of the lab work to analyse received water samples. The first three methods would be used for the models and scenarios by programming, and the last part involves the detailed apparatuses and processes for the measurement of significant parameters for industrial water samples, including pH, conductivity, turbidity, total alkalinity, total suspended solids (TSS), total dissolved solids (TDS), chemical oxygen demand (COD), total organic carbon (TOC), volatile fatty acids (VFA) and inorganic ion species.

2.1. ELECTRICAL CONDUCTIVITY OF AQUEOUS SOLUTIONS

Although the total dissolved solids (TDS) can be a more intuitive parameter to assess salinity in water systems, measurement of the electrical conductivity (EC) is still simpler and more cost effective. With the ion concentrations in an aqueous solution, the EC can be easily calculated. The EC of aqueous solutions has been regarded as a universal standard of salinity in solutions. EC basically depends on the number of ions that are able to move under an electrical force. According to Atkins et al., 2014, the molar ionic conductivity was defined as the conductivity divided by the molar concentration. Ionic conductivity can be directly calculated with Kohlrausch equation (Daintith, 2008):

$$\Lambda_i = \Lambda_i^0 - K\sqrt{c_i} \tag{2.1}$$

where Λ_i is the molar ionic conductivity of ion i in the unit of $mS\ m^2/mol$, Λ_i^0 is the limiting molar conductivity in the unit of $mS\ m^2/mol$, c_i is the concentration of the electrolyte in mol/L, and K is an empirical coefficient known as the Kohlrausch coefficient, whose unit can be deducted as $mS\ m^{\frac{7}{2}}/mol^{\frac{3}{2}}$.

There has been much research on the solution EC, and several equations have been used by previous researchers to calculate solution EC. Visconti et al., 2010 assessed six commonly used equations with three ionic properties, i.e. analytical concentration, ionic activity and free ion concentration. It was proved that the best means to calculate conductivity at least up to 40 dS/m is based on Eq.2.2 (Reluy et al., 2004), where n is the total number of different ionic species, z_i is the charges carried by ion i in eq/mol, λ_i is the ionic conductivity the same as Λ_i in Eq.2.1 in the unit of $mS\ m^2/mol$, and c_i is the analytical concentration in mol/L. The calculation would be more precise using free ion concentration instead of analytical concentration. But in the bottle washers, it was assumed that the ionic activity should have minor influence on the conductivity. And the analytical concentrations were used to calculate EC in the baths for simplification but still accurate.

$$EC = \sum_{i=1}^{n} |z_i| \lambda_i c_i \tag{2.2}$$

Molar ionic conductivity of aqueous H^+, OH^- and Na^+ ions that would be used in the modelling are listed below:

Table 2.1: Ionic conductivity of H^+, OH^- and Na^+ (Adamson, 2012)

Ions	λ_i $(mS\ m^2/mol)$
H^+	34.982
OH^-	19.8
Na^+	5.011

2.2. MASS BALANCE OF WATER AND IONS IN A BATH IN THE BOTTLE WASHER

Mass balancing is a useful method to help understand the material flows into and out from a defined system boundary. With respect to the bottle washer, the mass balance can be established for the physical processes in each bath. The chemical reactions were not included in the model, thus, the OH^- was assumed not reacted in any bath. For the logic of the following Python models, a local mass balance in the n^{th} bath focusing on certain substances, including water, ions, and possibly contaminants in the future, in the baths can be expressed as iterated differential equations over time t:

- Water balance expressed in volume:

$$\frac{dV_n}{dt} = Q + Q_d - Q - Q_l = Q_d - Q_l \tag{2.3}$$

  Since the solution volumes in baths should be always kept within the bath volumes and avoid overwhelming, V_n can be taken as a constant for simplification.

- Na^+ balance:

$$\frac{dC_{n,Na^+}}{dt} \cdot V_n = Q \cdot C_{n-1,Na^+} + Q_d \cdot C_{d,Na^+} - Q \cdot C_{n,Na^+} + Q_l \cdot C_{n,Na^+} \tag{2.4}$$

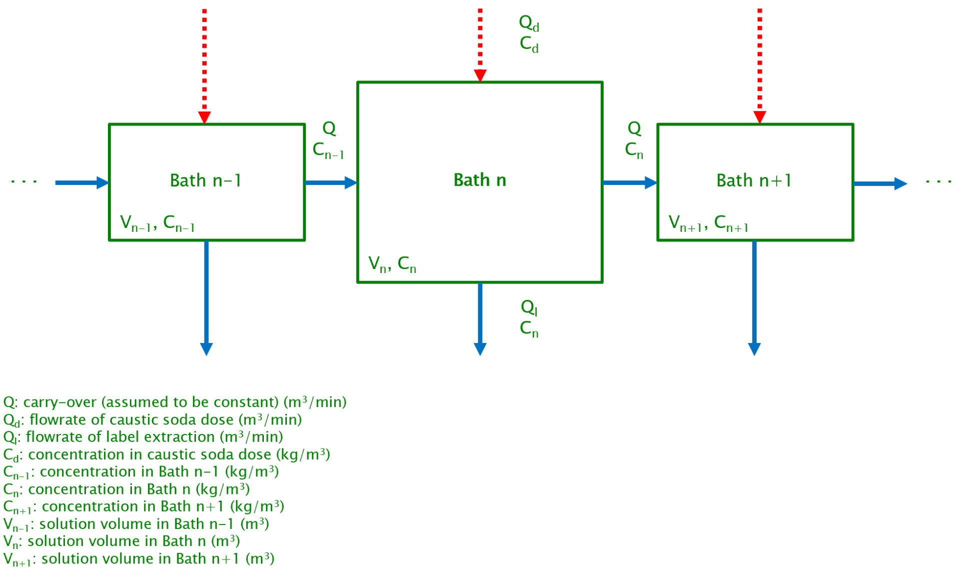


Figure 2.1: Local mass balance of physical processes related to the n^{th} bath in a bottle washer

- OH^- balance:

$$\frac{dC_{n,OH^-}}{dt} \cdot V_n = Q \cdot C_{n-1,OH^-} + Q_d \cdot C_{d,OH^-} - Q \cdot C_{n,OH^-} + Q_l \cdot C_{n,OH^-} \tag{2.5}$$

where V_n is the volume in the n^{th} bath in m^3, C_n is the concentration of Na^+ or OH^- ions in the bath in kg/m^3 Q is the constant flowrate of carry-over solutions on bottles in m^3/min, C_n is the concentration of Na^+ or OH^- ions in kg/m^3, Q_d is the volume of caustic soda solution automatically dosed if needed in m^3/min, Q_l is the label extraction flow rate in m^3/min.

For an operational cycle with a time span of T min and N baths in total, at the beginning of the operation when $t = 0$, caustic soda only exists in the caustic baths. At the end of the operational cycle when $t = T$, caustic soda exists in both caustic bats and water baths due to carry-over. The sum of $\frac{dC_n}{dt} \cdot V_n$ over the whole time span T for the bath should equal to the difference of total mass at the beginning and the end over the lifetime. Then this bath shall be considered as mass balanced for the substance. C_n can be the concentration of either Na^+ or OH^-. The full mass balance is presented in Appendix.A.

$$C_{n,t=T} \cdot V_n - C_{n,t=0} \cdot V_n - \int_{t=0}^{t=T} (\frac{dC_n}{dt} \cdot V_n)\, dt = 0 \tag{2.6}$$

The mass balance can also be extended to other components in the bottle washers, for example, organic compounds and trace elements. The chemical reaction consumption, such as the reaction of OH^- with organic impurities and CO_2, can also be included based on a thorough survey of the bottle washer solution composition to make it a more complete model for the future.

2.3. MODELLING WITH PYTHON

Modelling is a method to simulate a certain process based on input variables and predict the theoretical results in graphs or numbers. One of the biggest advantage to build models with programming is that programs can be trained to adapt to variable scenarios a big research (Maxville, 2018). Python was used as the programming language to build all the two models and following scenarios in this research, and the models can be used by future researchers for further improvement. In order to simulate the influence of carry-over solutions on the surface of beer bottles, the author built a model and generated graphs with respect to time series. There are multiple tools for modelling, and Python programming is one of them. In this research, Python will be used to complete the modelling part. The benefits of Python programming includes but not limited to:

- Mature language that is flexible and easy to use;
- Open source programming leads to high accessibility;
- Automatically handle low-level tasks which must be handled manually in some traditional languages (Lutz, 2001);
- The improvement and optimisation of the process are also more convenient and fast by modelling compared with experiments
- Able to track variables at any specific time unit.

The procedures of the modelling process started with the general study on current bottle washers. Common components of bottle washers were studied based on samples from breweries and bottle washer suppliers. By analysing the water flows within the bottle washers, an preliminary model was built based on an imaginary bottle washer, which could be modified for other types of bottle washers in the future. The second step was to test the model with changing variables. On the one hand, the performance of the model can be tested on extreme variables. On the other hand, it could be regarded as a simple sensitivity test on the model.

When the model was ensured with the changing variables, it was applied to a real-life case. A questionnaire containing significant questions regarding the bottle washer operation was designed and distributed to breweries. Based on the answers collected from cooperate breweries, the first model would be adapted to the real-life cases. The outcome of the questionnaire would be the second model, which was built with operational data provided by a Spanish brewery, and a real bottle washer was then simulated. Comparing the modelling results and real-life data, some primary conclusions could be drawn on the caustic soda loss. To solve the problem of high loss of caustic soda, several optimisation scenarios were simulated and compared to find out solutions.

In total, there would be two models and nine scenarios, four scenarios for the imaginary bottle washer model and five scenarios for the real-life model respectively. The models and scenarios are listed below with abbreviations and working conditions:

1. **Base scenario (BS):** Imaginary model with high adaptability (simple and full)
   1.5% 2% caustic soda, 1.5 $mL/bottle$ *carry-over, intermittent dosing*

- **Test Scenario 1 (TS-1):** Extreme carryovers
  [0.15, 1.5, 15] mL/bottle carry-over
- **Test Scenario 2 (TS-2):** Continuous dosing
  2% caustic concentration maintained, 15 mL/bottle carry-over
- **Test Scenario 3 (TS-3):** Various carry-overs
  [10, 15, 20] mL/bottle carry-over with continuous dosing
- **Test Scenario 4 (TS-4):** Various caustic concentrations
  [1%, 1.5%, 2%] caustic concentrations with continuous dosing

2. **Valencia model (V):** Real life operational data (1 week and 3 months)
   1.5% 2% caustic soda, 10 mL/bottle carry-over, internal recirculation

   - **Optimised Scenario 1 (OS-1):** Reduced rinsing flowrates
     [75%, 75%, 75%, 150%] of original rates
   - **Optimised Scenario 2 (OS-2):** Increased water bath volume
     3 times of original volume
   - **Optimised Scenario 3 (OS-3):** Label extraction recirculation
     90% reuse of label extraction effluent
   - **Optimised Scenario 4 (OS-4):** Reduced carry-over
     7 mL/bottle carry-over
   - **Optimised Scenario 5 (OS-5):** Reduced caustic concentrations
     1.0% 1.5% caustic soda concentrations

2.4. LAB ANALYSIS ON WATER SAMPLES: APPARATUSES AND PROCESSES

Due to the lack of information on the compositions of caustic beer bottle washer effluent, a lab analysis on three caustic bath water samples was carried out. The water samples were obtained from another cooperate brewery located in Belgium. Basic parameters that are significant for industrial wastewater analysis, including pH, conductivity, turbidity, total alkalinity, total suspended solids (TSS), total dissolved solids (TDS), chemical oxygen demand (COD), total organic carbon (TOC), volatile fatty acids (VFA) and inorganic ion species, were measured from the samples. According to the analysis results, the possibilities of several treatment solutions can be discussed.

Bulk water samples were stored in three separate plastic containers under room temperature for one and half months, then transferred into a cold cell under 6 $^{\circ}C$ for at least 48 hours' sedimentation to simulate the common pre-treatment process in the breweries. Before all the measurement, samples were taken out from the cold cell to maintain the room temperature for accuracy.

2.4.1. pH, ELECTRICAL CONDUCTIVITY AND TOTAL ALKALINITY

The pH and conductivity of water samples were measured by Multimeter model IDS 9430, with SenTix® 94x(-P) pH probe and TetraCon® 325 conductivity sensor respectively. The pH meter was calibrated before use with standard buffer solutions of pH

4.01, 7.00, and 10.00 respectively. The temperature was measured together with the pH probe. Turbidity was measured with Hach® 2100N laboratory turbidimeter with well mixed samples.

Alkalinity of a water body is the buffering capacity to resist acidity (Addy et al., 2004). Total alkalinity A_T of a solution can be defined as the excess of H^+ acceptors over H^+ donors regarding to zero level of H^+ where the dissociation constant of acids $K = 10^{-4.5}$ (Dickson, 1981). With non-conservative ions, whose concentrations change with pH, solutions gain some buffering capacity against pH change.

The total alkalinity of water samples were measured by titration. Attribute to the high pH, 1 mol/L, instead of 0.1 mol/L, hydrochloric acid solution was used. Titration started from the original pH until the alkalinity equivalence point of pH 4.3, where $A_T = 0$ (Wolf-Gladrow et al., 2007). The titration device used for the analysis was SM Titrino 702. In the built-in program, the pH meter of this device could only be calibrated with 4.01 and 7.00 standard buffer solutions. Therefore, the starting pH of the samples were taken from the pH meters instead of directly from the titration device. Samples were well mixed and 50 mL of each sample was transferred into a beaker for titration. The samples were continuously stirred during the whole titration process. The alkalinity could be calculated according to the acid volumes V_a, sample volumes V_s and normality of the acid N_a. Normality is defined as the product of molarity (mol/L) and the number of hydrogen exchanged in a reaction (eq/mol) (Harvey, 2000). With the following equation (Metrohm, 2020), where the normality of hydrochloric acid equalled to 1 eq/L, A_T could be calculated into $CaCO_3$ equivalent:

$$\frac{V_a\,(L) \times N_a\,(eq/L) \times 50\,(g\ CaCO_3/eq)}{V_s\,(L)} = A_T\,(g\ CaCO_3/L) \tag{2.7}$$

All the parameters above were measured only once for the samples, and parameters below were measured with three duplicates for each water sample to ensure accuracy.The average values were calculated as the final results, if the bias of the results from three duplicates was within an acceptable range of 5% of the average. If the result from one duplicate was obviously different from the others, the analysis of that duplicate would be repeated to eliminate the error.

2.4.2. Total Suspended Solid and Total Dissolved Solid

The traditional way to measure TSS (Cole-Parmer, 2021) and TDS (Environmental Express, 2021) is to filter the water samples with filter paper. With TSS, the samples were filtered with 0.4 μm filter paper, and 0.2 μm filters for TDS measurement. The results can be calculated according to the weight difference of the filter papers or water sample containers before and after drying.

TSS were measured twice during the lab analysis with different volumes of samples and filter paper of different pore sizes. For the first time, 100 mL water samples were filtered with glass fibre filter paper Whatman® GF/F 1825-070 with 0.7 μm pore size, and 250 mL samples with 0.4 μm filter paper MN® 85/220 BF for the second time. Before filtration, the filter papers were weighed with their own containers. The weights were noted as the initial value. After weighing, filter papers were put on the vacuum filters and wetted by demi-water. Water samples were poured on the filter paper with vacuum, and the samples remained on the filter were washed off onto the filter paper with demi-water. Then the filter papers were collected from the filters back to the specific containers, and dried under 104 $°C$ for at least 1 hour until the filter papers had been fully dried. After drying, the filter papers with containers were weighed again at room temperature for the final weight. TSS contents could be calculated with the following equation (Cole-Parmer, 2021):

$$\frac{Weight_{final}\,(g) - Weight_{initial}\,(g)}{Sample\ volume\,(mL)} \times 10^6 = TSS\,(mg/L) \tag{2.8}$$

TDS were measured with similar filtration process as TSS, while the filtrate was transferred into a container to dry and weigh. Before vacuum filtration, the empty containers were weighed as the initial value. Water samples were filtered with glass fibre filter paper MN® 85/220 BF with 0.4 μm pore size, and then CHROMAFIL Xtra PA with 0.2 μm pore size. There was no demi-water rinsing process during filtration to ensure that TDS content in the filtrate could be maintained the same as in the feed. 20 mL filtrate was transferred to each container, after which the containers were dried under 180 $°C$ for at least 1 hour until no liquid was left in the containers. After drying, the containers with solids were weighed again at room temperature for the final weight. TDS in the bottle washer wastewater was expected to be relatively higher with the impurities, thus, the unit of g/L might be more appropriate. TDS contents could be calculated with the following equation (Environmental Express, 2021):

$$\frac{Weight_{final}\,(g) - Weight_{initial}\,(g)}{Sample\ volume\,(mL)} \times 10^3 = TDS\,(g/L) \tag{2.9}$$

2.4.3. CHEMICAL OXYGEN DEMAND AND TOTAL ORGANIC CARBON

Hach® test kits were used to determine the COD and TOC concentrations in the water samples. Based on a preliminary estimation of COD content in the water samples, a test was carried out with Hach® LCK514 kits with range of 100-2,000 $mg\ O_2/L$, where it was indicated that the COD concentration in the sample was out of range. Then LCK014 kits with a higher COD range of 1,000-10,000 $mg\ O_2/L$ were used to get accurate measurement. For TOC measurement, LCK387 kits were used with range of 300-3,000 $mg\ C/L$. All the procedures were carried out following the instructions of respective kits mentioned above.

2.4.4. ION CONCENTRATIONS

During the operation of bottle washers, sodium hydroxide is dosed along with the washing process. OH^- ions are consumed for cleaning, whereas Na^+ ions are not. Therefore, the ions with highest concentrations in the water samples were expected to be Na^+ and OH^-, whereas OH^- concentrations were directly calculated from pH. Due to the high difference between the concentrations of Na^+ and other ions, samples were tested twice with different dilution factors, 10 and 1,000 respectively, with Ion Chromatography (IC) produced by Metrohm®. The IC was equipped with 919 auto-sampler, 818 anion system, 883 cation system and MagIC Net software. A Supp 5 150/4.0 column was used as a standard anion column, and a C6 Cation 150/4.0 column was used as a standard anion column. With standard solutions, anions including F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}, as well as cations including Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} were detectable in IC samples. Samples were filtered with 0.2 μm CHROMAFIL Xtra PA filters before dilution. In the 10 times demi-water diluted samples, all the ions except for Na^+ were measured. In the demi-water 1,000 times diluted samples, only Na^+ concentration were measured.

2.4.5. VFA

VFA concentrations in water samples were measured with Gas Chromatography (GC) produced by Agilent®. The dilution factor was two for all the three water samples with internal standard pentanol solutions (325.8 mg/L) for the column. 1.5 mL vials were used to prepare the samples. Samples were filtered with 0.2 μm CHROMAFIL Xtra PA filters. 750 μL filtered samples were added to 750 μL standard pentanol solutions in the vials, and another 10 μL formic acid (purity higher than 99%) was added. The samples were measured with GC method FREE FATTY ACIDS3.M.

3

Base Scenario Modelling with Testing Scenarios

So far, there has been limited study on the water and chemical flows within a bottle washer. To better understand how water and chemicals travel through and leave the bottle washer, a Python model can be helpful. The model can also be used to evaluate how much water and chemicals are lost during operation, and where are the loss points.

In this chapter, a Python model was built based on an imaginary bottle washer structures and operational variables, noted as the Base Scenario (BS) model. This model was built from a simple structure with two baths and then extended to a relatively more complicated structure with ten baths. It would only provide an insight about how much caustic soda could be lost only due to carry-over but not consumed in chemical reactions. Therefore, the results should not be directly related to any real-life problems. The BS model could also be easily modified to simulate other bottle washers by modifying the structure of baths and rinses, as well as assigning new values to the operational variables.

The results of this first Python model and its four following Testing Scenarios (TS-1 to TS-4) will be presented in graphs and tables with analysis. The BS model showed the very basic working mechanisms of a typical bottle washer, and was tested by changing different operational variables in the scenarios. The possible chemical reactions in a caustic bath from a bottle washer will be discussed at the end of this chapter as well.

3.1. Aim of Modelling and Operational Variables

From the industrial field, it is easy to quantify chemical consumption according to the procurement data. However, the chemical flows in an industry can be complicated. In the beer bottle washers, caustic soda solutions are dosed for bottle washing. Caustic soda is either consumed by impurities or lost in the wastewater due to physical reasons such as carry-over and label extraction. By identifying the different components that contributed to the total caustic soda consumption, it will be more clear on how much caustic soda can be conserved from each component. Consequently, the improvement and optimisation towards chemical footprint reduction can be more individualised. Carry-over is one of the components that are regarded significantly related to caustic soda loss from bottle washers. Nevertheless, it is difficult to measure the exact caustic soda loss that is only due to carry-over during daily operations. Therefore, modelling is needed to investigate how much influence carry-over has on the overall caustic soda consumption in a bottle washer.

To build models for bottle washers with programming, understanding how they are operated is the preliminary task. Although there is not much research on the performance of bottle washers, some information can already be obtained from empirical daily operation:

- The range of caustic soda that is universally used in most bottle washers is approximately 1.5% to 2%, and caustic soda can be dosed automatically when the concentration is detected below 1.5% or when EC is detected below a certain value.
- 25% concentrated caustic soda as make-up materials.
- Solutions in caustic baths can be shifted forward after cycle time of one to two weeks, and solution from the first caustic bath will be discharged to sedimentation.
- The wastewater of final rinse can be reused in the pre-rinse, and then will be discharged to treatment plant.
- The inner surface of bath tanks will be completely cleaned every two to three months.

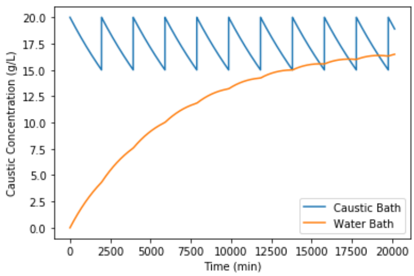
Based on the information, a simple model was established with only one caustic bath and one water bath of 17 m^3 without any chemical reactions, then it was expanded to a full BS model with five caustic baths followed by five water baths of 17 m^3 without any chemical reactions. The simulated operation cycle had a time span of 14 days with intervals of 1 min. The range of caustic soda concentration was 1.5% to 2%, i.e. 1.5 to 2.0 $g\ NaOH/L$, as a typical operation parameter for most bottle washers. The flowrate for both pre-rinse and final rinse was 10 m^3/h where the effluent of final rinse was reused for pre-rinse. It was assumed that the caustic soda concentration would be raised to 2.0 $g\ NaOH/L$ with the automatic dose. It was assumed that caustic soda was dosed as solid form with molecular weight of 40 g/mol containing sodium of 23 g/mol. Therefore, the volume change due to caustic soda dose did not exist in this model. Water and caustic soda loss between baths was neglected and the change in temperature was not taken into consideration as minor influencing variables. The density of 2.0% caustic soda solution should be 1.019 kg/L and the density used in the models was 1 kg/L, the minor difference was neglected. For the BS model, it was possible to change the volume of any bath, the range of caustic soda concentrations in caustic baths, number of baths, operational time span, time interval, carry-over per bottle, and the speed of bottle inflow.

Studying the caustic soda carry-over, the target substance for the mass balance would be the mass of caustic soda. Thus, in water baths, there will be no automatic caustic soda dose. In the first caustic bath, the caustic concentration in the inflow equalled to zero at the beginning of simulation for Eq.2.4 and Eq.2.5 because it was assumed that bottles enter the bottle washer without any caustic.

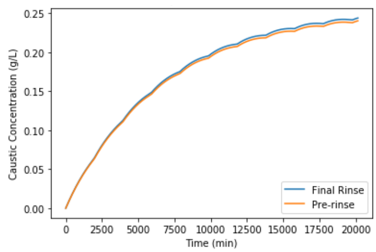
3.2. BASE SCENARIO (BS) MODEL

In this section, the BS model will be elaborated. This was a basic model for an imaginary bottle washer with assumed operational variables and without chemical reactions. By modifying the structure or variables in this model could it be adapted to other bottle washers as well. The model started from a simple setup, and expanded to a more complicated setup afterwards.

3.2.1. SIMPLE BS MODEL WITH TWO BATHS



(a) Caustic concentrations in the baths of the simple BS model



(b) Caustic concentrations in the rinse effluents in the simple BS model

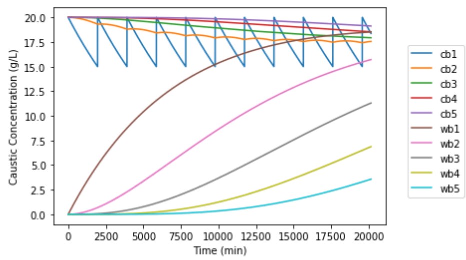
Figure 3.1: Caustic soda concentrations in baths and rinse effluent in the simple BS model

With the results from the simple model in Fig.3.1a, it was clear that there was periodical fluctuations in the water bath when caustic soda was dosed in the caustic bath. This could be seen from the serrated curve of the caustic concentration in the caustic bath, and the small fluctuation in the water bath. Every serration in the blue curve was an automatic dose of caustic soda triggered by low caustic concentration in the caustic bath. With the increasing caustic concentration in the water bath, the difference of caustic concentration between the caustic bath and the water bath decreased with time. Therefore, the rate of increase in the water bath caustic concentration decreased with time, and the curve was convex. After simulation of about nine days, which equalled to about 12,960 min in 3.1a, the caustic concentration in the water bath reached the same level as caustic bath.

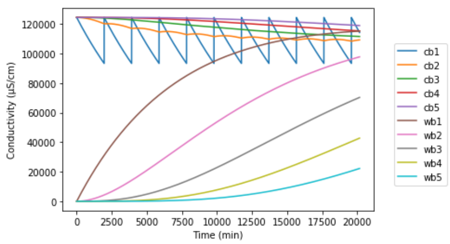
The the concentration at the end of the simulation was 16.527 g/L. This made it possible to shift the water bath forward and serve as a caustic bath after the operational cycle. However, due to the high caustic concentration in the water bath, the total caustic soda loss over the time span was calculated as up to 597.628 kg, which was quite significant compared with the total dose of 850.340 kg. The average caustic soda consumption was defined as the total caustic soda dose divided by the total number of bottles entering the bottle washer over the whole simulation, calculated as 2.531×10^{-5} $kg/bottle$. In Fig.3.1b, minor differences could be noticed between the effluent from pre-rinse and final rinse. This was caused by the delay in the reuse of final rinse effluent. Both of the curves were concave, with the similar shape of caustic concentration curve in water bath in Fig.3.1a. The total loss of caustic soda was then calculated as the sum of discharge of pre-rinse and the carry-over from final rinse, summing up to 588.852 kg.

The mass balance for the caustic and water baths were calculated as -0.004 kg and 0.045 kg respectively. The differences could be caused by the bias in the millions of calculations in the model. The results of mass balance were too low to be regarded as open mass balance compared with the total dose of 850.34 kg. Based on these minor differences, this model could be regarded as mass balanced.

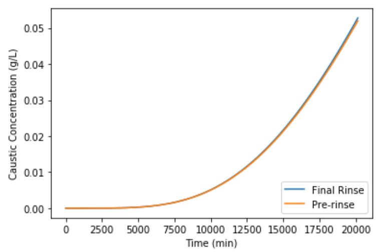
3.2.2. FULL BS MODEL WITH TEN BATHS



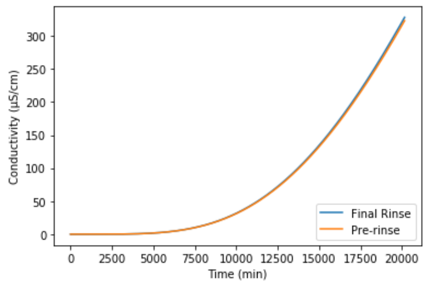
(a) Caustic concentrations in the baths of the full BS model



(b) Conductivity in the baths of the full BS model



(c) Caustic concentrations in the rinse effluents of the full BS model



(d) Conductivity in the rinse effluents of the full BS model

Figure 3.2: Caustic concentrations and conductivity in the full BS model ("cb" for caustic bath, "wb" for water bath)

The results from the full BS model without considering chemical reactions are shown in Fig.3.2. Basically only the curve for the first caustic bath was the same as in the simple model, thus the caustic dose was the same as well. In the legend, "cb" stands for caustic bath and "wb" stands for water bath.

It was good to notice that, caustic soda was dosed only in the first caustic bath. In the following four caustic baths, caustic soda was made up by the previous caustic bath, thus the caustic concentrations never declined to 1.5%. Only in the second caustic bath could the caustic concentration fluctuations due to automatic caustic soda dose in the first caustic bath be obviously observed. From the third caustic bath and on-wards, the curves were visually smooth. The final caustic soda concentrations also increased from the second caustic bath to the fifth, from 17.559 $g\ NaOH/L$ to 19.124 $g\ NaOH/L$. As a result, it should be possible to shift the last 4 caustic baths forward after the time span. The convex shape of the curves for water baths became less obvious along the sequence.

This was because the caustic concentration in the first water bath was increasing rapidly, and there would be a delay in the following four baths to go up. The final caustic soda concentration in the first water bath was already 18.520 $g\ NaOH/L$ which was higher than in the simple model due to the higher caustic soda concentration maintained in the last caustic bath, and that in the last water bath was only 3.580 $g\ NaOH/L$.

Compared with the simple BS model, the total loss of caustic soda from the full BS model was much lower as 43.560 kg. This provided the information that the overall caustic loss could be limited by using several water baths after the caustic baths. The caustic concentration curve for the first water bath was clearly convex as shown in Fig.3.2a. However, the curves for the last two water baths, as well as the rinses, were concave. This could be explained by the rapid increase in caustic concentrations in the previous water baths, and the delay in concentration increase in the last two water baths.

Daily loss of caustic was modelled to be an increasing trend, due to the increasing caustic concentration in the last water bath. The total loss of caustic soda was then calculated as the sum of discharge of pre-rinse and the carry-over from final rinse, summing up to 42.917 kg, which was much less than the simple model. The major part of 42.273 kg was discharged to the wastewater treatment plant as effluent from pre-rinse.

This full BS model could be considered as mass balanced with the following calculation results according to Eq.2.6. The final mass balances of each bath can be found in Table 3.1.

Table 3.1: Overall caustic soda mass balance of each bath in the BS model

Baths	Mass Balance (kg)
Caustic Bath 1	-0.004
Caustic Bath 2	-0.002
Caustic Bath 3	0.001
Caustic Bath 4	0.002
Caustic Bath 5	0.001
Water Bath 1	0.046
Water Bath 2	0.039
Water Bath 3	0.028
Water Bath 4	0.017
Water Bath 5	0.009

In chemical reactions between organics and caustic soda, which will be explained in the end of this chapter, the effective part is the hydroxy radicals which help with the decomposition of organics. The sodium ions were assumed to just remain in the solutions. Thus, with the current results, it was already enough to track the sodium flows and concentrations within the bottle washing system. During the 14 days' operation, there was still 24.677 kg sodium lost from the system. The major part of 24.307 kg was discharged to the wastewater treatment plant as effluent from pre-rinse after an operation of the full BS model for 14 days. This value might be very large, and the real-life design of bottle washers could be greatly different from this BS model. Therefore, this BS model just provided a basic structure for future real-life modelling as stated in the aim, but should not directly be directly related to real-life cases.

The major chemical components for the bottle washers to study is caustic soda, i.e. $NaOH$. When caustic soda is dissolved in water, Na^+ and OH^- will be ionised from the it. The concentrations of Na^+, H^+ and OH^- can be calculated accordingly by solving Functions 3.3.

$$H_2O \longrightarrow H^+ + OH^- \tag{3.1}$$

$$NaOH + H_2O \longrightarrow Na^+ + OH^- \tag{3.2}$$

$$\begin{cases} c_{Na^+} + c_{H^+} = c_{OH^-} \\ c_{Na^+} \times c_{OH^-} = 10^{-14} \end{cases} \tag{3.3}$$

After solving the above functions, c_{H^+} and c_{OH^-} can be interpreted by c_{Na^+} which will be directly calculated by the models:

$$\begin{cases} c_{H^+} = \dfrac{-c_{Na^+} + \sqrt{c_{Na^+}^2 + 4 \times 10^{-14}}}{2} \\ c_{OH^-} = \dfrac{2 \times 10^{-14}}{-c_{Na^+} + \sqrt{c_{Na^+}^2 + 4 \times 10^{-14}}} \end{cases} \tag{3.4}$$

3.3. Testing Scenarios with Different Carry-over, Dosing Pattern and Caustic Concentrations

To test with different operational variables, different values were assigned to compare the total caustic dose, loss and average consumption in the modelling results. With the four testing scenarios TS-1 to TS-4, the impact of changing different variables could be concluded.

TS-1: Extreme carry-overs

Table 3.2: TS-1: Caustic soda dose and loss with extreme carry-overs

	Carry-over (mL/bottle)			Unit
	0.15	1.5	15	
Total Dose	85.003	850.340	7833.324	kg
Average Consumption	2.530×10^{-3}	2.531×10^{-2}	2.311×10^{-1}	g/bottle
	7.667×10^{-4}	7.670×10^{-3}	7.064×10^{-2}	g/hL beer
Total Loss	0 (0%)	42.917 (5.05%)	6615.477 (84.45%)	kg

As the main target of this modelling, carry-over greatly influenced the loss of caustic soda. With extreme carry-overs to magnify its influence, it could be concluded that the higher carry-over, the more caustic soda were lost, with both higher quantities and higher loss percentage.

Table 3.3: TS-2: Caustic soda dose and loss with continuous and intermittent dosing pattern

	Dosing Pattern		Unit
	Continuous	Intermittent	
Total Dose	9128.914	7833.324	kg
Average Consumption	2.717×10^{-1}	2.311×10^{-1}	g/bottle
	8.233×10^{-2}	7.064×10^{-2}	g/hL beer
Total Loss	7430.922 (81.40%)	6615.477 (84.45%)	kg

TS-2: CONTINUOUS DOSING PATTERN

With continuous dosing and automatic dosing according to the caustic concentrations in the caustic baths, the dosing pattern did not greatly influence the percentage of caustic soda loss, which could be greatly determined by carry-over. Nevertheless, continuous dosing pattern led to higher dosage demand and consequently higher caustic loss.

TS-3: VARIOUS CARRY-OVERS

Table 3.4: TS-3: Caustic soda dose and loss with different carry-overs

	Carry-over (mL/bottle)			Unit
	10	15	20	
Total Dose	6304.735	9128.914	11808.593	kg
Average Consumption	1.876×10^{-1}	2.717×10^{-1}	3.514×10^{-1}	g/bottle
	5.686×10^{-2}	8.233×10^{-2}	1.065×10^{-1}	g/hL beer
Total Loss	4606.079 (73.06%)	7430.922 (81.40%)	10111.278 (85.63%)	kg

By comparing the caustic loss with varying carry-overs within relatively reasonable range for industries, the obvious difference in caustic loss was still obvious. With a fixed difference of 5 mL in carry-over, the caustic loss varied greatly in quantity but slightly in percentage. It could be concluded that the higher carry-over, the more caustic soda would be lost with both higher quantities and higher loss percentage. With the same change in carry-over, the higher carry-over, the lower influence it had on the caustic loss, both in quantity and percentage.

TS-4: VARIOUS CAUSTIC CONCENTRATIONS

Table 3.5: TS-4: Caustic soda dose and loss with different caustic soda concentrations in caustic baths

	Caustic soda concentrations (%)			Unit
	1.0	1.5	2.0	
Total Dose	3152.367	4728.551	6304.735	kg
Average Consumption	9.382×10^{-2}	1.407×10^{-1}	1.876×10^{-1}	g/bottle
	2.843×10^{-2}	4.265×10^{-2}	5.686×10^{-2}	g/hL beer
Total Loss	2303.040 (73.06%)	3454.560 (73.06%)	4606.079 (73.06%)	kg

To clearly present the influence of caustic concentrations on caustic loss, continuous dosing pattern was used to maintain uniform concentrations in caustic baths. The percentage of caustic soda varied within a normally used range of 1.0% to 2.0%. It was clear that caustic soda loss was not influenced by concentrations, but the higher concentration, the higher loss.

Summary for Testing Scenarios

The total amount of caustic soda dosage was influenced by the carry-over, concentrations used in caustic baths, and dosing pattern. The percentage of caustic soda loss from total dosage was greatly influenced by the carry-over, slightly influenced with continuous dosing, and not influenced by the concentrations in caustic baths. The testing scenarios could also be regarded as a basic sensitivity analysis of caustic soda dosage and percentage of loss over different operational variables.

3.4. Chemical Reactions in Caustic Baths

Although the chemical components of bottle washer wastewater has not been thoroughly studied yet, the main ions can be deduced according to the working mechanism. Two predominant ion species are mainly from the caustic soda, which is used for cleaning bottles, and possibly returned bottles themselves. From bottles, a small amount of beer residue may still exist in the first caustic bath. A more important problem comes from the labels and glue. Cellulose and glue also dissolve in the highly alkaline solutions. With caustic soda dosage, there will be a large amount of Na^+ and OH^- in the caustic baths. A very small portion of the ions might be Ca^{2+}, Mg^{2+} and CO_3^{2-} from beer residue, and can be negligible after pre-rinse.

The chemical reactions can be divided into organic and inorganic reactions. Organic compounds can be roughly distinguished as sugar, protein and lipid. Sugar basically does not react with caustic soda. Protein can be hydrolysed into amino acids, and lipids into fatty acids. Some possible chemical reactions that happen in the caustic baths, consuming OH^-, may include:

- Neutralisation: (including VFA, LCFA and amino acids)
  $H^+ + OH^- \longrightarrow H_2O$
- CO_2 dissolution:
  $CO_2 + OH^- \longrightarrow HCO_3^-$
  $HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$
- Ester hydrolysis:
  $R-COO-R' + OH^- \longrightarrow R-COO^- + R'-OH$

Besides reactions mentioned above, scaling is also happening when Ca^{2+} and Mg^{2+} combine with CO_3^{2-} to form scale in baths and on the conveying belt. Therefore, the hardness of water used in bottle washers is critical.

4

Real-life Case Modelling: Valencia

Although an imaginary BS model had been built which could be applied with different operational variables, it was important to utilise it in some real-life cases to test its adaptability with a more realistic and complicated structure. A questionnaire for breweries was designed to collect operational information from industries to establish the real-life model. Answers to the questions were received from a Spanish brewery. The questionnaire with answers can be found in Appendix.B. In this chapter, the real-life model, based on the Heineken® Espana brewery Quart de Poblet, which will be noted as "Valencia brewery" for short in the following sections, located in Valencia, Spain, will be introduced. By analysing the modelling results and comparing with the real-life data, the conclusion on significance of carry-over on the overall chemical consumption could be drawn.

4.1. Quart de Poblet (Valencia): Basic Information

In the brewery, both 33 cl and 25 cl returnable bottles are accepted. According to the questionnaire completed by Quart de Poblet, the annual beer production in Valencia brewery from Year 2020 was 13,549,770 L in 42,137,232 bottles. Some beer produced was filled into new bottles, and the rest into recyclable bottles, which were first cleaned with their bottle washers. Around 37,693,273 bottles of 33 cl and 444,396 bottles of 25 cl were used in Year 2020. Therefore, the 33 cl bottles would be considered as majority and used for the Valencia Python model. The daily consumption of 25% caustic soda solution is around 3.6 m^3/day, which equals to 900 $kg\ NaOH/day$. At present, there is no chemical recovery process on site in Valencia. Wastewater from label extractions and caustic baths is transferred to sedimentation tank directly for 48 hours' sedimentation, and the effluent from pre-rinse is directly sent to a treatment plant.

In the Valencia brewery, there are several production lines, and the reply on the questionnaire was provided based on Line 32 for returnable bottles. The bottle wash-

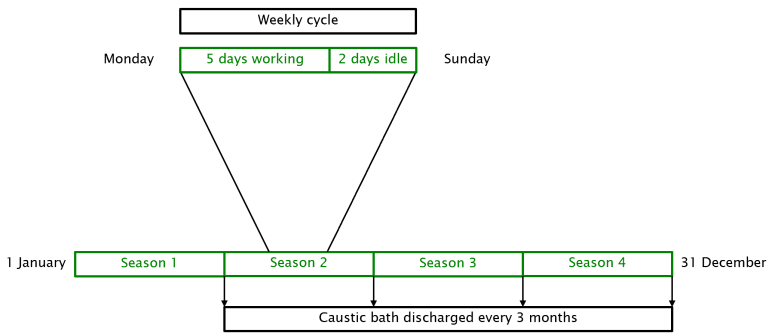
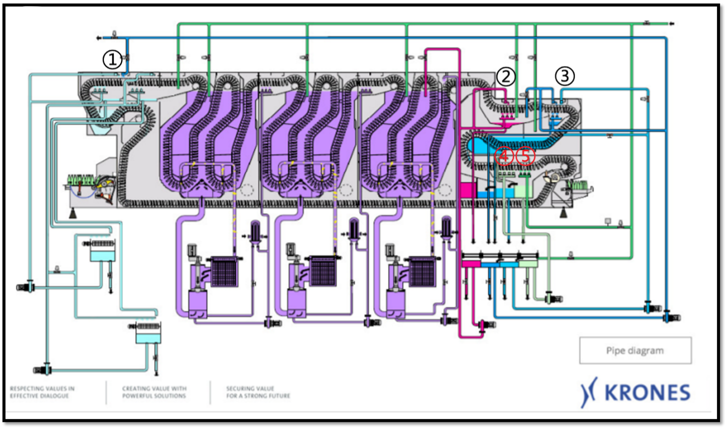


Figure 4.1: Example for Valencia bottle washer annual working periods

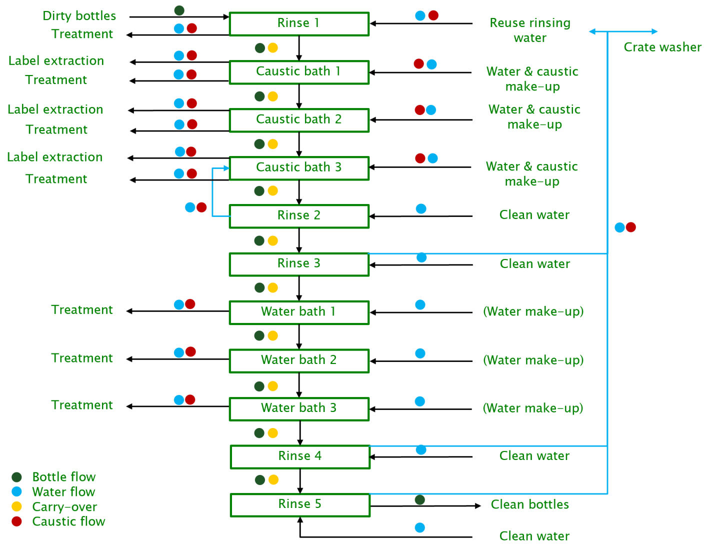
ers work from Monday to Friday, and stop during weekends when there are no staff on site. There are effluents from the label extractors, which are positioned in all the caustic baths as shown in Fig.4.2, every hour during working. The wet waste labels are pressed and then disposed. Discharge of caustic bath wastewater happens approximately every three months, and a thorough cleaning of the bottle washers follows. These bottle washers were purchased from KRONES®, one of the most popular suppliers in food and beverage industries in Europe. The section view of a bottle washer from Valencia is shown in Fig.4.2a, and the bottle washing process is presented in Fig.4.2b as a flow chart. Compared with the originally modelled bottle washers, some differences, besides different operational variables, were noticed in Valencia bottle washers:

- There were two rinsing processes between the last caustic bath and the first water bath, presented in Fig.4.2a as ② and ③ respectively.
- There were two final rinsing processes after the water baths, presented in Fig.4.2a as ④ and ⑤ respectively.
- The volume of water baths was much smaller than the original model, and all the three baths were indicated as hot water baths with specified temperature of 65 $°C$ and 55 $°C$. One cold water bath, whose temperature was lower than 45 $°C$, was positioned at the very end, with volume of 0.52 m^3, and was considered to be negligible.
- Another water recirculation occurs within Valencia bottle washer from the second rinse to the last caustic bath to reduce loss of caustic soda.
- The label extraction was also modelled in the Valencia bottle washer.
- The concentration of make-up caustic solution is specified in Valencia. In the real-life modelling, the caustic supplement was considered as solution rather than solid. Changes in volume in caustic baths were therefore modelled as well.

4



(a) Sectional view of the KRONES® bottle washer purchased by Valencia with water flows



(b) Conceptual process with water and caustic soda flows in a Valencia bottle washer

Figure 4.2: Valencia bottle washer: Section view and flow scheme

Some caustic loss points could be identified with the scheme: the label extraction, rinsing effluents, and the carry-over at the outlet of bottles, which was really small compared to the other two parts and could be neglected. Caustic wastewater was generated from the label extraction, with as high concentration as in the caustic baths, and pre-rinse effluent, with a relatively lower concentration. With the Valencia brewery, the full scale model was adapted with the bottle washers used in Valencia.

4.2. OPERATIONAL VARIABLES FOR MODELLING

Since the previous BS model could be modified to simulate other bottle washers by adapting the operational variables, a Python model was built based on the information provided by Valencia. According to the questionnaire from Valencia, the bottle washers clean 92,000 bottles per hour. The volume of the three caustic baths is 48.08 m^3. With several rinses after the caustic baths, the volumes of the water baths can be designed to be very small, 1.44 m^3, 6.74 m^3, and 1.57 m^3 respectively. The lifetime in the Valencia model was five days, corresponding to the weekly beer production cycle with returnable bottles. The range of caustic soda concentration was 1.5% to 2%, i.e. 15 to 20 $g\ NaOH/L$.

Besides the information above, some assumptions were made according to practical experience for the unknown operational variables. The carry-over was assumed to be 10 $mL/bottle$. The effluent from the second rinse was directly returned to the last caustic bath. 25 m^3 of rinsing water from the last three rinses were reused for the pre-rinse continuously. The water pressure used for rinses was 1.4 to 1.6 bar, but the flowrate was not measured by the brewery. This was assumed to be 40 $mL/bottle$, i.e. 3.68 m^3/h for the last four rinses.

The working mode for Valencia bottle washers is periodic according to the operation of beer production line with recyclable bottles. In generally, the bottle washers work five days a week, and the caustic baths are discharged every three months. Therefore, the lifetime in the one-week Valencia model was five days, and was then expanded to 60 days as the full cycle of three months operation including weekend idle. The total wastewater generation and caustic consumption were calculated both weekly and trimonthly.

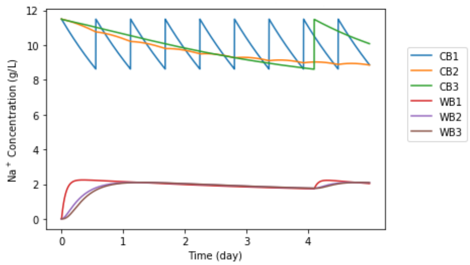
4.3. MODELLING RESULTS AND DISCUSSIONS

With Python it is possible to define the caustic soda dosage and loss due to rinses and carry-over. To quantify the chemical reactions, however, is difficult without any information on the composition of the solutions in the caustic baths or the label and glue. A basic insight of the operation for the first five days of a Valencia bottle washer, with sodium concentrations in both six baths and five rinsing effluents, and daily consumption of caustic soda, was presented with the Valencia model. An estimation of caustic soda consumed by the chemical reactions would be given based on the difference between the model and the real-life data.

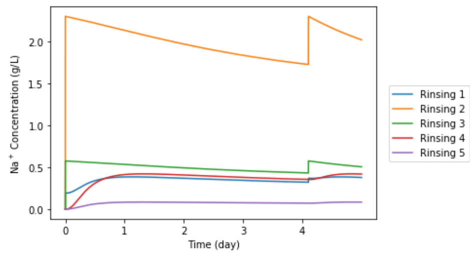
4.3.1. ONE-WEEK OPERATION

With the model of operation for only five days, more details of the changes in sodium concentrations, caustic dose and caustic loss could be noticed. Similar as the models before, the periodic patterns in sodium concentrations in caustic baths were obvious, due to automatic caustic dosage. In the water baths, the concentrations of sodium were stable at around 2 g/L. The first water bath reached the stable value very quickly, and it took the other two baths around one day operation to reach stable. This stable sodium concentration for water baths was even higher than that in the rinsing effluent before it, which meant that the bottles got more polluted in the water baths after the third rinsing.

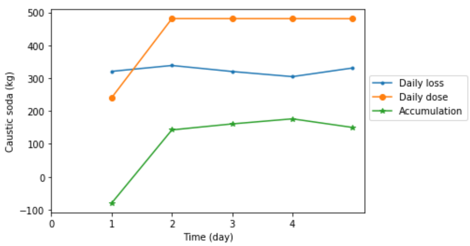
In Fig.4.3b, compared with the other four rinsing effluents, the sodium concentration was much higher in the second rinsing effluent, which was directly after the last caustic



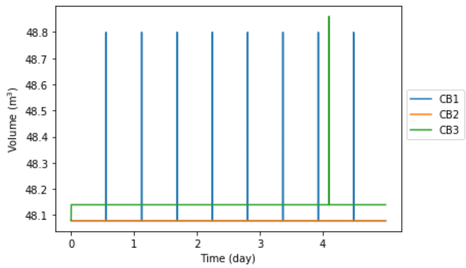
(a) Sodium concentrations in the baths of Valencia bottle washer for one week



(b) Sodium concentrations in the rinsing effluents of Valencia bottle washer for one week



(c) Daily caustic soda loss of Valencia bottle washer for one week



(d) change in caustic bath volumes of Valencia bottle washer for one week

Figure 4.3: Sodium concentrations in the baths and the rinsing effluents, daily caustic loss and chagne in caustic bath volumes of one-week Valencia bottle washer model ("CB" for caustic bath, "WB" for water bath)

bath. Thus, it was reasonable that in the Valencia brewery daily operation, the effluent from the second rinse was directly recirculated to the last caustic bath to prevent too much loss in caustic soda. However, this recirculation also diluted the concentration in the last caustic bath to some extent, since the sodium concentration in the rinsing effluent was much lower than that in the caustic bath, which was always above 8.6 g/L. This also explained why the sodium concentration depressed faster in the third caustic bath, and there was no caustic dosage in the second caustic bath but one in the third caustic bath within the one week modelling.

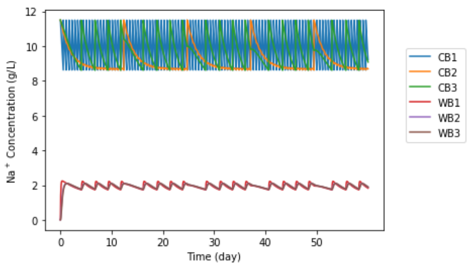
From Fig.4.3c and Fig.4.3d, the automatic dosage of caustic soda was presented clearly. On the first day of operation, the starting caustic concentration in the three baths was directly the highest range, thus, the dosage on the first day was lower than later. And the solution volumes in the three caustic baths were kept within an acceptable range of 1 m^3.

With the Valencia model of one week, it could be calculated that 2,164.39 kg as $NaOH$ was dosed into the bottle washer, and 1,614.69 kg was lost. With this result, with every 1 hL beer produced for returnable bottles, 0.06 g caustic soda will be lost only due to carry-over. The daily caustic consumption due to carry-over was 432.88 kg/day in the model, and the actual daily consumption in total is 900 kg/day. The difference can be regarded as the chemical reaction part, which consumes approximately 467.12 kg/day.

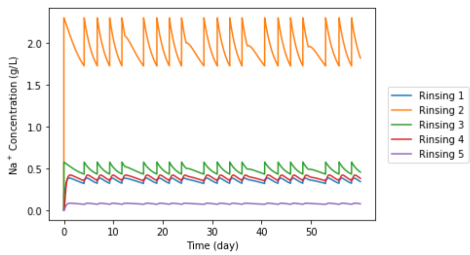
4.3.2. 60-DAY OPERATION

With the operation model for 60 continuous working days, excluding the weekends, it was more clear to see the overall patterns of the caustic consumption within in a Valencia bottle washer during the three months of operation. Expanded from the one-week model, it was good to make sure that the sodium concentrations in the three water baths already reached the stable level within the first week, and the pattern showed a dynamic equilibrium. Caustic soda was more frequently dosed in the last caustic bath than the second due to the dilution from rinsing water recirculation. The same pattern was also observed in the sodium concentrations in the five rinsing effluents, and a periodic cycle of around 12 days was palpable, especially from the second rinse. The direct reason for this was the caustic dosage in the last caustic bath, and the primary cause was the dosage in the second caustic bath. This was more obvious in Fig.4.5 when the sodium concentrations of the second caustic bath, the third caustic bath, and the second rinsing effluent were presented in the same graph. And the dosage also contributed to the high daily caustic dose of around 700 kg in Fig.4.4c. The daily caustic loss was very stable from the label extraction, which also showed the small influence of the caustic loss from carry-over compared to it. When the dose increased, the accumulation also increased along, which then led to a decreased dose in the caustic baths afterwards. This phenomenon could be regarded as a feedback within the bottle washer based on the caustic concentration.

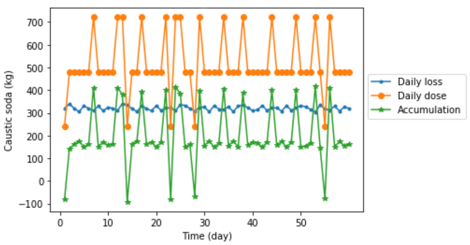
4



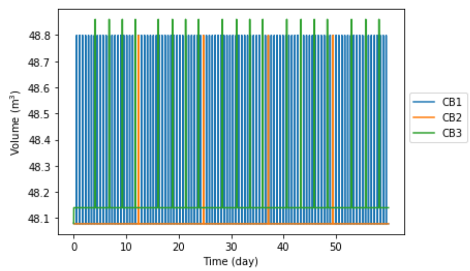
(a) Sodium concentrations in the baths of Valencia bottle washer for 60 days



(b) Sodium concentrations in the rinsing effluents of Valencia bottle washer for 60 days



(c) Daily caustic soda loss of Valencia bottle washer for 60 days



(d) Change in caustic bath volumes of Valencia bottle washer for 60 days

Figure 4.4: Sodium concentrations in the baths and the rinsing effluents, daily caustic loss and chagne in caustic bath volumes of 60-day Valencia bottle washer model ("CB" for caustic bath, "WB" for water bath)

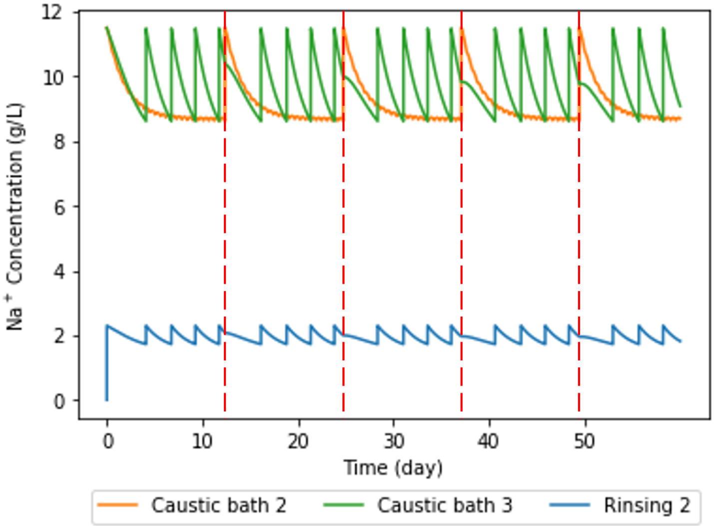


Figure 4.5: Sodium concentrations in caustic baths 2, 3, and rinsing 2 of Valencia bottle washer for 60 days

In total, the caustic dose in the 60-day operation model was summed up to 31,024.31 kg as $NaOH$, and the loss was 19,229.78 kg. The average caustic loss per 1 hL of beer was 0.07 g, similar to the results from the one-week model. Before cleaning the bottle washer at the end of the cycle, another 3,842.22 kg caustic soda would be disposed by emptying the caustic baths.

4.3.3. Annual Estimation and Conclusion

The wastewater discharged from the bottle washer could be traced to the pre-rinse effluent and the label extraction. As for wastewater generation, 175 $m^3/week$ was discharged from the bottle washer based on the fact of 25 m^3/day pre-rinse consumption with reused rinsing effluent and 10 m^3/day label extraction discharge. The annual wastewater generation could be estimated to 9,016 m^3 for the whole year. On average, 0.052 hL of wastewater was discharged per 1 hL beer production. With the assumption of 40 $mL/bottle$ rinsing flowrate with fresh water, 1,766.4 $m^3/week$ and 84,787.2 $m^3/year$ would be consumed for rinsing bottles.

Based on the model for 60 days operation, the annual caustic consumption due to label extraction and carry-over could be estimated. With four cycles per year, the total caustic loss due to physical reasons was summed up to 86,079.81 kg, including the disposal from caustic baths. As around 900 kg/day caustic consumption from Valencia in real-life operation, the total demand was 216,000 $kg/year$. Assuming the difference between modelling dosage and real-life dosage would be consumed by impurities, around 41.21% was consumed with chemical reactions, and 39.85% ended up in the wastewater and is eventually wasted. The rest was lost with carryovers on outlet bottles or due to the adjustment on the volume changes.

5

Optimised Scenarios and Sustainability Study

From the modelling results in the last Chap.4, it was clear that a significant amount of caustic soda was lost in the bottle washer in the brewery. To improve the situation and help with the industrial sustainability, some optimisation scenarios were simulated by varying operational variables in a reasonable range. With the comparisons among different scenarios, Sustainability is a very complex topic. In this research, only water footprint (WFP) and chemical footprint were focused on.

5.1. Sustainability Indicators

To carry out a sustainable study, a baseline scenario should be presented as a benchmark, and compare other optimised scenarios with it. First, the sustainability indicators should be introduced. As for bottle washers, possible sustainability indicators include the water footprint (WFP), energy consumption, chemical consumption, emissions and cost. In this study, WFP and chemical consumption are the most important indicators and will be the criteria for the optimisations.

5.2. Baseline Scenario and Optimisations

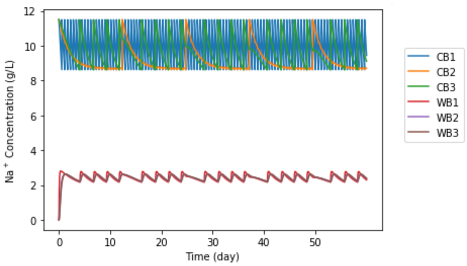
This baseline scenario was the 60-day Valencia model. Making use of the results from the testing scenarios in Chap. 2, five optimised scenarios, noted as OS-1 to OS-5 respectively, would be given based on possible measures to increase the sustainability of the bottle washer according to the criteria to reduce WFP and caustic consumption. In each scenario, controlled variable were used, and there would be only one assigning different values to the operational variables. For each scenario, several trials within reasonable ranges of values assigned to the certain operational variables were taken, and the results were presented as the most effective ones.

5.2.1. OS-1: REDUCING WFP BY RINSING FLOWRATE ADJUSTMENT

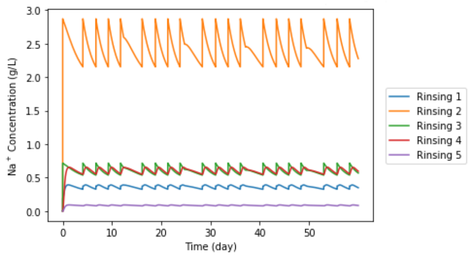
From the analysis of Valencia bottle washer, a huge amount of clean water was used for rinsing bottles every day. One of the measures that could be raised to reduce the WFP of bottle washer operation was to adjust the rinsing flowrate. This measure could be the easiest, by changing the nozzles inside the bottle washer or the pressure for clean water supply. But the limitation is that the cleanness of outgoing bottles should never be compromised.

In this scenario, the pre-rinse was still 25 m^3/day, which was not counted in the WFP due to the reuse of other rinsing effluent. The flowrate of rinses 2, 3 and 4 was reduced to 75% of the original value. To maintain the bottle outlet as the same level of caustic residue of 0.13 g/L from the last rinsing effluent, the last rinse was increased to 150% and the new concentration was acceptable at 0.15 g/L. The consumption of clean water was reduced from 21,196.8 m^3 to 19,872 m^3 during the operation for 60 days, and in total 88.32 $m^3/year$ could be saved compared to the original settings. Overall, 93.75% of the original flowrate was used, thus, 6.25% of the total clean water can be save despite of the exact flowrate.

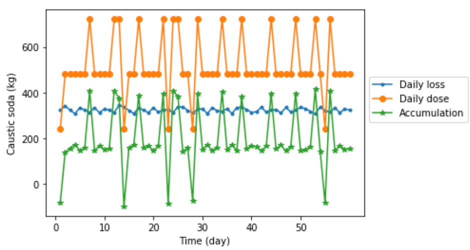
The change in caustic dose was negligible, from 31,024.31 kg to 31,025.87 kg, however, the caustic loss increased from 19,229.78 kg to 19453.37 kg, which led to an increase in caustic loss by 894.36 $kg/year$ at the same time.



(a) Sodium concentrations in the baths of OS-1 ("CB" for caustic bath, "WB" for water bath)



(b) Sodium concentrations in the rinsing effluents of OS-1



(c) Daily caustic soda loss of OS-1

Figure 5.1: OS-1: Sodium concentrations in the baths and the rinsing effluents, and daily caustic loss in the optimised model with reducing rinsing flowrate to 93.75%

5

5.2.2. OS-2: REDUCING CAUSTIC LOSS BY ENLARGING WATER BATHS

According to the Valencia bottle washer purchased from KRONES®, the water baths are very small. From the BS model it was suggested that more water baths could reduce the loss of caustic soda by trapping it within the bottle washer. Another possibilities is to change the volume of the water baths, if increasing the number of water baths is not possible. This is more difficult since changes need to be taken in the structure of bottle washers, and will be a suggestion for the bottle washer manufacturers. With enlarged water baths, more caustic soda can be kept and prevent part of the lost.

Assuming the water baths were three times larger for the Valencia bottle washer, and the rinsing flowrate maintains the same, the caustic dose actually increased from 31,024.31 kg to 31,266.56 kg, but the caustic loss was cut down from 19,229.78 kg to 16,910.75 kg by 12.0%. This was because more caustic soda went into the water baths, and the caustic accumulation inside the whole bottle washer went from 11,794.39 kg to 14,355.67 kg. This made it possible to also collect the wastewater from water baths at the end of the cycle, and reuse or recycle caustic soda in the caustic baths for the next cycle. The last rinsing effluent contained $NaOH$ of 0.13 g/L, the same as the baseline scenario. Therefore, it is possible to make the change of water bath volumes without affecting the cleaning result. But the clean water demand for water baths would increase by two times.

5

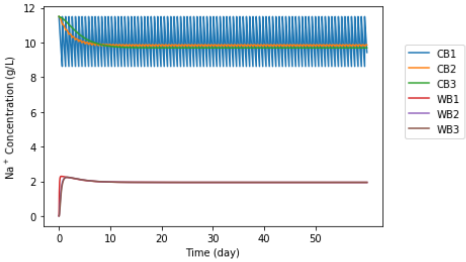
5.2.3. OS-3: REDUCING CAUSTIC LOSS BY REUSING FROM LABEL EXTRACTION

The biggest contribution of caustic loss during daily operation is from the label extraction, which is actually avoidable. The wastewater, containing waste label and the same caustic concentration as the caustic baths, is directly discharged after sieving.

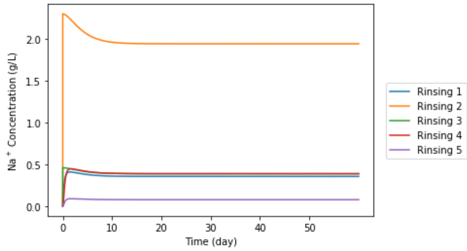
This scenario would like to reuse 90% from the label extraction discharge by sieving and squeezing the solid part, and return the liquid directly to the caustic baths. The eventual discharge from the label extraction would be only 1 m^3/day. This measure also requires some changes in the structure of the machine. The caustic dose decreased from 31,024.31 kg to 22,375 kg by 27.9%, and the caustic loss was cut down from 19,229.78 kg to 10,303.67 kg by 46.4%. This was because the recirculation of label extraction discharge prevented unnecessary caustic loss and kept the caustic in the water baths, and the caustic accumulation inside the whole bottle washer went from 11,794.39 kg to 12,071.58 kg. It was noticed from Fig.5.2a that no caustic dose was needed for the second and third caustic baths with minimised label extraction discharge, and the overall caustic consumption could be directly cut down. This directly cut off the caustic loss to a great extent, and therefore the caustic consumption was reduced. The caustic concentration in the last rinsing effluent was also the same as the baseline scenario.

5.2.4. OS-4: REDUCING CAUSTIC LOSS BY MINIMISING CARRY-OVER

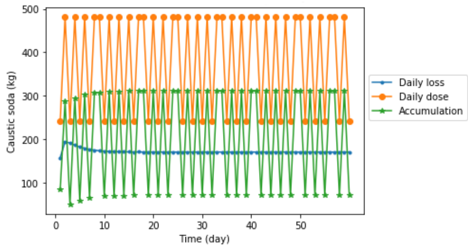
Another contribution of caustic loss is the carry-over on bottles and in the pockets. It is not easy to control how much water is adhesive onto bottle surfaces, but the pockets can be designed to minimise the water carry-over. A reduced carry-over of 7 $mL/bottle$ was assumed in this scenario, and the caustic loss was directly decreased from 19,229.78 kg to 14,911.05 kg by 22.5%. The caustic dose decreased from 31,024.31 kg to 25,009.07



(a) Sodium concentrations in the baths of OS-3 ("CB" for caustic bath, "WB" for water bath)



(b) Sodium concentrations in the rinsing effluents of OS-3



(c) Daily caustic soda loss of OS-3

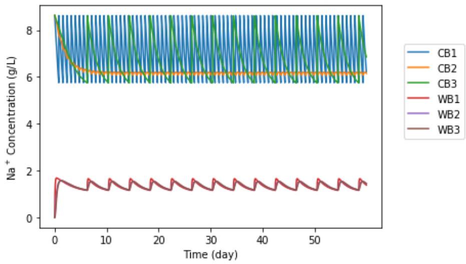
Figure 5.2: OS-3: Sodium concentrations in the baths and the rinsing effluents, and daily caustic loss in the optimised model with reusing 90% label extraction discharge

kg by 19.4%, and the caustic accumulation inside the whole bottle washer went from 11,794.39 *kg* to 10,097.89 *kg*. The caustic concentration in the last rinsing effluent was 0.05 g/L, which made it possible to reduce the rinsing flowrate for the last two rinses accordingly and reduce the WFP at the same time.

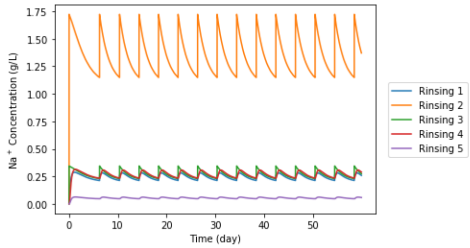
5.2.5. OS-5: Reducing Caustic Consumption by Reducing Caustic Concentrations

The caustic concentrations in caustic baths can be different from breweries. If the cleaning effect can be guaranteed, the caustic concentrations should be lowered as much as possible to prevent over use of chemicals. Several tests might need to be carried out to find the critical points.

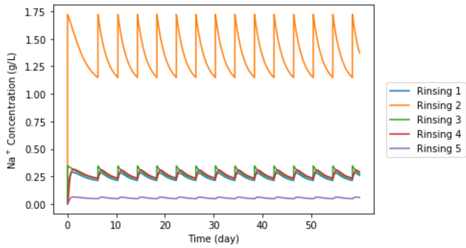
In this scenario, the caustic concentration was limited within the range of 1.0% to 1.5%. The caustic contained in the carry-over reduced accordingly, and there was no automatic dose in the second caustic bath as shown in Fig.5.3a, and the 12-day periodic pattern also disappeared compared with the baseline. The caustic dose decreased from 31,024.31 *kg* to 21,401.66 *kg* by 31.0%, and the caustic loss decreased from 19,229.78 *kg* to 13,348.15 *kg* by 30.6%. Due to the low caustic concentration, the caustic accumulation greatly decreased from 11,794.39 *kg* to 8,053.41 *kg* by 31.7%. The caustic concentration in the last rinsing effluent was 0.10 g/L.



(a) Sodium concentrations in the baths of OS-5 ("CB" for caustic bath, "WB" for water bath)



(b) Sodium concentrations in the rinsing effluents of OS-5



(c) Daily caustic soda loss of OS-5

Figure 5.3: OS-5: Sodium concentrations in the baths and the rinsing effluents, and daily caustic loss in the optimised model with lower caustic concentrations at 1.0% to 1.5%

5.3. SUMMARY FOR OPTIMISED SCENARIOS

Among the five optimised scenarios above, OS-1 focused on the WFP reduction, OS-2 to OS-4 focused on the CFP, where OS-2 to OS-4 aimed to prevent caustic loss, and OS-5 was able to reduce caustic consumption straightly.

Table 5.1: Summary of changes of caustic soda dose, loss and accumulation in the five optimised scenarios in 60 days

Model	Changes Made	Changes in Caustic Soda		
		Dose	Loss	*Acc
OS-1	Rinsing water reduced by 6.25% in total	0.005%	1.16%	-1.88%
OS-2	Water baths enlarged to 3 times	0.78%	-12.06%	21.72%
OS-3	**Label extraction effluent reused by 90%**	**-27.88%**	**-46.42%**	2.35%
OS-4	Carry-over reduced by 30%	-19.39%	-22.46%	-14.38%
OS-5	**1.0% to 1.5% caustic concentrations**	**-31.02%**	**-30.59%**	**-31.72%**

**Acc: Accumulation*

From OS-1 it was clear that there was not much space to reduce clean water consumption by reducing the rinsing flowrate. This was decided by the cleanness of the outgoing beer bottles. To ensure the bottles were cleaned to certain standard, the rinsing flowrate could not be conserved to a great extent. OS-3 and OS-5 showed the greatest

Table 5.2: Summary of changes of caustic soda dose, loss and accumulation in the five optimised scenarios, estimated for annual

Model	Changes Made	Changes in Caustic Soda	
		Dose	Loss
OS-1	Rinsing water reduced by 6.25% in total	0.005%	1.18%
OS-2	Water baths enlarged to 3 times	0.76%	-9.55%
OS-3	**Label extraction effluent reused by 90%**	**-27.25%**	**-40.70%**
OS-4	Carry-over reduced by 30%	-18.95%	-19.35%
OS-5	**1.0% to 1.5% caustic concentrations**	**-30.88%**	**-30.39%**

potential to reduce CFP as caustic soda, by either recirculating the label extraction effluent or reducing the caustic soda concentrations in caustic baths by 5%. Both methods were able to reduce the caustic dose and loss by around 30% to even 40%. However, the accumulation was not much influenced by recirculating label extraction effluent, but also greatly decreased by reducing caustic soda concentrations. It was also possible to reduce caustic soda loss by reducing carry-over, while it might not be easy to achieve. The annual results estimated from the scenarios were similar to the results for 60-day operations.

6

Caustic Recovery: Possibilities and Challenges

To improve the current bottle washing system in a more sustainable way, on the one hand, bottle washers themselves can be improved regarding with other possible operation and recirculation; on the other hand, caustic soda can also be reclaimed from the wastewater. From the Valencia model, it was surprising that almost half of the total caustic soda consumption of the bottle washer was lost due to the carry-over and the label extraction, ending up in the wastewater. Therefore, there should be a considerable potential to recover caustic soda from the bottle washer wastewater, consisting of label extraction effluent and caustic baths disposal, and greatly reduce the annual caustic consumption in breweries. If this could be achieved successfully, similar techniques can be used for clean-in-place (CIP) wastewater for chemical recovery as well.

6.1. Composition of Caustic Bath Solutions

To obtain basic knowledge on the composition of bottle washer effluent, three water samples were provided by Heineken® from respectively three caustic baths in a bottle washer in Alken Maes, a brewery located in Belgium. The samples were taken after around two months' operation, and some analysis were carried out in the Water Lab from TU Delft. According to Cotruv et al., 2013, at least turbidity, TOC, TDS and pH should be monitored at the end of industrial water utilisation. Moreover, parameters including conductivity, total alkalinity, TSS, COD, VFA and inorganic ion species were measured. The final results are summarised in Table 6.1 and Table 6.2. The original data can be found in Appendix.D. Concentrations of volatile fatty acids (VFA), Br^-, NO_3^-, and Mg^{2+} were too low in the samples to measure. Thus, these information would not be included in the final results.

Since the water samples under analysis were obtained from a different brewery, with different bottle washers and operational variables, the analysis results were not comparable with the previous bottle washers data or modelling results. The compositions of the water samples only served as a reference for the discussion over possible caustic soda reclamation techniques.

It was expected that the pH of the water samples might not be as high as 13 due to the conductivity monitoring for automatic caustic soda dosage. As the operation going on, the accumulated impurities also contributed to the conductivity in caustic baths. Therefore, when the conductivity reached the standard of caustic soda concentration, the actual concentration could be lower than the standard. It could be assumed that the majority ion in the samples were OH^- and Na^+ due to the caustic soda dosage. Within in a caustic bath, the anions could be ranked according to their abundance as: OH^- $> CO_3^{2-} > SO_4^{2-}$ or $CO_3^{2-} > OH^- > SO_4^{2-}$, and HCO_3^- would not exist if the pH in the water exceeded 12. The cations could be ranked according to their abundance as: $Na^+ >$ $Mg^{2+}/Ca^{2+} >> H^+$. Among the three samples, the first sample could contain the most impurities and the last one with least impurities due to the operational sequence.

6.1.1. LAB ANALYSIS RESULTS

Table 6.1: Characteristics of bottle washer caustic bath water samples from Alken Maes

	Sample 1	Sample 2	Sample 3
pH	13.4	13.4	13.4
Temperature ($°C$)	17.4	17.2	17.3
Conductivity (mS/cm)	67.4	72.9	70.6
Turbidity (NTU)	165	189	206
Alkalinity ($g\ CaCO_3/L$)	61.61	66.89	66.08
TDS (g/L)	24.03	27.82	29.47
COD (mg/L)	3125	3882	4798
TOC (mg/L)	1038	1307	1591

To restore the occasion on site where wastewater is usually sent to sedimentation tanks before the treatment plant, the water samples were all measured after at least 48 hours' sedimentation. The solids within the water samples were highly unevenly distributed in the vertical scale. Therefore, the difference in TSS among the three duplicates, which were taken from different layers of the same sample, were too large after sedimentation to include as reliable results. According to Ait Hsine et al., 2005, TSS in bottle washing effluents could be around 0.15 g/L.

Regarding the low VFA content in the samples, the concentrations of volatile species were under the detect limit of GC. Thus the results from GC-VFA measurement were not able to be calculated. This might because of the long time preservation before measurement, which was not avoidable due to the situation. Attribute to the same reason, the TOC contents could also be higher in the original samples before the possible decomposition during preservation. However, it could be assumed that TOC and VFA concentrations should be higher in the original samples due to alcohols and aromatic substances in beers.

Table 6.2: Ionic concentrations in bottle washer water samples (unit: mg/L)

		Sample 1	Sample 2	Sample 3
Anions	F^-	70.58	90.90	117.46
	Cl^-	29.17	30.72	32.51
	PO_4^{3-}	15.78	19.69	21.90
	SO_4^{2-}	61.97	64.33	68.59
Cations	Na^+	12919.33	14954.00	14793.67
	NH_4^+	20.30	21.90	15.04
	K^+	18.85	21.25	22.88
	Ca^{2+}	10.58	14.57	19.34

6.1.2. CHARGE BALANCE

To maintain the electroneutrality of solutions, the sum of positive charges equals the sum of negative charges. In this section, the number of moles of positive charges and negative charges will be calculated for each water sample, based on the analysis results.

According to the definition, alkalinity is the buffering capacity of a water body to resist acidity (Addy et al., 2004). Ions that are able to combine with H^+ added into the solutions, until pH 4.3, can be all counted into alkalinity. In a buffering system, Some common H^+ donors include H_3PO_4, HSO_4^-, and HF, and common H^+ acceptors include HCO_3^-, CO_3^{2-}, $B(OH)_4^-$, HPO_4^{2-}, PO_4^{3-}, $H_3SiO_4^-$, HS^- and NH_3 (Wolf-Gladrow et al., 2007).

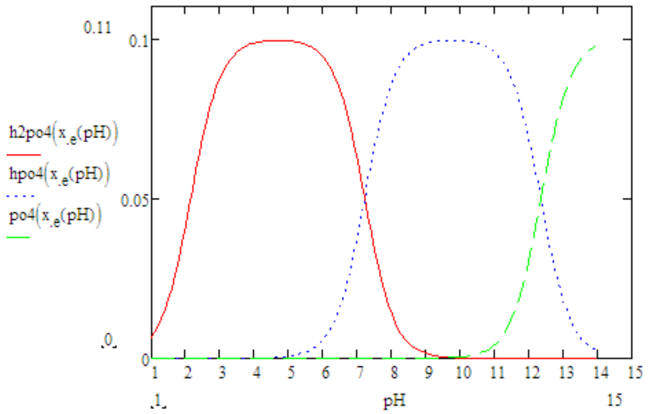
The H^+ acceptors that could be identified from the samples were OH^-, CO_3^{2-}, PO_4^{3-}, and HPO_4^{2-}. According to Fig.6.1, $H_2PO_4^-$, HCO_3^- and H_2CO_3 did not present in the samples of pH 13.4, thus there was no H^+ donors except for H^+ itself. The pH of the samples was extremely high, and the concentration of the major species of phosphate PO_4^{3-} at pH 13.4 was relatively very low. It could be assumed that under this pH, concentrations of H^+ and the minor phosphate species HPO_4^{2-} were too low so that the two species could be neglected. Until pH 4.3, the species of phosphate is $H_2PO_4^-$. Thus, the equivalent H^+ that could be accepted by every 1 mol of PO_4^{3-} in alkalinity titration was 2 mol. The A_T in the samples could be expressed as Eq.6.1 with the ionic concentrations of the four H^+ acceptor species. Based on the ionic concentrations given by pH test and IC analysis, the estimated concentration of CO_3^{2-} could be calculated.

$$A_T = [OH^-] + 2[CO_3^{2-}] + 2[PO_4^{3-}] - [H^+] \tag{6.1}$$

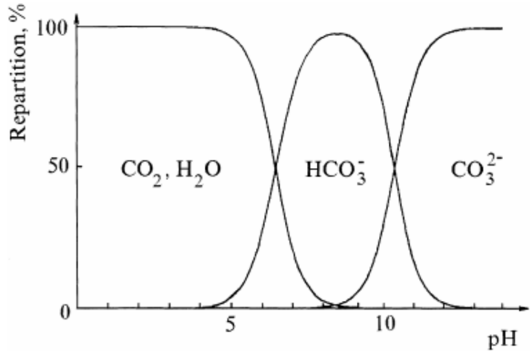
6.1.3. DISCUSSION OVER THE RESULTS

First of all, it was beyond the expectation that the pH in the caustic baths was almost as high as calculation, which was around pH 13.57 to pH 13.70 for 15 to 20 g/L caustic soda concentration. It might due to the inaccurate monitoring with higher caustic concentration applied in brewery Alken Maes, or the monitoring method for the bottle washers in the brewery was not only based on conductivity to increase accuracy.

The conductivity of the samples was lower than the modelled bottle washer, which was between 90 to 120 mS/cm without impurities. This attracted attention on the EC



(a) Concentration changes of phosphate species ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) in varying pH conditions (Wang et al., 2018)



(b) Concentration changes of carbonate species (H_2CO_3/CO_2, HCO_3^-, CO_3^{2-}) in varying pH conditions (Pismenskaya et al., 2001)

Figure 6.1: Non-conservative ion concentration changes with varying pH

calculations in the models. The previous method for EC calculation was not correct that some more aspects, such as ionic activity, should be taken into consideration for further improvement.

According to the IC analysis and calculation from pH, the majority ion species in the water samples were OH^- and Na^+. However, concentrations of CO_3^{2-} were much higher than expected. It could be possible that some CO_2 were taken into the samples during bottle washer operation, or before and during lab analysis due to the very high pH. CO_2 in the air could be easily taken into the samples when they were continuously stirred at high pH for the alkalinity measurement with titration. Some carbonate might already present inside the caustic baths from beer residue or decomposition of organic compounds. However, the K_{sp} of $CaCO_3$ is 4.8×10^{-9}, which was exceeded of the product of Ca^{2+} and CO_3^{2-} concentrations. Based on the Ca^{2+} concentrations, CO_3^{2-} had to be at approximately 10^{-2} $mmol/L$ to avoid precipitation. Therefore, the CO_3^{2-} concentra-

Table 6.3: Charge balance in three water samples (unit: $mmol/L$)

Ion Species and Charges	Sample 1	Sample 2	Sample 3
OH^-	251.19	251.19	251.19
*CO_3^{2-}	490.32	543.12	534.96
F^-	3.71	4.78	6.18
Cl^-	0.82	0.87	0.92
PO_4^{3-}	0.17	0.21	0.23
SO_4^{2-}	0.65	0.67	0.71
Total Negative Charges	-1238.15	-1345.04	-1330.32
Na^+	561.95	650.46	643.48
NH_4^+	1.12	1.21	0.83
K^+	0.48	0.54	0.59
Ca^{2+}	0.26	0.36	0.48
Total Positive Charges	564.09	652.94	645.87
Overall Charge Balance	**-674.06**	**-692.10**	**-684.45**

**The concentrations were calculated from total alkalinity and might not be correct.*

tions calculated from A_T were not correct for the samples, probably due to other species which also contributed to alkalinity. There might be other unknown ion species which contributed to A_T. It was also possible that CO_2 from the atmosphere were taken by the samples as a consequence of the continuous stirring during titration.

A problem that deserved attention was that, according to the parameters in Table 6.1 and Table 6.2, it seemed that the last caustic bath contained the most impurities and Na^+ ions and the first bath contained the least after a period of operation. This could be explained with the different retention time of inlet bottles in the three caustic baths, which was part of the lack information. The higher Na^+ concentration in Sample 3 also indicated that more caustic soda had been dosed in the bath.

It was clear that the charges in all the three samples were not balanced. Samples were more negatively charged according to the calculation, which was not rational for electroneutral solutions. There could be three reasons. One was the inaccurate assumption of the existence of HPO_4^{2-}, whose concentration should not be neglected but measured in the lab. However, this could only contribute to a small part. Another reason could be the presence of other positive ions which were beyond the measurement range of the IC used for analysis.

This lab analysis was carried out for only one bottle washer from one brewery. Accordingly, the results could only serve as an insight of the possible compositions of bottle washer caustic baths, but should not be regarded as typical or representative.

6.2. ALTERNATIVE TECHNOLOGIES

The concept of caustic recovery can be regarded as an ion fractionation process to separate the ionised caustic soda, more specifically, OH^- ions, from other unwanted ion species. The other ions should be eliminated as much as possible, to avoid pollution accumulation in the bottle washer machine. Possible technologies include ion exchange, membrane filtration and electrodialysis. Ion exchange has been widely used for industrial application to purify water, however, to regenerate the resins usually consumes a large amount of effluent (Zhang et al., 2012). Moreover, the high sodium concentration can be the obstacle for divalent ion exchange. Moreover, the high concentration of Na^+ is highly competitive for other divalent or multivalent cations such as Ca^{2+} (Zagorodni, 2007), which are the target of removal. Thus, ion exchange will not be discussed in this report due to the lack of sustainability and efficiency.

According to the lab analysis, it has been proved that the pH of real bottle washer wastewater can be higher than 13. The high pH might be one of the biggest obstacles for the application of currently available technologies.

The product of caustic recovery will be used as the caustic dosed into caustic baths. Therefore, on the one hand, the recovered solutions should be concentrated to avoid too much liquid dosage which may leads to big water level fluctuations in the baths. On the other hand, there should not be too much unwanted contents in the recovered solutions to avoid impurity accumulation along with caustic recirculation.

6.2.1. Membrane Technologies

Membrane technologies have been rapidly developed for industrial use. Some conventional membranes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes. Flat sheet, tube and hollow fibre are the common forms of NF membrane modules. The first two forms are not self-supporting, but are placed against porous external support to withstand the pressure and drain the permeate (Schäfer et al., 2005).

Among these types of membrane, plate sheets with frames can only provide limited filtration surface per volume, and the size of the module will be constrained by the high pressure for nanofiltration. The replacement of such membranes is sheet by sheet, which is labour intensive. Therefore, this membrane is only practical for application in small scale. The spiral wound module is made by flat sheets rolling around a central tube for permeate. such membranes can be made for UF, NF and RO, and are very popular nowadays for large scale use. The tubular membranes are usually used for medium scale, and the characterisation of such modules is the possibility for water with particles since they can be easily cleaned with foam balls. The self-supported hollow fibre NF modules are still under development.

As presented in Fig.6.2 the decisive difference among the membranes is the different pore sizes. The index for membranes to quantify the pore size is the molecular weight cut-off (MWCO) in the unit of dalton (Da), which means the molecular weight of the molecule that is 90% retained by the membrane (Singh, 2006). Some tight NF or loose RO membranes are able to separate monovalent from multivalent ions. Such membranes seem to be ideal for caustic soda recovery by separating Na^+ and OH^- from other multivalent ions and pollution with larger molecules. However, RO membranes are usually made into spiral wound modules with polymeric materials such as cellulose acetates and polyamides (Buschow, 2010). Under very low or high pH, polymers would start hydrolysis when $C=O$ or $C-N$ are destroyed by H^+ or OH^- (Jiang et al., 2019). As a result, current RO membranes are not available to treat the bottle washer wastewater due to the pH tolerance.

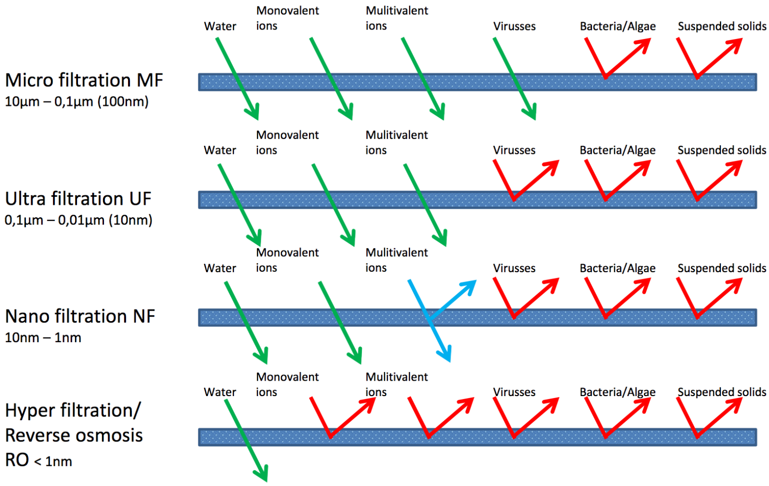


Figure 6.2: Pore sizes of conventional membranes (Logisticon Water Treatment b.v., n.d.)

An investigation was carried out in the current NF membrane market, and the pH requirement for many popular used membranes was below 11. Similar to the RO membranes, the compositions of most commercially available commercial NF membranes are also amide or cellulose acetate, limiting the pH tolerance in the range of around 2 to 12 (Daems et al., 2018). There are also ceramic membranes that are able to operate at as high pH as 14, but with some disadvantages to limit their wide application in industries. The disadvantages include very low permeability, limited temperature range, and high MWCO (Freger et al., 2005; Lee et al., 2017; Lee et al., 2015). For the treatment of bottle washer wastewater, the narrow temperature range of around 10 to 80 $°C$ should not a problem. The water temperature in the caustic bath is usually around 65 to 70 $°C$, and after discharge, the wastewater can be further cooled down during the sedimentation of 24 to 48 hours. The high MWCO may reduce the efficiency of caustic soda recovery by allowing other unwanted chemicals into the permeate. Nevertheless, with the significantly higher concentration of OH^- than unwanted ions, this may not be a big problem for caustic soda recovery. The low permeability might also not be the obstacles for the wastewater to be filtered with such nanofiltration membranes. Taking a current bottle washer from Valencia brewery for example, with a low NF membrane permeability of less than 1.5 $L/(h\ m^2\ bar)$, it would be challenging to handle the 175 $m^3/week$ wastewater, equivalent to 1458.3 L/h with five working days per week. Every three months, another 144.24 m^3 of caustic wastewater from caustic baths will be transferred to the treatment. If a decent pressure of approximately 10 bar will lead to a membrane surface area of around 20 m^2, which can be designed overlapped to reduce the space occupied.

Regarding the lab analysis, turbidity of bottle washer wastewater can be too high to be directly filtrated by membranes. Generally a turbidity of around 10 NTU or higher has already a profound influence on the efficiency of membrane filtration (Thompson, 2001). As a result, it might be significant to pre-treat the wastewater before nanofiltration. A pre-treatment process before the membrane can increase the efficiency of nanofiltration with higher feed water quality, and enhance the reusing and recycling opportunities of wastewater (Hashlamon et al., 2017). Pre-treatment such as rapid gravity filtration (RGF) may be needed to retard fouling in membranes (Moran, 2018).

As a conclusion, although there is a certain type of nanofiltration membranes which tolerate high pH of the wastewater discharged from beer bottle washers, divalent ions such as Ca^{2+} and CO_3^{2-} can not be removed from the product. The purity of recovered caustic soda solution still need extra treatment to raise the concentration and eliminate impurities.

6.2.2. ELECTRODIALYSIS

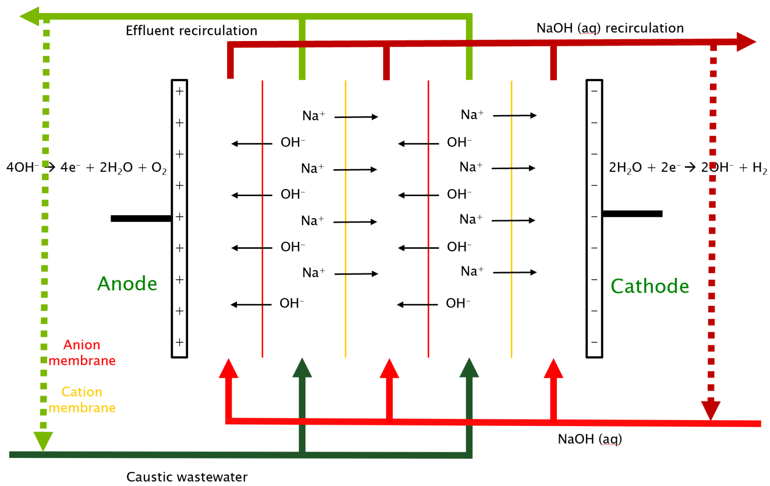


Figure 6.3: Sodium hydroxide recovery from caustic wastewater scheme with electrodialysis

The other alternative for caustic soda recovery is electrodialysis, with which the possibility to recover valuable metals, acids or bases from industrial wastewater can be increased (Scarazzato et al., 2020). Electrodialysis is also a membrane separation process, where the driving force is the difference in electrical potential, to transport ions from different solutions through semipermeable membranes (Scarazzato et al., 2017). Connected to an external power source, electrical forces are formed between the two electrodes. Driven by electrical forces, salt ions carrying different charges transport toward different directions and through the ion exchange membranes. The cation exchange membranes (CEM) and anion exchange membranes (AEM) are composed of backbones that has anions and cations active fixed groups on the structures respectively (Scarazzato et al., 2020). Counter-ions of the fixed groups are able to pass the semipermeable membrane, while co-ions are not. Under the category of electrodialysis, it can be further divided into conventional electrodialysis, selectrodialysis, and bipolar membrane electrodialysis (Chen et al., 2018).

Wastewater effluent needs some pre-treatment as well, to avoid fouling and increase the purity of product. The treated wastewater and product can be collected from different compartments as shown in Fig.6.3 as the very conventional setup of electrodialysis.

The advantage for the caustic wastewater to be treated with electrodialysis is the high conductivity, which can enhance the movement of charged ions and therefore the treatment efficiency. Electrodialysis is also possible to produce concentrated $NaOH$ solutions of around 15% to 20%. However, electrodialysis is more favourable for divalent ions compared with monovalent ions due to the bigger electrical force. According to Severin and Hayes, 2019, when monovalent ions are present together with multivalent ions, the concentrating process is usually more effective for divalent ions, even if they are of much lower concentrations. By a ratio of around 1.4:1 are the multivalent ions more preferred than monovalent, on a charge basis. Therefore, if the multivalent ions can not be removed in the pre-treatment process, they will not be eliminated in the electrodialysis. Due to the unknown concentration of carbonate, there might be scaling possibilities in both electrodialysis and the bottle washers if impurities accumulate along with recirculation.

Selectrodialysis, which is able to separate monovalent and divalent ions (Zhang et al., 2012), is possible for divalent and monovalent ion removal. However, research on the pH tolerance of selectrodialysis is limited at present. Current research of selectrodialysis is usually carried out with approximately neutral solutions. Therefore, it still need to be studied whether current selectrodialysis is able to handle high pH wastewater.

6.3. Solutions for the Future

Comparing the two techniques discussed above, electrodialysis seems to be more suitable for concentrating recovered caustic soda solutions. Nevertheless, neither technique can eliminate divalent and multivalent ions from the desired products. To compensate for the drawbacks from the two available techniques above, several measures could be considered for future applications.

First of all, the composition of caustic wastewater from bottle washers should be examined in detail, to provide more thorough information to treatment process designers.

Second, the surface of some NF membranes can be rebuilt or coated with special materials to enhance the rejection of divalent ions, or for loose RO membranes to increase pH tolerance, the possibility of using membrane filtration to recover caustic soda will largely increase. Such membranes can be used either directly for ion separation for the pre-treated wastewater, or after electrodialysis to purify the concentrated caustic soda solutions.

Third, highly pH tolerant selectrodialysis can be studied to recover caustic soda instead of conventional electrodialysis. Membranes with high pH tolerance need to be developed for selectrodialysis for caustic soda reclamation.

Moreover, the two techniques can be combined in practice. It is possible to dilute the pre-treat wastewater until pH 10 or pH 11, which is suitable for monovalent selective membranes, and then concentrate with conventional electrodialysis.

The most important, experiments of different possible setups should be carried out in lab scale first, testing with real caustic wastewater. By comparing the results from different techniques, setups can be improved and the optimised solution can be selected. and apply for industrial use.

7

Conclusion and Reflection

In this research, a few initiatives were completed with practical industrial information and water samples from Heineken®. A Python model was built for an imaginary bottle washer, and tested with difference operational variables under the four testing scenarios (TS-1 to TS-4). Based on the operational information from the Spanish brewery Quart de Poblet, a second Python model was built for the real-life case study, which was then optimised with several operational variables to reduce either WFP or CFP as caustic soda in five optimisation scenarios (OS-1 to OS-5). With three water samples from three caustic baths from another bottle washer operated in a Belgian brewery Alken Maes, a composition analysis on significant water parameters was carried out in the Water Lab in TU Delft. This lab analysis gave a basic insight of the compositions of caustic wastewater from bottle washers, and provided possibility to discuss the treatment methods.

7.1. Answers to Research Questions

1. **Can a model be built based on mass balance for a typical bottle washer to simulate caustic soda loss due to carry-over?**
   It can be hard to define what a typical bottle washer is, however, the basic units included can be similar including rinses, caustic baths and water baths. The mass balance can be calculated for every single bath within a bottle washer, and also for the whole bottle washer. Equations for mass balances can be related to water flows or substances. With checking the mass balance it is easy to know if any material flow is missing from the model. Basic Python models were built, and future programmers can easily modify them into other bottle washers to simulate the carry-over based on mass balance.

2. **What is the typical composition of caustic effluent from the bottle washers?**
   It is difficult to define a typical caustic effluent. Based on the analysis of the water samples, it was clear that the pH in bottle washer caustic baths could reach higher than 13. The concentrations of Na^{+}, OH^{-} and CO_3^{2-} could possibly be the highest among the inorganic species, while the concentrations of other ions were

significantly lower. The Na^+ and OH^- concentration could reach as high as about 600 $mmol/L$ and 250 $mmol/L$ respectively, while other ion species might not exceed 10 $mmol/L$. Conductivity and TDS of the caustic solutions were high due to caustic soda dosage and the accumulated impurities.

3. **Can the model of bottle washer be applied for different operational variables and structures?**
   It is possible to build a model with Python to adapt for most bottle washers, by modifying the structure of the bottle washer and assigning new values to operational variables. The number of baths and rinses, addition of label extraction, and internal recirculation can be changed from the BS model to fit the model in another bottle washer. All the operational variables can be assigned with different values, and creating new variables is simple as well. It is handy to simulate different scenarios with the same methods above once a model is built up for a certain type bottle washer.

4. **What are the most suitable methods for bottle washers to reduce the total caustic soda consumption?**
   There stated two different ways to reduce caustic soda consumption from bottle washers: during daily operation and to reclaim caustic soda from wastewater. On the one hand, the bottle washers themselves can be further improved in operation or structure, to reduce caustic soda consumption by recirculating label extraction discharge and lower the caustic soda concentrations in caustic baths. On the other hand, techniques are available to recover caustic soda from the wastewater. Membrane filtration and electrodialysis are not perfectly suitable for caustic soda reclamation, but with further adaptation on pH tolerance and charge selectivity will the technologies work out better.

7

7.2. CONCLUSIONS

The "3 R's principle" for waste management, i.e. reduce, reuse and recycle, can be applied to the waste caustic soda from the bottle washers. To improve the overall performance of bottle washers, changes can be made from either the bottle washers themselves by reducing caustic soda concentrations and reusing caustic soda from label extractors, or external chemical recovery processes connected between the wastewater discharge and automatic caustic soda dose to caustic baths.

According to the scenarios tested by using the Python models, some method could be raised to reduce the caustic consumption in a brewery:

1. Reduce the carry-over with pockets and conveying belt;

2. Reduce caustic strength in caustic baths if possible;

3. Recirculate the label extraction effluent to caustic baths after eliminating paper and glues to directly reuse the caustic soda;

4. Build more or larger water baths within reasonable budget;

Furthermore, the modelling method can greatly help with industrial operations such as bottle washers to simulate designed scenarios within a short time and without real-life experiments. But the validation in real-life practice of the final models is still needed.

7.3. Recommendations for Future Research

As for the modelling part, other modelling methods are also appreciated if they work more professionally than Python. The calculation towards EC has been examined as not accurate in the current models. Therefore, in the future models, the EC calculation should be improved by including more considerations, such as ionic activity and free ion concentrations, rather than using the theoretical values. To simulate the full situations in a real bottle washer, chemical reactions are strongly recommended to be added by defining the initial impurity concentrations according to real-life analysis, and reaction constants according to previous research. The reaction rates will depend on the temperature in the baths, and the concentrations after reaction are closely related to the retention time. Therefore, variables of impurity concentrations, temperature and retention time should be defined for each bath in the future model as well.

Besides, theoretical models still need qualification and validation with real-life data or experiments, from which real-life results can be obtained. This work was not done yet in this research. During the real-life operations, it is not possible to directly measure the caustic loss with carry-over. Therefore, the aim of the models was to simulate the caustic soda loss due to carry-over along the operational life span. The model was expected to get information which could not be directly obtained from real-life operations. But when the model is completed with all the other variables and built the same as real-life operation, the validation will become possible.

For the breweries as one of the stakeholders, here are some further suggestions, which also help with the improvement in sustainability, to help with future research and their operation of bottle washers:

- Lab analysis on the bottle washer wastewater is recommended for each brewery, or several breweries that are equipped with similar bottle washers. The analysis is preferred to be carried out on site to ensure the accuracy of the concentrations of organic compounds. More inorganic ion species should be measured. The content of VFA, which was missing in this research, should be paid much attention;

- Improve the monitoring system for the bottle washers to control the rinsing flowrate. The conductivity sensor is not enough since the impurities also contribute to the conductivity, leading to the possibly lower caustic soda concentrations than standards;

- Cooperate with research institutions and technical companies to actively improve their industrial processes;

- Replace $NaOH$ with KOH where potassium can be utilised by crops, but can be more expensive than $NaOH$. With KOH the possibility of wastewater reuse can be expanded to agriculture. The net cost will depend on the profit selling potassium rich wastewater.

This research can be referred to by future researchers. A multi-criteria optimisation with professional mathematical models is expected to built for bottle washers, with adequate information on wastewater composition and operational parameters from the breweries. In the future models, more parameters such as the working hours and chemical concentrations should be included to complete the current model from this research. Currently available techniques should be discussed and selected if caustic soda reclamation is expected to be achieved, so that the recovered caustic soda can be reused in the bottle washers. Tests on the membranes or electrodialysis in lab scales should be carried out to optimise the recovery solution for further industrial practice. CAPEX and OPEX should be evaluate as well to judge if the caustic soda reclamation scheme is cost wise. Similarly, the research can also be carried out regarding the CIP wastewater in the breweries, which is also expected to be highly caustic and contains more organic components.

Furthermore, sustainability is not only related to the WFP and CFP, but also a social problem. With optimised WFP or CFP are the bottle washers partially improved to be more sustainable. The work done in this research should be regarded as only a small and initial step towards sustainability, but more factors need to be involved in the future. A "sustainable" bottle washer could influence many stakeholders including the breweries, the suppliers, the market and even every consumer. The project should be carried on by future researchers. A thorough sustainability study, involving goal and scope definition, inventory assessment, and optimisation, is recommended as well.

8

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Yiyi Zhang (Annie),
Delft, March 2022

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A

Full Mass Balance

To present the full mass balance of a bottle washer, an example with pre-rinse, two caustic baths, one water bath and final rinse will be included in this appendix. The automatic caustic dose and label extraction will also be taken into consideration.

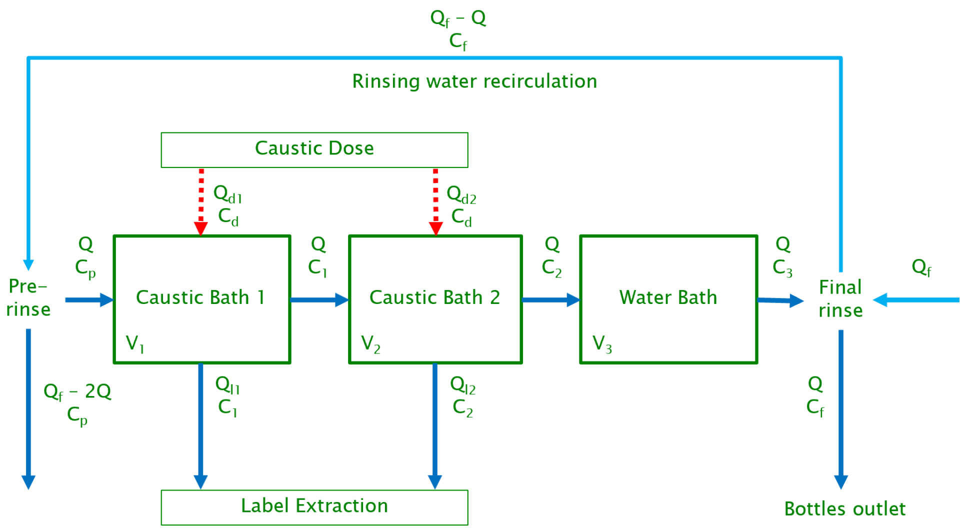

Figure A.1: Full mass balance of physical processes with pre-rinse, two caustic baths, one water bath and final rinse

In the mass balance model, notations are used to represent water flows and concentrations within the boundary:
Q: carry-over (assumed to be constant) (m^3/min)
Q_{d1}: flowrate of caustic soda dose in Caustic Bath 1 (m^3/min)
Q_{d2}: flowrate of caustic soda dose in Caustic Bath 2 (m^3/min)

A

Q_{l1}: flowrate of label extraction from Caustic Bath 1 (m^3/min)
Q_{l2}: flowrate of label extraction from Caustic Bath 2 (m^3/min)
Q_f: flowrate of clean water used for final rinsing (m^3/min)
C_d: concentration in caustic soda dose (kg/m^3)
C_1: concentration in Caustic Bath 1 (kg/m^3)
C_2: concentration in Caustic Bath 2 (kg/m^3)
C_3: concentration in Water Bath (kg/m^3)
C_p: concentration in the water after pre-rinse (kg/m^3)
C_f: concentration in the water after final rinse (kg/m^3)
V_1: solution volume in Caustic Bath 1 (m^3)
V_2: solution volume in Caustic Bath 2 (m^3)
V_3: solution volume in Water Bath (m^3)

The dosage of caustic soda are based on the demand in the caustic baths. In the ideal case, not considering evaporation or other losses, the differential equations of the full mass balance model can be described as:

- Water balance expressed in volume:

$$\frac{dV_1}{dt} = Q + Q_{d1} - Q - Q_{l1} = Q_{d1} - Q_{l1} \tag{A.1}$$

$$\frac{dV_2}{dt} = Q + Q_{d2} - Q - Q_{l2} = Q_{d2} - Q_{l2} \tag{A.2}$$

$$\frac{dV_3}{dt} = Q - Q = 0 \tag{A.3}$$

Since there should not be too much fluctuation in the solution volumes in baths, V_n can be taken as a constant for simplification. It can be more accurate if the fluctuation percentage in the caustic baths is known to make V_n also a variable.

- Na^+ balance:

$$\frac{dC_{1,Na^+}}{dt} \cdot V_1 = Q \cdot C_{p,Na^+} + Q_{d1} \cdot C_{d,Na^+} - Q \cdot C_{1,Na^+} + Q_{l1} \cdot C_{1,Na^+} \tag{A.4}$$

$$\frac{dC_{2,Na^+}}{dt} \cdot V_2 = Q \cdot C_{1,Na^+} + Q_{d2} \cdot C_{d,Na^+} - Q \cdot C_{2,Na^+} + Q_{l2} \cdot C_{2,Na^+} \tag{A.5}$$

$$\frac{dC_{3,Na^+}}{dt} \cdot V_3 = Q \cdot C_{2,Na^+} - Q \cdot C_{3,Na^+} \tag{A.6}$$

- OH^- balance:

$$\frac{dC_{1,OH^-}}{dt} \cdot V_1 = Q \cdot C_{p,OH^-} + Q_{d1} \cdot C_{d,OH^-} - Q \cdot C_{1,OH^-} + Q_{l1} \cdot C_{1,OH^-} \tag{A.7}$$

$$\frac{dC_{2,OH^-}}{dt} \cdot V_2 = Q \cdot C_{1,OH^-} + Q_{d2} \cdot C_{d,OH^-} - Q \cdot C_{2,OH^-} + Q_{l2} \cdot C_{2,OH^-} \tag{A.8}$$

$$\frac{dC_{3,OH^-}}{dt} \cdot V_3 = Q \cdot C_{2,OH^-} - Q \cdot C_{3,OH^-} \tag{A.9}$$

The overall mass balance of a bottle washer with N baths over an operational time span T can be expressed with integration. The total mass flows in deducted by the total mass flows out and the net accumulation of mass in the certain bath should equal 0:

$$\int_{n=1}^{n=N} (C_{n,t=T} \cdot V_n)\, dn - \int_{n=1}^{n=N} (C_{n,t=0} \cdot V_n)\, dn - \int_{n=1}^{n=N} \int_{t=0}^{t=T} (\frac{dC_n}{dt} \cdot V_n)\, dt\, dn = 0 \quad \text{(A.10)}$$

B

Brewery Questionnaire

The Questionnaire was designed for cooperative breweries to fill in. The breweries would provide their operational information on their bottle washers for this research and their Python model. In this appendix, questions in the questionnaire and answers from the Valencia brewery brewery Quart de Poblet will be presented. Questions without answers were not answered by the brewery, and the name of the contact person was hidden.

B.1. Introduction of the Questionnaire

Dear Sir/Madam,

This is Annie from TU Delft working on the MSc thesis on sustainable bottle washers. At the same time, this is also a very important project for Heineken to promote sustainability in their breweries.

To complete the project, we sincerely invite you to share your data with us by filling this questionnaire. I will only use your data for this project, and not anywhere else. The dissertation will be handed in to the university after I finish it. Please help us to provide data according to this questionnaire in the "Basic info", "Bottle Washers" and "Chemical" Tab. Details are always welcome.

You can put your answers in the "Answers" column and extra information you would like to provide in the "Remarks" column. Some examples may be already given. You can also change the units according to your data. You may need some laboratory tests to answer the "Chemical" Part. There is a scheme of the bottle washers for your better understanding.

If there is any question that you do not have information so far, please also let me know.

Thank you very much for your time!

Sincerely yours, Annie

B.2. Basic Information

Contact Information

1. Name of the brewery
   Valencia

2. Location
   Spain

3. Contact person

Background Information

Data from 2020 from LINE 32 (returnable bottle)

1. Do you have bottle washers on site? (Yes/No)
   Yes

2. What is the supplier for your bottle washer? (Name of the supplier)
   KRONES®

3. How much beer do you annually produce? (in *L*)
   13,549,770 L

4. How many bottles of beer do you annually produce?
   42,137,232 bottles

5. What are the volumes of your returnable bottles? (0.5, and 0.33 for e.g., in *L*)
   33cl and 25cl

6. How much beer do you put in these bottles in 2020? (in *L*)
   -33cl: 12,438,780 L; 25cl: 1,110,990 L

B.3. Bottle Washer Operation

Operation Overview

1. What is the operational lifetime for your bottle washers? (The lifetime is the duration when you empty the first caustic bath and shift solutions of following baths forward, in $days$)

2. For how long time do you completely clean the baths? (This is the time duration when you thoroughly clean all the baths, in $days$)

3. How many caustic baths do you have?
   3

4. How many water baths do you have?
   3

5. What is the volume of the baths? (in m^3)
   48 m^3

B

6. Do you have any insight on the carry-over per bottle? (in $mL/bottle$)

7. How many water loss points do you expect in the bottle washer? Please explain where and how much is the loss. (position of loss point, how much water is discharged)
   No.
   (Remark: But we consume aprox. 36 hl of caustic solution (25%) per day)

8. How many caustic loss points do you expect in the bottle washer? Please explain where and how much is the loss. (position of loss point, how much caustic soda is discharged)
   We may consider we lose water (and caustic) in:Label extraction system (10 m^3/day), pre-rinse system (that reuse water from the last water baths you may see in the image 1) 25 m^3/day, without consider the liquid absolved by the paper, Crate washer, from the same system of the pre-rinse (pumps and pipes) 50 m^3, and by the normal carry-over from bath to bath.
   Remark: aprox. 328 m^3/day

RINSING

1. What is the flowrate of pre-rinse and final rinse? (in m^3/h)
   We dont have the flowrate, just the working pressure, that is 1.4 -1.6 bar

2. Do you reuse the effluent from final rinse in pre-rinse? (Yes/No, with any treatment?)
   Yes, with no intermediate treatment

BOTTLE WASHER OPERATIONS

1. How many bottles do you put in the bottle washers per hour? (in $bottles/h$)
   92,000 $bottles/h$

2. How long is the retention time in each bath? (in min)
   we don't have the time in each bath, the total time of treatment is 20 min

3. What is the temperature in the caustic baths? (in $^\circ C$)
   1: 65 $^\circ C$;2: 75 $^\circ C$; 3: 70 $^\circ C$

4. What do you use as make-up caustic? (liquid/solid, purity %)
   We receive caustic solution on 50%, that are diluted to 25%

5. How do you dose caustic soda into caustic baths? Please explain the working mode in detail (continuous dosing or automatic intermittent dosing? when the concentration or conductivity reaches which certain value?)
   automatic intermittent dosing when the conductivity is right below the set point. Then it makes 1 min of dosification.

6. What is the range of caustic concentration in caustic baths? (in g/L)
   1.5 - 2 g/L

7. What is the concentration of caustic soda that you use for automatic dosing? (in g/L)
   80 mS to 90 mS

8. What is the starting caustic soda concentration in the caustic baths? (in g/L)
   2 g/L

9. What is the starting conductivity in the caustic baths? (in $\mu S/cm$)
   1: 85 mS;2: 90 mS; 3: 85 mS

10. How much caustic soda do you consume per operational cycle? (in kg)
    per day 36 hl from caustic solution of 25%

11. How much caustic soda do you loss from bottle washer per operational cycle? (in kg)
    per day 36 hl from caustic solution of 25%

12. Do you think the difference in the last two questions all goes to the chemical reactions with organic matters in caustic baths?
    As I don't have a way to know how much soda is "consumed" by the normal carry-over or the chemical reactions, I have put the same 36 hl in both.
    Remark: I do believe that most of the caustic is consumed in chemical reactions and in the label extraction system (this last one due to the paper absorption). But it would be good make some tests

13. Do you have label extraction in caustic baths (how many)? How does it work?
    Yes we do have in all 3 baths.

14. What is the temperature in the water baths? (in $°C$)
    Hot water 1: 65°C Hot water 2: 55°C; Cold Water < 45°C

AFTER-USE

Now a day we do not have the decantation system working ,it was desacvated 10 years ago. Now we are on going with a project to recover this system. So, in every 3 months we discharge all tanks from the Bottle Washer.

1. How many sedimentation tanks do you have for the caustic wastewater after every operational cycle?

2. What is the volume of each sedimentation tanks? How much sediments do you usually get for how long period? (in m^3)

3. How long is the sedimentation time? (in h)

4. What do you do after the sedimentation? Treatment or discharge or reuse?

5. How much water is discharged with sediments (solids) and how much recycled?

6. Do you currently have any water/chemical recovery process on site? (Yes, what process? /No)
   No

B.4. CHEMICAL

GENERAL

1. What onsite monitoring tools do you have?
   We just do carbonates concentration and caustic soda concentration.

B

2. What parameters are you monitoring with these tools?
   We just do carbonates concentration and caustic soda concentration.

3. Do you carry out lab test of wastewater/bath solutions regularly?
   just in the 3 caustic solution baths, were we check the 2 parameter commented above

4. Are you clear about the chemical reactions happening in caustic baths?
   not entirely

5. Do you know what is the major consumer of caustic in the baths?
   No

6. If so, how much caustic soda is consumed per bottle or per kg COD? (or based on other chemical format)

LAB TEST SECTION (UNITS MODIFIABLE)

1. Conductivity ($\mu S/cm$)
2. Sodium Na^+ (g/L)
3. COD (g/L)
4. TSS (g/L)
5. VFA (g/L)
6. TOC (g/L)
7. Turbidity (NTU)
8. pH
9. Other trace elements (g/L)
   - Calcium Ca^{2+}
   - Magnesium Mg^{2+}
   - Carbonate CO_3^{2-}
   - Sulphate SO_4^{2-}

C

Python Codes for Models

C.1. Simple Model

```
import numpy as np
import matplotlib.pyplot as plt
# import scipy as sp
# from pandas import read_csv
from pandas import DataFrame
# from IPython.display import display
# import random

mc_Na = 0.05011*10**6
mc_H = 0.34982*10**6
mc_OH = 0.1986*10**6
# molar conductivity in  S *L/mol/cm

# operational parameters

days = 14      # lifetime in days
lifetime = days * 24 * 60      # lifetime in minutes
v_caustic = 17      # volume of caustic bath in m3
v_water = 17      # volume of water bath in m3
caustic_low = 0.015      # lowest range of caustic concentration
caustic_high = 0.02      # highest range of caustic concentration
carryover = 1.5      # carry-over in mL/bottle
bpm = 100000 / 60      # bottles (per hour to) per min
density = 1000      # water density 1000 kg/m3 = 1 kg/L
rinse_flow = 10 / 60      # rinse flowrate (m3/h to) m3/min
```

C

```
loss = bpm * carryover / (10**6)      # losses due to carry-over in
    m3/min
cmin = caustic_low * v_caustic * density      # critical
    concentration for auto-dose
cmax = caustic_high * v_caustic * density      # max caustic
    concentration in the bath

# model parameters

dc = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), '
    caustic_co': np.zeros(lifetime), 'dose': np.zeros(lifetime), '
    dmdt': np.zeros(lifetime), 'conductivity': np.zeros(lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry
    -over in kg, automatical caustic dose in kg, electrical
    conductivity in  S /cm
dw = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), '
    caustic_co': np.zeros(lifetime), 'dmdt': np.zeros(lifetime), '
    conductivity': np.zeros(lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry
    -over in kg, electrical conductivity in  S /cm
dr = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), '
    caustic_co': np.zeros(lifetime), 'conductivity': np.zeros(
    lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry
    -over in kg, electrical conductivity in  S /cm

caustic = DataFrame(data=dc)      # time series for caustic bath
water = DataFrame(data=dw)      # time series for water bath
prinse = DataFrame(data=dr)      # time series for pre rinse
    discharge (wastewater)
frinse = DataFrame(data=dr)      # time series for final rinse
    discharge

caustic.content[0] = cmax
# caustic.content2[0] = caustic.content[0]
caustic.conc[0] = caustic.content[0] / v_caustic
caustic.caustic_co[0] = caustic.conc[0] * loss
na = caustic.conc[0] / 40      # Na+ concentration in mol/L
h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
caustic.conductivity[0] = (na * mc_Na) + (oh * mc_OH) + (h * mc_H)

for i in np.arange(lifetime-1):
    # caustic bath
    # caustic.content[i+1] = (caustic.content[i] + caustic.content2[
```

```
    i]) / 2 - caustic.caustic_co[i]

# if caustic.content[i+1] < cmin:
#     caustic.dose[i+1] = cmax - caustic.content[i+1]
#     # caustic.content[i+1] = cmax

# caustic.content2[i+1] = caustic.content[i+1] + caustic.dose[i
    +1]
# caustic.conc[i+1] = (caustic.content[i+1] + caustic.content2[i
    +1]) / 2 / v_caustic
# caustic.caustic_co[i+1] = caustic.conc[i+1] * loss

# # water bath
# water.content[i+1] = (water.content[i] + water.content2[i]) /
    2 - water.caustic_co[i]     # taking in carry-over from
    caustic bath and giving out
# water.content2[i+1] = water.content[i+1] + caustic.caustic_co[
    i+1]
# water.conc[i+1] = (water.content[i+1] + water.content2[i+1]) /
     2 / v_water
# water.caustic_co[i+1] = water.conc[i+1] * loss


# caustic bath
caustic.content[i+1] = caustic.content[i] + prinse.caustic_co[i]
     - caustic.caustic_co[i]

if caustic.content[i+1] < cmin:
    caustic.dose[i+1] = cmax - caustic.content[i+1]

caustic.content[i+1] = caustic.content[i+1] + caustic.dose[i+1]
caustic.conc[i+1] = caustic.content[i+1] / v_caustic
caustic.caustic_co[i+1] = caustic.conc[i+1] * loss
caustic.dmdt[i+1] = caustic.dose[i+1] - caustic.caustic_co[i+1]
na = caustic.conc[i+1] / 40
h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
caustic.conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h *
    mc_H)

# water bath
water.content[i+1] = water.content[i] - water.caustic_co[i] +
    caustic.caustic_co[i]     # taking in carry-over from caustic
     bath and giving out
water.conc[i+1] = water.content[i+1] / v_water
```

```
    water.caustic_co[i+1] = water.conc[i+1] * loss
    water.dmdt[i+1] = caustic.caustic_co[i+1] - water.caustic_co[i
        +1]
    na = water.conc[i+1] / 40
    h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
    oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
    water.conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h *
        mc_H)

    # rinse
    frinse.content[i+1] = water.caustic_co[i+1]
    frinse.conc[i+1] = frinse.content[i+1] / (rinse_flow + loss)
    frinse.caustic_co[i+1] = frinse.conc[i+1] * loss
    na = frinse.conc[i+1] / 40
    h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
    oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
    frinse.conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h *
        mc_H)
    prinse.content[i+1] = frinse.content[i] - frinse.caustic_co[i]
    prinse.conc[i+1] = prinse.content[i+1] / (rinse_flow + loss)
    prinse.caustic_co[i+1] = prinse.conc[i+1] * loss
    na = prinse.conc[i+1] / 40
    h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
    oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
    prinse.conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h *
        mc_H)

caustic_start = caustic.conc[0] * v_caustic
caustic_end = caustic.conc[lifetime-1] * v_caustic + water.conc[
    lifetime-1] * v_water
# caustic_total = caustic_start + np.sum(caustic.dose) - caustic_end
        # total caustic consupmtion over life time in kg
caustic_loss = np.sum(frinse.caustic_co) + np.sum(prinse.conc) *
    rinse_flow
caustic_ave = np.sum(caustic.dose) / (bpm * lifetime)     # average
    caustic consumption per bottle in kg
# print(caustic_loss)

# mass_balance = caustic_start + np.sum(caustic.dose) - caustic_end
    - np.sum(water.caustic_co)
# mass_balance_1 = caustic_start + np.sum(caustic.dose) - caustic.
    conc[lifetime-1] * v_caustic - np.sum(caustic.caustic_co)
# mass_balance_2 = np.sum(caustic.caustic_co) - np.sum(water.
    caustic_co) - water.conc[lifetime-1] * v_water
# print(mass_balance, mass_balance_1, mass_balance_2)
```

```
# mbc = caustic.content[lifetime-1] - caustic.content[0] - np.sum(
    caustic.dmdt)
# mbw = water.content[lifetime-1] + water.content[0] - np.sum(water.
    dmdt)
# print(mbc, mbw)

# plt.figure()
# plt.plot(caustic.conc)
# plt.plot(water.conc)
# plt.title(f'Caustic concentrations for {days}-day operation in
    caustic and water baths')
# plt.xlabel('Time (min)')
# plt.ylabel('Caustic Concentration (g/L)')
# plt.legend(['Caustic Bath', 'Water Bath'], loc=4)

# plt.figure()
# plt.plot(frinse.conc)
# plt.plot(prinse.conc)
# plt.title(f'Caustic concentrations for {days}-day operation in pre
    -rinse and final rinse effluent')
# plt.xlabel('Time (min)')
# plt.ylabel('Caustic Concentration (g/L)')
# plt.legend(['Final Rinse', 'Pre-rinse'], loc=4)

plt.figure()
plt.plot(caustic.conductivity)
plt.plot(water.conductivity)
plt.title(f'Electrical conductivity for {days}-day operation in 
    caustic and water baths')
plt.xlabel('Time (min)')
plt.ylabel('Electrical Conductivity ( S /cm)')
plt.legend(['Caustic Bath', 'Water Bath'], loc=4)

plt.figure()
plt.plot(frinse.conductivity)
plt.plot(prinse.conductivity)
plt.title(f'Electrical conductivity for {days}-day operation in pre-
    rinse and final rinse effluent')
plt.xlabel('Time (min)')
plt.ylabel('Electrical Conductivity ( S /cm)')
plt.legend(['Final Rinse', 'Pre-rinse'], loc=4)
```

C.2. FULL SCALE MODEL

C

```
import numpy as np
import matplotlib.pyplot as plt
# import scipy as sp
# from pandas import read_csv
from pandas import DataFrame
# from IPython.display import display
# import random

mc_Na = 5.011*10**4
mc_H = 34.982*10**4
mc_OH = 19.86*10**4
# molar conductivity in  S *L/mol/cm

# operational parameters

days = 14      # lifetime in days
lifetime = days * 24 * 60      # lifetime in minutes
ncaustic = 5      # number of caustic baths
nwater = 5      # number of water baths
v_caustic = np.ones(ncaustic) * 17      # volume of each caustic bath
     in m3
v_water = np.ones(nwater) * 17      # volume of each water bath in m3
# caustic_low = 0.015      # lowest range of caustic concentration
# caustic_high = 0.02      # highest range of caustic concentration
caustic_high_range = [0.01, 0.015, 0.02]      # highest range of
    caustic concentrations
carryover = 10      # carry-over in mL/bottle
# carryover_range = [10, 15, 20]      # carry-over in mL/bottle
bpm = 100000 / 60      # bottles (per hour to) per min
density = 1000      # water density 1000 kg/m3 = 1 kg/L
bottle_volume = 3.3      # bottle volume in hL

# model parameters

# caustic balance

for caustic_high in caustic_high_range:
    rinse_flow = 10 / 60      # rinse flowrate (m3/h to) m3/min
    # cmin = caustic_low * v_caustic * density      # critical
        content for auto-dose in kg
    cmax = caustic_high * v_caustic * density      # max caustic
        content in the bath in kg
    dose_total = 0      # the total caustic dose in caustic baths in
        kg
```

```
loss_total = 0      # the total caustic loss from the whole system in kg
loss_cb = 0      # the total caustic loss from caustic baths to water baths in kg
loss = bpm * carryover / (10**6)      # losses due to carry-over in m3/min

dc = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), 'caustic_co': np.zeros(lifetime), 'dose': np.zeros(lifetime), 'dmdt': np.zeros(lifetime), 'conductivity': np.zeros(lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry-over in kg, automatical caustic dose in kg, electrical conductivity in  S /cm
dw = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), 'caustic_co': np.zeros(lifetime), 'dmdt': np.zeros(lifetime), 'conductivity': np.zeros(lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry-over in kg, electrical conductivity in  S /cm
dr = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), 'caustic_co': np.zeros(lifetime), 'conductivity': np.zeros(lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry-over in kg, electrical conductivity in  S /cm
cb = []
wb = []
for c in np.arange(ncaustic):
    cb.append(DataFrame(data=dc))
    cb[c].content[0] = cmax[c]
    # cb[c].content2[0] = cb[c].content[0]
    cb[c].conc[0] = cb[c].content[0] / v_caustic[c]
    cb[c].caustic_co[0] = cb[c].conc[0] * loss
for w in np.arange(nwater):
    wb.append(DataFrame(data=dw))

prinse = DataFrame(data=dr)      # time series for pre rinse discharge (wastewater)
frinse = DataFrame(data=dr)      # time series for final rinse discharge
prinse.conductivity[0] = frinse.conductivity[0] = 10**(-7) * (mc_H + mc_OH)

for i in np.arange(lifetime-1):

    # caustic bath:
```

```
cb[0].content[i+1] = cb[0].content[i] + prinse.caustic_co[i]
      - cb[0].caustic_co[i]
if cb[0].content[i+1] < cmax[0]:
        cb[0].dose[i+1] = cmax[0] - cb[0].content[i+1]
        dose_total = dose_total + cb[0].dose[i+1]
cb[0].content[i+1] = cb[0].content[i+1] + cb[0].dose[i+1]
cb[0].conc[i+1] = cb[0].content[i+1] / v_caustic[0]
cb[0].caustic_co[i+1] = cb[0].conc[i+1] * loss
cb[0].dmdt[i+1] = cb[0].dose[i+1] - cb[0].caustic_co[i+1]

for c in np.arange(ncaustic)[1:]:
    cb[c].content[i+1] = cb[c-1].caustic_co[i] + cb[c].
        content[i] - cb[c].caustic_co[i]

    if cb[c].content[i+1] < cmax[c]:
        cb[c].dose[i+1] = cmax[c] - cb[c].content[i+1]
        dose_total = dose_total + cb[c].dose[i+1]
        # cb[c].content[i+1] = cmax[c]

    cb[c].content[i+1] = cb[c].content[i+1] + cb[c].dose[i
        +1]
    cb[c].conc[i+1] = cb[c].content[i+1] / v_caustic[c]
    cb[c].caustic_co[i+1] = cb[c].conc[i+1] * loss
    cb[c].dmdt[i+1] = cb[c-1].caustic_co[i+1] + cb[c].dose[i
        +1] - cb[c].caustic_co[i+1]

# water bath:
wb[0].content[i+1] = wb[0].content[i] + cb[ncaustic-1].
    caustic_co[i+1] - wb[0].caustic_co[i]
wb[0].conc[i+1] = wb[0].content[i+1] / v_water[0]
wb[0].caustic_co[i+1] = wb[0].conc[i+1] * loss
wb[0].dmdt[i+1] = cb[ncaustic-1].caustic_co[i+1] - wb[0].
    caustic_co[i+1]

for w in np.arange(nwater)[1:]:
    wb[w].content[i+1] = wb[w].content[i] + wb[w-1].
        caustic_co[i+1] - wb[w].caustic_co[i]      # taking
        in carry-over from caustic bath and giving out
    wb[w].conc[i+1] = wb[w].content[i+1] / v_water[w]
    wb[w].caustic_co[i+1] = wb[w].conc[i+1] * loss
    wb[w].dmdt[i+1] = wb[w-1].caustic_co[i+1] - wb[w].
        caustic_co[i+1]

# rinse:
frinse.content[i+1] = wb[nwater-1].caustic_co[i+1]
```

```
        frinse.conc[i+1] = frinse.content[i+1] / (rinse_flow + loss)
        frinse.caustic_co[i+1] = frinse.conc[i+1] * loss
        na = frinse.conc[i+1] / 40      # Na+ concentration in mol/L
        h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2      # H+
            concentration in mol/L
        oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
                # OH- concentration in mol/L
        frinse.conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h
            * mc_H)

        prinse.content[i+1] = frinse.content[i] - frinse.caustic_co[
            i]
        prinse.conc[i+1] = prinse.content[i+1] / rinse_flow
        prinse.caustic_co[i+1] = prinse.conc[i+1] * loss
        na = prinse.conc[i+1] / 40      # Na+ concentration in mol/L
        h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2      # H+
            concentration in mol/L
        oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
                # OH- concentration in mol/L
        prinse.conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h
            * mc_H)

        # caustic loss:
        loss_cb = loss_cb + cb[ncaustic-1].caustic_co[i+1]
        loss_total = loss_total + (prinse.conc[i+1] * rinse_flow) +
            frinse.caustic_co[i+1]

# calculation at the end of life time

# caustic_start = 0      # starting caustic content in caustic
    baths
# caustic_end_cb = np.zeros(ncaustic)      # end caustic content
    in caustic baths
# caustic_end_wb = np.zeros(nwater)      # end caustic content in
     water baths
# mb = np.zeros(ncaustic+nwater)

# na = np.zeros(lifetime)
# h = np.zeros(lifetime)
# oh = np.zeros(lifetime)

# plt.figure()
# for n in np.arange(ncaustic):
#     caustic_start = caustic_start + cb[n].conc[0] * v_caustic[
    n]
```

```
#      caustic_end_cb[n] = cb[n].conc[lifetime-1] * v_caustic[n]
#      mb[n] = cb[n].content[lifetime-1] - cb[n].content[0] - np.
    sum(cb[n].dmdt)
#      na = cb[n].conc / 40       # Na+ concentration in mol/L
#      h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
#      oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
#      cb[n].conductivity = (na * mc_Na) + (oh * mc_OH) + (h *
    mc_H)
#      print(cb[n].conc[lifetime-1])
#      plt.plot(cb[n].conc / 40 * 23)       # Na+ concentration
     # plt.plot(cb[n].conductivity)
# plt.legend(['cb1', 'cb2', 'cb3', 'cb4', 'cb5'], loc=4)
# plt.title(f'Sodium concentrations in caustic baths for {days}-
    day operation')
# plt.xlabel('Time (min)')
# plt.ylim((-1,21))
# plt.ylabel('Sodium Concentration (g/L)')

# plt.figure()
# for n in np.arange(nwater):
#      caustic_end_wb[n] = wb[n].conc[lifetime-1] * v_water[n]
#      mb[ncaustic+n] = wb[n].content[lifetime-1] - wb[n].content
     [0] - np.sum(wb[n].dmdt)
#      na = wb[n].conc / 40       # Na+ concentration in mol/L
#      h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
#      oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
#      wb[n].conductivity = (na * mc_Na) + (oh * mc_OH) + (h *
    mc_H)
#      print(wb[n].conc[lifetime-1])
#      plt.plot(wb[n].conc / 40 * 23)       # Na+ concentration
#      # plt.plot(wb[n].conductivity)
# plt.xlabel('Time (min)')
# plt.ylabel('$\mathregular{Na^+}$ Concentration (g/L)')
# # plt.ylabel('Conductivity ( S /cm)')
# # # # plt.legend(['wb1', 'wb2', 'wb3', 'wb4', 'wb5'], loc=2)
# plt.title(f'Sodium concentrations in water baths for {days}-
    day operation')
# plt.legend(['cb1', 'cb2', 'cb3', 'cb4', 'cb5', 'wb1', 'wb2', '
    wb3', 'wb4', 'wb5'], bbox_to_anchor=(1.05, 0.85))
# # # # plt.title(f'$Na^+$ concentrations in caustic and water
    baths for {days}-day operation')
# # plt.title(f'Conductivity for {days}-day operation in caustic
     and water baths for {days}-day operation')

# plt.figure()
```

```
    # plt.plot(frinse.conc / 40 * 23)
    # plt.plot(prinse.conc / 40 * 23)
    # plt.title(f'$Na^+$ concentrations for {days}-day operation in
        pre-rinse and final rinse effluent')
    # plt.xlabel('Time (min)')
    # plt.ylabel('$\mathregular{Na^+}$ Concentration (g/L)')
    # plt.legend(['Final Rinse', 'Pre-rinse'], loc=4)

    daily_caustic_loss = np.zeros(days)      # daily caustic loss sum
        -ups
    daily_caustic_dose = np.zeros(days)      # daily caustic dose sum
        -ups
    for n in np.arange(days):
        a = n * 24 * 60
        b = (n + 1) * 24 * 60
        # loss = final rinse + pre-rinse - pre-rinse carryover +
            label extraction
        daily_caustic_loss[n] = np.sum(frinse.caustic_co[a:b]) + np.
            sum(prinse.content[a:b]) - np.sum(prinse.caustic_co[a:b
            ])
        for i in np.arange(ncaustic):
            daily_caustic_dose[n] = np.sum(cb[i].dose[a:b])
    # print(daily_caustic_loss)
    # daily_acc = daily_caustic_dose - daily_caustic_loss
    # plt.figure()
    plt.plot(daily_caustic_loss/40*23, label=f'{caustic_high*100}%')
    # plt.plot(daily_caustic_dose, label='Daily dose')
    # plt.plot(daily_acc, label='Accumulation')
plt.title(f'Daily␣sodium␣loss␣for␣{days}-day␣operation␣with␣
    different␣caustic␣concentrations')
plt.xlabel('Time␣(day)')
plt.ylabel('Sodium␣(kg)')
plt.legend(loc=0)
    # caustic_bottle = dose_total / (bpm * lifetime)      # average
        caustic consumption per bottle in kg
    # caustic_beer = caustic_bottle / bottle_volume      # average
        caustic consumption hL of beer in kg
    # print(f'Total loss {loss_total} kg, total dose {dose_total} kg
        , {caustic_bottle} kg/bottle, {caustic_beer} per hL beer. ')

# plt.title(f'Daily caustic soda loss for {days}-day operation with
    different carryover rates')
# plt.xlabel('Time (day)')
# plt.ylabel('Caustic soda loss (kg)')
# plt.legend(loc=4)
```

```
# plt.figure()
# plt.plot(frinse.conductivity)
# plt.plot(prinse.conductivity)
# plt.title(f'Conductivity for {days}-day operation in pre-rinse and final rinse effluent')
# plt.xlabel('Time (min)')
# plt.ylabel('Conductivity ( S /cm)')
# plt.legend(['Final Rinse', 'Pre-rinse'], loc=4)

# caustic_end = np.sum(caustic_end_cb) + np.sum(caustic_end_wb)

# # caustic_total = np.sum(caustic_start) + dose_total - caustic_end - loss_total     # total caustic consupmtion over life time in all the baths in kg

# mass_balance = caustic_start + dose_total - caustic_end - loss_total
# mass_balance_cb = caustic_start + dose_total - loss_cb - np.sum(caustic_end_cb)
# mass_balance_wb = loss_cb - np.sum(caustic_end_wb) - loss_total
# print(mass_balance, mass_balance_cb, mass_balance_wb)
# print(mb)
```

C.3. VALENCIA MODEL

```
import numpy as np
import matplotlib.pyplot as plt
# import scipy as sp
# from pandas import read_csv
from pandas import DataFrame
# from IPython.display import display
# import random

# mc_Na = 5.011*10**4
# mc_H = 34.982*10**4
# mc_OH = 19.86*10**4
# molar conductivity in  S *L/mol/cm

# operational parameters

days = 60      # 5 days as a cycle
lifetime = days * 24 * 60      # lifetime in minutes
ncaustic = 3      # number of caustic baths
```

```
nwater = 3      # number of water baths
caustic_volume = 48.08      # volume of each caustic bath in m3
v_caustic = np.ones(ncaustic) * caustic_volume      # volume of each
    caustic bath in m3
v_water = [1.44, 6.74, 1.57]      # volume of each water bath in m3
caustic_low = 0.015      # lowest range of caustic concentration
caustic_high = 0.02      # highest range of caustic concentration
# caustic_high_range = [0.01, 0.015, 0.02]      # highest range of
    caustic concentrations
carryover = 10      # carry-over in mL/bottle
# carryover_range = [10, 15, 20]      # carry-over in mL/bottle
bpm = 92000 / 60      # bottles (per hour to) per min
density = 1000      # water density 1000 kg/m3 = 1 kg/L
bottle_volume = 3.3      # bottle volume in hL
le = 10/3/24/60      # label extraction loss in each caustic bath 10
    m3/day to m3/min
rinsings_total = 5      # total number of rinsings
caustic_make_up_conc = 0.25      # 25% caustic soda solution
caustic_density = 100 / (75 / density)      # density of 25% caustic
    soda solution
le_loss_total = np.zeros(lifetime)

# model parameters

# caustic balance

rinse_flow = 3.68/60      # rinse flowrate m3/min
pre_rinse_flow = 25/24/60      # 25 m3/day reuse from the other four
    rinses
cmin = caustic_low * v_caustic * density      # critical content for
    auto-dose in kg
cmax = caustic_high * v_caustic * density      # max caustic content
    in the bath in kg
dose_total = 0      # the total caustic dose in caustic baths in kg
loss_total = 0      # the total caustic loss from the whole system in
    kg
loss_cb = 0      # the total caustic loss from caustic baths to water
    baths in kg
loss = bpm * carryover / (10**6)      # losses due to carry-over in
    m3/min

dc = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), '
    caustic_co': np.zeros(lifetime), 'dose': np.zeros(lifetime), '
    dmdt': np.zeros(lifetime), 'conductivity': np.zeros(lifetime), '
    v': np.zeros(lifetime), 'le_loss': np.zeros(lifetime)}
```

```
# caustic content in kg, concentration in g/L = kg/m3, caustic carry
    -over in kg, automatical caustic dose in kg, electrical
    conductivity in  S /cm, volume of water in m3, caustic soda in
    kg
dw = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), '
    caustic_co': np.zeros(lifetime), 'dmdt': np.zeros(lifetime), '
    conductivity': np.zeros(lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry
    -over in kg, electrical conductivity in  S /cm
dr = {'content': np.zeros(lifetime), 'conc': np.zeros(lifetime), '
    caustic_co': np.zeros(lifetime), 'conductivity': np.zeros(
    lifetime)}
# caustic content in kg, concentration in g/L = kg/m3, caustic carry
    -over in kg, electrical conductivity in  S /cm
cb = []
wb = []
rinse = []
for c in np.arange(ncaustic):
    cb.append(DataFrame(data=dc))
    cb[c].content[0] = cmax[c]
    cb[c].conc[0] = cb[c].content[0] / v_caustic[c]
    cb[c].caustic_co[0] = cb[c].conc[0] * loss
    cb[c].v = v_caustic[c] * np.ones(lifetime)
for w in np.arange(nwater):
    wb.append(DataFrame(data=dw))
for r in np.arange(rinsings_total):
    rinse.append(DataFrame(data=dr))

# prinse = DataFrame(data=dr)       # time series for pre rinse
    discharge (wastewater)
# frinse = DataFrame(data=dr)       # time series for final rinse
    discharge
# prinse.conductivity[0] = frinse.conductivity[0] = 10**(-7) * (mc_H
     + mc_OH)

for i in np.arange(lifetime-1):

    # caustic bath:
    cb[0].content[i+1] = cb[0].content[i] + rinse[0].caustic_co[i] -
         cb[0].caustic_co[i] - cb[0].conc[i] * le
    if cb[0].content[i+1] < cmin[0]:
        cb[0].dose[i+1] = cmax[0] - cb[0].content[i+1]
        dose_total = dose_total + cb[0].dose[i+1]
        cb[0].v[i+1] = cb[0].v[i+1] + cb[0].dose[i+1] / 0.25 /
            caustic_density
```

```
cb[0].content[i+1] = cb[0].content[i+1] + cb[0].dose[i+1]
cb[0].v[i+1] = cb[0].v[i+1] - le
cb[0].conc[i+1] = cb[0].content[i+1] / cb[0].v[i+1]
cb[0].caustic_co[i+1] = cb[0].conc[i+1] * loss
cb[0].le_loss[i+1] = cb[0].conc[i+1] * le
le_loss_total[i+1] = le_loss_total[i+1] + cb[0].le_loss[i+1]
# cb[0].dmdt[i+1] = cb[0].dose[i+1] - cb[0].caustic_co[i+1]

for c in np.arange(ncaustic)[1:]:
    cb[c].content[i+1] = cb[c-1].caustic_co[i] + cb[c].content[i
        ] - cb[c].caustic_co[i] - cb[c].conc[i] * le

    if c == ncaustic-1:
        cb[c].content[i+1] = cb[c].content[i+1] + rinse[1].
            content[i+1]
        cb[c].v[i+1] = cb[c].v[i+1] + rinse_flow
        cb[c].conc[i+1] = cb[c].content[i+1] / (cb[c].v[i+1] +
            rinse_flow)

    if cb[c].content[i+1] < cmin[c]:
        cb[c].dose[i+1] = cmax[c] - cb[c].content[i+1]
        dose_total = dose_total + cb[c].dose[i+1]
        cb[c].v[i+1] = cb[c].v[i+1] + cb[c].dose[i+1] / 0.25 /
            caustic_density

    cb[c].content[i+1] = cb[c].content[i+1] + cb[c].dose[i+1]
    cb[c].v[i+1] = cb[c].v[i+1] - le
    cb[c].conc[i+1] = cb[c].content[i+1] / cb[c].v[i+1]
    cb[c].caustic_co[i+1] = cb[c].conc[i+1] * loss
    cb[c].le_loss[i+1] = cb[c].conc[i+1] * le
    le_loss_total[i+1] = le_loss_total[i+1] + cb[c].le_loss[i+1]
    # cb[c].dmdt[i+1] = cb[c-1].caustic_co[i+1] + cb[c].dose[i
        +1] - cb[c].caustic_co[i+1]

# water bath:
wb[0].content[i+1] = wb[0].content[i] + rinse[2].content[i] - wb
    [0].caustic_co[i]
wb[0].conc[i+1] = wb[0].content[i+1] / v_water[0]
wb[0].caustic_co[i+1] = wb[0].conc[i+1] * loss
# wb[0].dmdt[i+1] = cb[ncaustic-1].caustic_co[i+1] - wb[0].
    caustic_co[i+1]

for w in np.arange(nwater)[1:]:
    wb[w].content[i+1] = wb[w].content[i] + wb[w-1].caustic_co[i
        +1] - wb[w].caustic_co[i]      # taking in carry-over
```

C

C

```
            from caustic bath and giving out
        wb[w].conc[i+1] = wb[w].content[i+1] / v_water[w]
        wb[w].caustic_co[i+1] = wb[w].conc[i+1] * loss
        # wb[w].dmdt[i+1] = wb[w-1].caustic_co[i+1] - wb[w].
            caustic_co[i+1]

    # rinse:
    rinse[1].content[i+1] = cb[ncaustic-1].caustic_co[i+1]
    rinse[1].conc[i+1] = rinse[1].content[i+1] / (rinse_flow + loss)
    rinse[1].caustic_co[i+1] = rinse[1].conc[i+1] * loss
    # na = rinse[3].conc[i+1] / 40      # Na+ concentration in mol/L
    # h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2      # H+
        concentration in mol/L
    # oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
            # OH- concentration in mol/L
    # rinse[3].conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h
        * mc_H)

    rinse[2].content[i+1] = rinse[1].caustic_co[i]
    rinse[2].conc[i+1] = rinse[2].content[i+1] / (rinse_flow + loss)
    rinse[2].caustic_co[i+1] = rinse[2].conc[i+1] * loss

    rinse[3].content[i+1] = wb[nwater-1].caustic_co[i+1]
    rinse[3].conc[i+1] = rinse[3].content[i+1] / (rinse_flow + loss)
    rinse[3].caustic_co[i+1] = rinse[3].conc[i+1] * loss

    rinse[4].content[i+1] = rinse[3].caustic_co[i]
    rinse[4].conc[i+1] = rinse[4].content[i+1] / (rinse_flow + loss)
    rinse[4].caustic_co[i+1] = rinse[4].conc[i+1] * loss

    rinse[0].conc[i+1] = (rinse[2].content[i] + rinse[3].content[i]
        + rinse[4].content[i]) / (rinse_flow * 3)
    rinse[0].caustic_co[i+1] = rinse[0].conc[i+1] * loss
    # na = rinse[0].conc[i+1] / 40      # Na+ concentration in mol/L
    # h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2      # H+
        concentration in mol/L
    # oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
            # OH- concentration in mol/L
    # rinse[0].conductivity[i+1] = (na * mc_Na) + (oh * mc_OH) + (h
        * mc_H)

    # caustic loss (for mass balance):
    # loss_cb = loss_cb + cb[ncaustic-1].caustic_co[i+1]
    loss_total = loss_total + (rinse[0].conc[i+1] * rinse_flow * 3)
        + rinse[4].caustic_co[i+1] + le_loss_total[i+1] - rinse[0].
```

```
        caustic_co[i+1]

# calculation at the end of life time

caustic_start = 0      # starting caustic content in caustic baths
caustic_end_cb = np.zeros(ncaustic)      # end caustic content in
    caustic baths
caustic_end_wb = np.zeros(nwater)      # end caustic content in water
     baths
# mb = np.zeros(ncaustic+nwater)

# na = np.zeros(lifetime)
# h = np.zeros(lifetime)
# oh = np.zeros(lifetime)

plt.figure()
print('End concentrations in caustic baths: ')
for n in np.arange(ncaustic):
    caustic_start = caustic_start + cb[n].conc[0] * v_caustic[n]
    caustic_end_cb[n] = cb[n].conc[lifetime-1] * v_caustic[n]
    # mb[n] = cb[n].content[lifetime-1] - cb[n].content[0] - np.sum(
        cb[n].dmdt)
    # na = cb[n].conc / 40      # Na+ concentration in mol/L
    # h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
    # oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
    # cb[n].conductivity = (na * mc_Na) + (oh * mc_OH) + (h * mc_H)
    print(f'Caustic Bath {n+1}: {cb[n].conc[lifetime-1]:.2f} g NaOH/
        L, {cb[n].conc[lifetime-1]/40*23:.2f} g Na+/L')
    plt.plot(cb[n].conc / 40 * 23)      # Na+ concentration
    # plt.plot(cb[n].conductivity)
# plt.legend(['cb1', 'cb2', 'cb3'], loc=4)
# plt.title(f'Sodium concentrations in caustic baths for {days}-day
    operation')
# plt.xlabel('Time (min)')
# plt.ylim((-1,21))
# plt.ylabel('$\mathregular{Na^+}$ Concentration (g/L)')

# plt.figure()
print('End concentrations in water baths: ')
for n in np.arange(nwater):
    caustic_end_wb[n] = wb[n].conc[lifetime-1] * v_water[n]
    # mb[ncaustic+n] = wb[n].content[lifetime-1] - wb[n].content[0]
        - np.sum(wb[n].dmdt)
    # na = wb[n].conc / 40      # Na+ concentration in mol/L
    # h = (np.sqrt(na**2 + 4 * 10**(-14)) - na) / 2
```

```
    # oh = 2 * 10**(-14) / (np.sqrt(na**2 + 4 * 10**(-14)) + na)
    # wb[n].conductivity = (na * mc_Na) + (oh * mc_OH) + (h * mc_H)
    print(f'Water␣Bath␣{n+1}:␣{wb[n].conc[lifetime-1]:.2f}␣g␣NaOH/L,
        ␣{wb[n].conc[lifetime-1]/40*23:.2f}␣g␣Na+/L')
    plt.plot(wb[n].conc / 40 * 23)      # Na+ concentration
    # plt.plot(wb[n].conductivity)
# plt.xticks(np.arange(days)*60*24, np.arange(days))
plt.xticks(np.arange(days/10)*60*24*10, np.arange(int(days/10))*10)
# plt.vlines(np.arange(days)*60*24, 0, 11.8, ls='--')
plt.xlabel('Time␣(day)')
plt.ylabel('$\mathregular{Na^+}$␣Concentration␣(g/L)')
# plt.ylabel('Conductivity ( S /cm)')
# # # plt.legend(['wb1', 'wb2', 'wb3', 'wb4', 'wb5'], loc=2)
plt.title(f'Sodium␣concentrations␣in␣water␣baths␣for␣{days}-day␣
    operation')
plt.legend(['CB1', 'CB2', 'CB3', 'WB1', 'WB2', 'WB3'],
    bbox_to_anchor=(1.05, 0.85))
# # # plt.title(f'$Na^+$ concentrations in caustic and water baths
    for {days}-day operation')
# plt.title(f'Conductivity for {days}-day operation in caustic and
    water baths for {days}-day operation')

print('End␣concentrations␣in␣rinse␣effluent:␣')
plt.figure()
for r in np.arange(rinsings_total):
    print(f'Risne␣{r+1}:␣{rinse[r].conc[lifetime-1]:.2f}␣g␣NaOH/L,␣{
        rinse[r].conc[lifetime-1]/40*23:.2f}␣g␣Na+/L')
    plt.plot(rinse[r].conc / 40 * 23, label=f'Rinsing␣{r+1}')
# plt.xticks(np.arange(days)*60*24, np.arange(days))
plt.xticks(np.arange(days/10)*60*24*10, np.arange(int(days/10))*10)
plt.title(f'$Na^+$␣concentrations␣for␣{days}-day␣operation␣in␣
    rinsing␣effluents')
plt.xlabel('Time␣(day)')
plt.ylabel('$\mathregular{Na^+}$␣Concentration␣(g/L)')
plt.legend(bbox_to_anchor=(1.3, 0.65))

plt.figure()
for n in np.arange(ncaustic):
    plt.plot(cb[n].v, label=f'CB{n+1}')
# plt.xticks(np.arange(days)*60*24, np.arange(days))
plt.xticks(np.arange(days/10)*60*24*10, np.arange(int(days/10))*10)
plt.title('Volume␣change␣in␣caustic␣baths')
plt.xlabel('Time␣(day)')
plt.ylabel('Volume␣($\mathregular{m^3}$)')
plt.legend(bbox_to_anchor=(1, 0.65))
```

```
daily_caustic_loss = np.zeros(days)      # daily caustic loss sum-ups
daily_caustic_dose = np.zeros(days)      # daily caustic dose sum-ups
daily_caustic_vol = np.zeros(days)      # daily caustic dose volumes
for n in np.arange(days):
    a = n * 24 * 60
    b = (n + 1) * 24 * 60
    # caustic loss = 3 rinse effluent + LE + outlet carry-over - pre
        -rinse carry-over
    daily_caustic_loss[n] = np.sum(rinse[4].caustic_co[a:b]) + np.
        sum(rinse[0].conc[a:b]) * rinse_flow * 3 - np.sum(rinse[0].
        caustic_co[a:b])
    for i in np.arange(ncaustic):
        # loss = final rinse + pre-rinse - pre-rinse carryover +
            label extraction
        daily_caustic_loss[n] = daily_caustic_loss[n] + np.sum(cb[i
            ].conc[a:b]) * le
        daily_caustic_dose[n] = daily_caustic_dose[n] + np.sum(cb[i
            ].dose[a:b])
        daily_caustic_vol[n] = daily_caustic_dose[n] / 0.25 /
            caustic_density
# print(daily_caustic_loss)
daily_acc = daily_caustic_dose - daily_caustic_loss
plt.figure()
plt.plot(np.arange(days)+1, daily_caustic_loss, marker='.', label='
    Daily loss')
plt.plot(np.arange(days)+1, daily_caustic_dose, marker='o', label='
    Daily dose')
plt.plot(np.arange(days)+1, daily_acc, marker='*', label='
    Accumulation')
# plt.xticks(np.arange(days), np.arange(days))
plt.xticks(np.arange(days/10)*10, np.arange(int(days/10))*10)
plt.title(f'Daily caustic soda loss for {days}-day operation')
plt.xlabel('Time (day)')
plt.ylabel('Caustic soda (kg)')
plt.legend(bbox_to_anchor=(1, 0.7))
caustic_bottle = dose_total / (bpm * lifetime)      # average caustic
     consumption per bottle in kg
caustic_beer = caustic_bottle / bottle_volume      # average caustic
    consumption hL of beer in kg

# plt.figure()
# plt.plot(rinse[3].conductivity)
# plt.plot(rinse[0].conductivity)
# plt.title(f'Conductivity for {days}-day operation in pre-rinse and
```

```
    final rinse effluent ')
# plt.xlabel('Time (min)')
# plt.ylabel('Conductivity ( S /cm)')
# plt.legend(['Final Rinse', 'Pre-rinse'], loc=4)

print(f'Total loss {loss_total:.2f} kg, total dose {dose_total:.2f} 
    kg, {caustic_bottle*1000:.2f} g/bottle, {caustic_beer*1000:.2f} 
    g/hL beer, net accumulation {np.sum(daily_acc):.2f} kg. ')

if days == 5:
    # wastewater generation = pre rinses effluent + label extraction
        + caustic bath discharge
    ww_week = (pre_rinse_flow * 60 * 24 + 10) * 5
    # wc_week = rinse_flow * 60 * 24 * 5 * 4 +
    ww_season = ww_week * 12 + np.sum(v_caustic) + np.sum(v_water)
    ww_annual = ww_season * 4
    # average water consumption = annual ww generation / (bottles/wk
        * 12 (wk/season) * 4 season/year)
    ww_ave = ww_annual / ((bpm * lifetime) * 12 * 4)      # m3 per
        bottle
    # 1 bottle = 330 mL = 3.3 hL
    ww_per_hL = ww_ave / (330 * 10**(-6))      # m3 per m3 beer = hL
        per hL beer
    print(f'Total wastewater generated: {ww_week} m3 per week, and {
        ww_season} m3 per season and annually {ww_annual} m3, i.e. {
        ww_ave} m3 per bottle and {ww_per_hL} hL per hL beer. ')

if days == 60:
    ww_season = (pre_rinse_flow * 60 * 24 + 10) * 60 + np.sum(
        v_caustic) + np.sum(v_water)
    ww_annual = ww_season * 4
    # average water consumption = annual ww generation / (bottles/wk
        * 12 (wk/season) * 4 season/year)
    ww_ave = ww_annual / ((bpm * lifetime) * 4)      # m3 per bottle
    # 1 bottle = 330 mL = 3.3 hL
    ww_per_hL = ww_ave / (330 * 10**(-6))      # m3 per m3 beer = hL
        per hL beer
    print(f'Total wastewater generated: {ww_season} m3 per season 
        and annually {ww_annual} m3, i.e. {ww_ave} m3 per bottle and
         {ww_per_hL} hL per hL beer. ')

    caustic_loss_annual = loss_total
    caustic_dose_annual = dose_total * 4 + np.sum(v_caustic) *
        caustic_high * 1000
    for c in np.arange(ncaustic):
```

```
        caustic_loss_annual = caustic_loss_annual + cb[c].conc[
            lifetime-1] * cb[c].v[lifetime-1]      # lost from daily
            operation and seasonly disposal
    for w in np.arange(nwater):
        caustic_loss_annual = caustic_loss_annual + wb[w].conc[
            lifetime-1] * v_water[w]
    caustic_loss_annual = caustic_loss_annual * 4      # 4 seasons
    print(f'Annually {caustic_dose_annual:.2f} kg dosed, and {
        caustic_loss_annual:.2f} kg lost. ')

# plt.figure()
# plt.plot(cb[1].conc/40*23, label='Caustic bath 2', color='C1')
# plt.plot(cb[2].conc/40*23, label='Caustic bath 3', color='C2')
# plt.plot(rinse[1].conc/40*23, label='Rinsing 2')
# plt.xticks(np.arange(days/10)*60*24*10, np.arange(int(days/10))
    *10)
# plt.title(f'$Na^+$ concentrations in caustic bath 2, 3 and rinsing
    effluent 2')
# plt.xlabel('Time (day)')
# plt.ylabel('$\mathregular{Na^+}$ Concentration (g/L)')
# plt.legend(bbox_to_anchor=(1.0, -0.15), ncol=3)

# print(loss_total, np.sum(daily_caustic_loss))

# print(f'Total wastewater generated: {wc_week} m3 per week, and {
    wc_season} m3 per season and annually {wc_annual} m3, i.e. {
    wc_ave} m3 per bottle and {ww_per_hL} hL per hL beer. ')
# print(np.sum(daily_caustic_dose), np.sum(daily_acc))

# caustic_end = np.sum(caustic_end_cb) + np.sum(caustic_end_wb)

# # caustic_total = np.sum(caustic_start) + dose_total - caustic_end
    - loss_total      # total caustic consupmtion over life time in
    all the baths in kg

# mass_balance = caustic_start + dose_total - caustic_end -
    loss_total
# mass_balance_cb = caustic_start + dose_total - loss_cb - np.sum(
    caustic_end_cb)
# mass_balance_wb = loss_cb - np.sum(caustic_end_wb) - loss_total
# print(mass_balance, mass_balance_cb, mass_balance_wb)
# print(mb)
```

C

D

ORIGINAL DATA FROM LAB ANALYSIS

The lab analysis was carried out for three water samples from brewery Alken Maes, located in Belgium. For some measurement, three duplicates for each sample were measured to ensure the accuracy. Samples were sedimented for at least 48 hours to simulate the sedimentation process after discharge. "1-1" stands for the first duplicate of the first sample, and "2-3" stands for the third duplicate of the second sample, etc. The average from the three duplicates will presented in the next row.

In the first section contains all the results from lab analysis, and the following sections contain the detailed data for TSS, TDS and alkalinity measurement, which involved more calculations from the very original data.

D.1. THE OVERALL LAB ANALYSIS RESULTS FOR THREE WATER SAMPLES

This table below contains the measured results from lab analysis of the water samples, with average calculations.

	Sample 1			Sample 2			Sample 3		
	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
Temperature (°C)	17.4			17.2			17.3		
pH	13.4			13.4			13.4		
Conductivity (mS/cm)	67.4			72.9			70.6		
Alkalinity ($g\ CaCO_3/L$)	61.61			66.89			66.08		
Turbidity (NTU)	167	164	165	191	188	187	206	206	205
	165.33			188.67			205.67		
*TSS (mg/L)	20	30	80	10	10	70	50	10	30
	43.33			30			30		
TDS (g/L)	24.20	24.15	23.75	28.25	27.05	28.15	28.85	29.55	30.00
	24.03			27.82			29.47		
COD (mg/L)	3124	3135	3117	3883	3853	3910	4818	4758	4819
	3125.33			3882			4798.33		
TOC (mg/L)	1015	1056	1043	1312	1289	1320	1563	1608	1602
	1038			1307			1591		
F^- (mg/L)	71.32	70.34	70.07	90.78	90.34	91.57	117.57	117.31	117.51
	70.58			90.90			117.34		
Cl^- (mg/L)	29.41	29.09	29.02	30.80	30.53	30.83	32.47	32.46	32.60
	29.17			30.72			32.51		
PO_4^{3-} (mg/L)	16.12	15.68	15.55	19.69	19.60	19.78	21.94	21.89	21.87
	15.78			19.69			21.90		
SO_4^{2-} (mg/L)	62.57	61.77	61.58	64.18	64.04	64.77	68.58	68.58	68.60
	61.97			64.33			68.59		
Na^+ (g/L)	11.14	13.60	14.02	14.84	15.08	14.94	15.10	14.35	14.93
	12.92			14.95			14.79		
NH_4^+ (mg/L)	20.15	20.34	20.40	21.79	22.47	21.45	15.49	14.52	15.11
	20.30			21.90			15.04		
K^+ (mg/L)	18.48	19.02	19.06	21.08	20.94	21.74	22.86	22.61	23.17
	18.85			21.25			22.88		
Ca^{2+} (mg/L)	7.12	10.07	14.55	12.99	14.74	15.98	19.04	19.36	19.61
	10.58			14.57			19.34		

**TSS results were too variable among the three duplicates, and would not be used for the analysis and discussion.*

D

D.2. TSS MEASUREMENT

The two table present the two measurements taken for water sample TSS respectively. The first measurement was performed by filtering 100 mL samples with 0.7 μm filtration papers, and the second by filtering 250 mL samples with 0.4 μm filtration papers. The results of both measurements were too diverse, thus were regarded as not reliable.

	Sample 1			Sample 2			Sample 3		
	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
Filtration paper (g)	2.470	2.499	2.474	2.460	2.512	2.473	2.632	2.623	2.603
Dried (g)	2.472	2.502	2.482	2.461	2.513	2.480	2.637	2.624	2.606
TSS (mg/L)	20	30	80	10	10	70	50	10	30
Average (mg/L)	24.44			26.67			13.33		

D

	Sample 1			Sample 2			Sample 3		
	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
Filtration paper (g)	3.186	3.192	3.214	3.092	3.122	3.221	3.237	3.205	3.216
Dried (g)	3.189	3.199	3.219	3.099	3.123	3.222	3.251	3.210	3.221
TSS (mg/L)	12	28	20	28	4	4	56	20	20
Average (mg/L)	5.33			10.67			16.00		

D.3. TDS MEASUREMENT

The measurement of TDS was performed by filtrating samples with 0.2 μm filters, and 20 mL filtrate for drying.

	Sample 1			Sample 2			Sample 3		
	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
Container (g)	1.011	1.027	1.022	1.021	1.025	1.015	1.013	1.012	1.014
Dried (g)	1.495	1.510	1.497	1.586	1.566	1.578	1.590	1.603	1.614
TDS (g/L)	24.20	24.15	23.75	28.25	27.05	28.15	28.85	29.55	30.00
Average (g/L)	24.03			27.82			29.47		

D.4. ALKALINITY

In the alkalinity measurement, 50 mL samples were titrated with 1 mol/L hydrochloric acid solution.

	Sample 1	Sample 2	Sample 3
Start pH	13.00	13.00	13.00
End pH	4.28	4.29	4.29
Acid volume (mL)	61.608	66.892	66.078
Alkalinity ($g\ CaCO_3/L$)	61.608	66.892	66.078