

Optimisation of chemicals usage in the production of colloidal silica

Master's thesis in Innovative and Sustainable Chemical Engineering

MARIA LIVRELL KLINGBERG

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the production of colloidal silica**

MARIA LIVRELL KLINGBERG



CHALMERS
UNIVERSITY OF TECHNOLOGY

Department of Chemistry and Chemical Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2020

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In collaboration with Nouryon Pulp and Performance Chemicals AB

Supervisors: Tallal Belkheiri, Johan Pettersson and Anders Josefsson, Nouryon

Supervisor: Derek Creaser, Division of Chemical Reaction Engineering

Examiner: Derek Creaser, Division of Chemical Reaction Engineering

Department of Chemistry and Chemical Engineering

Chalmers University of Technology

SE-412 96 Gothenburg

Telephone +46 (0)31 772 1000

Cover: Schematic image of the proposed optimisation of the process.

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MARIA LIVRELL KLINGBERG
Department of Chemistry and Chemical Engineering
Chalmers University of Technology

Abstract

For one of the process steps in the production of colloidal silica, a possible optimisation in the usage of chemical has been identified and investigated. The optimisation is done via reuse of chemical, that is found in the effluent after the process step without further reprocessing. The aim of this project was to investigate the feasibility of reusing a chemical in the process step. It was carried out by studying the current case on lab-scale and pilot-scale in order to isolate and study important quality parameters. Parameter B was determined to be a good indicator for which interval of effluent to collect and reuse. The collected chemical was used in the process step on its own to study its potential. With this knowledge, an equation for calculating the amount of fresh chemical to add on top in order to reach normal productivity of the process step was devised. The collection interval of old chemical was optimised, both in regard to quality and production practicalities. The combination of reused and fresh chemical was used in the process step without affecting process time or productivity. The amount of fresh chemical saved was extrapolated to the full-scale process step and the potential cost savings were calculated. The investment cost of implementing the optimisation step was calculated and compared to the cost savings. A payback time of between 0.4 and 1 year was estimated for the project.

Keywords: colloidal silica, silica sol, process optimisation.

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1

Introduction

Silicon and oxygen are the two most common elements in the earth's crust, and together they form silicon dioxide, or silica as it is called, found in such minerals as quartz [3, 4]. Silica is a well-known and widely used material that can be found in many natural and synthetic forms. One such is colloidal silica that is silica nanoparticles suspended in water. The particles have a high specific surface area that can be functionalised through a wide range of surface modifications, making them suitable for a large variety of uses. In applications ranging from food grade beverage clarifying [5] to catalysts in refineries [6], the different properties of the particles are being utilised. They are used for modifying surface properties, like increased friction in paper and films, and dirt-repellent abilities in paints and textiles [5]. Their innate ability to hold water is further used in the papermaking industry. One big market that is expanding is the polishing of electronic circuits and other components within the electronics industry. Colloidal silica is used in some of the world's most cutting-edge technologies, and the areas of use are ever-expanding [5].

To accommodate this expansion, the types of particles produced will have to develop, and the process steps will need to undergo continuous improvement. Innovation is the reason why the chemical industry today looks different from the chemical industry 100 years ago, even though the underlying principles are the same. The strive to develop, reduce, shorten, streamline and to overall advance, is the basis that drives this change forward in a highly competitive industry. Established processes are constantly improved in various ways to increase e.g. energy efficiency, materials usage efficiency and productivity. Innovations can lead to both technical and economic advantages over competitors. It can also result in reduced environmental impact, which has become an increasingly important task in the industry today.

This thesis is a collaboration with Nouryon Pulp and Performance Chemicals AB. At the Nouryon plant in Bohus, Sweden, colloidal silica is produced for many different customers and uses. The company is deeply invested in sustainability, which is in the core of its thinking around innovation. Development of the different process steps is constantly being evaluated and implemented, and it is one such evaluation that this thesis evolves around. During the production of colloidal silica, several chemicals are used in the different process steps. Possible cost-saving changes concerning the reduction of chemicals usage by reuse of chemical have been found in one of these steps. Besides the direct cost savings this would result in from requiring less chemical, such a reduction would also lower the cost of wastewater treatment. All in all, the changes could mean a reduction in the environmental impact of the process and make the process more sustainable.

1.1 Aim of thesis

This thesis aims to investigate the feasibility of reusing a chemical in one of the production steps of colloidal silica. The objectives are to first find the optimal interval of chemical collection for reuse by simulating the process on lab-scale. Then, to reuse the chemical without affecting the productivity, and subsequently the product quality, and thereby find the extent to which the chemical usage can be reduced. Following the analysis, the findings will be used to calculate what reuse of chemical would mean for the full-scale production in terms of reduced chemical usage and reduced wastewater treatment. Lastly, the economic feasibility of the investigated change will be determined by comparing the economic benefits of these reductions to the cost of building and implementing the process changes.

1.2 Questions

To structure the work as to not deviate from the aim of the thesis, questions were used to deconstruct the aim into smaller parts. Questions to be answered, but not limited to, are:

- How do the quality parameters vary during the process run?
- How do the level of the two main quality parameters affect the performance of the process step?
- Which interval of the effluent should be collected?
- How does the reused chemical perform on its own?
- How does the reused chemical perform together with new chemical?
- Can the lab-scale process behaviours and results be translated to the full-scale process?

1.3 Limitations

Within this process optimisation step, many different quality parameters could potentially be studied. These were narrowed down to two main ones, both to fit within the available time for this project but also because of difficulties in measuring some of the other parameters accurately, easily and/or continuously.

2

Theory

In order to put the optimisation project into a chemical perspective, here follows a general theory about silica and the production of colloidal silica. Of special interest for the understanding of the project, there is also a section dealing with the theoretical background specific to the production step that is the objective of this thesis. In this section, the terminology is the same as in the optimisation parts and will therefore not be of use beyond the scope of this report. Lastly, the theory behind the economic evaluation is presented and this section deals in depth with the different cost parameters used for the calculations.

2.1 Silicon dioxide and colloidal silica

Silicon dioxide, SiO_2 , is most abundant in the earth's crust, mainly in different forms of quartz, both common and rare [3, 7]. When being subjected to different pressures and temperatures, the silicon oxide changes between two crystalline structures and can as a material, either pure or with intergrowth, appear in a large variety of forms. Silica is the common name used for silicon dioxide, whether it is amorphous, crystalline, solvated or chemically bonded [3]. As a monomeric building block, it has seemingly endless possibilities, both in its various crystalline forms shortly mentioned, and in the amorphous phase in e.g. particles, as seen in this project. In the last few years, the ways in which the polymer particles are built up and the applications in which they are used, have expanded abruptly, with no end in sight [8].

Colloidal silica is a suspension of silica particles in water, where levels of up to 50 wt% silica have been produced [3]. The size of the particles, on a scale of a few to over a hundred nanometres [9], means that the suspensions vary in appearance between translucent colourless to white opaque, depending on particle size and concentration [3]. The particles are built up of silicon and oxygen bonded via siloxane bonds, $\equiv \text{Si}-\text{O}-\text{Si} \equiv$, with the surfaces covered with silanol groups, $\equiv \text{Si}-\text{O}-\text{H}$ [1]. The silica particles can be discrete or arranged in large networks that can hold a lot of water inside one aggregated particle or network.

The network structure and colloidal form of the particles mean they have a very large surface area compared to weight, giving the particles their unique abilities, especially after surface modifications [3]. Modifications include aluminate and silane functionalised surfaces. These modifications, together with surface charge and charge den-

sity, are all possible to tailor to suit different applications [3, 10]. The charges are stabilised by different counter ions, e.g. sodium, ammonia or chloride, depending on the area of use.

2.2 Stability of colloidal silica

Colloidal silica can be made stable across a wide range of pH, between 2-12 [9], but can over time aggregate and gel or sediment [1, 5]. Sedimentation also occurs in so-called stable colloidal silica systems when particle diameters are above circa 70 nm [3]. Gelling is the interparticle formation of siloxane bonds [3]. The forces that keep the particles from aggregating are electrostatic repulsion for charged particles and steric hindrance for particles with silane surface modifications. Silica is negatively charged in normal water and positively charged below pH 2 [1]. Around pH 2, the particles will reach the point of zero charges as well as the isoelectric point [1], changing the conditions drastically e.g. polymerisation of silica, the rate of which is at its lowest (see Section 2.3). In this interval, the particles experience a type of local maximum of stability, as seen in Figure 2.1. This might have to do with the polymerisation reaction being catalysed by either hydroxide or hydrogen ions on their respective sides around pH 2 [3], as is discussed further in Section 2.3. Around pH 2, therefore, as the surface will remain un-charged, the polymerisation reaction is efficiently prevented from reaching the first stage after the reaction seen in Equation 2.2.

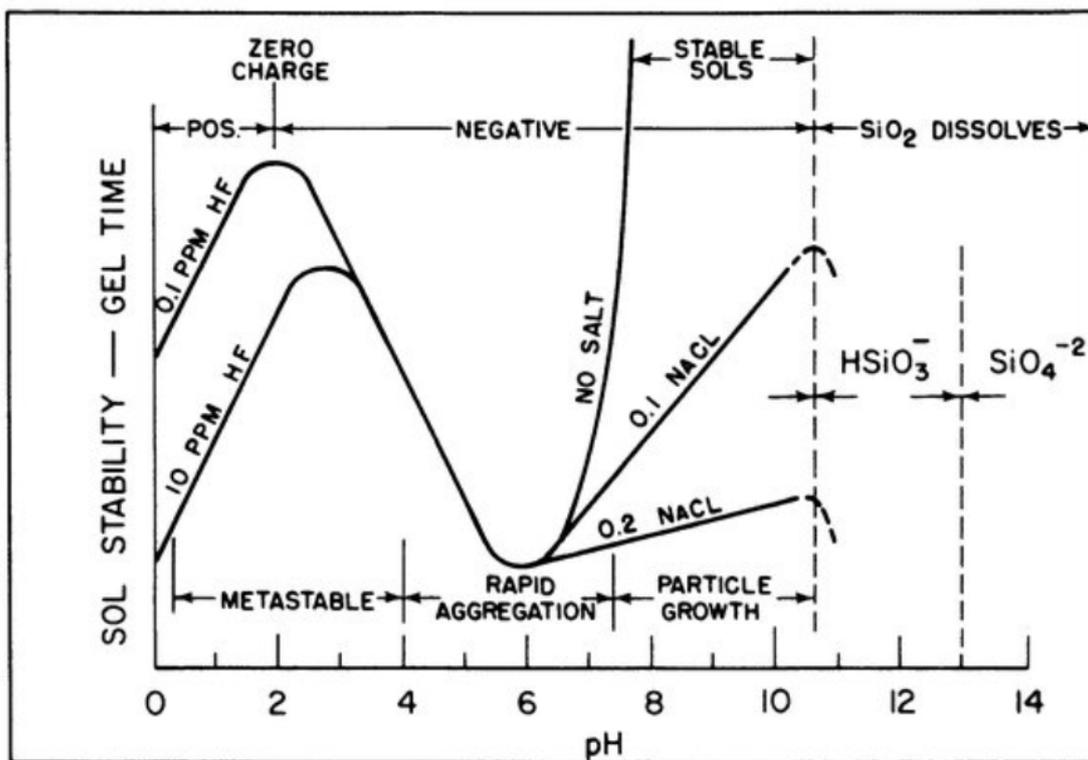
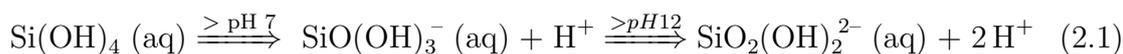


Figure 2.1. Stability of colloidal silica depending on pH-value. [1]

Between pH 9 and 10, the silica colloids are permanently stable, and above that, they dissolve in the high pH, as can be seen in Figure 2.1 [1]. In the interval between pH 5 and 7, the network aggregation is at its fastest and above pH 7 the particles have the fastest growth [1, 3]. This can be further seen in Figure 2.4.

2.3 Polymerisation of silica

The silicon monomer used for building these polymer particles and networks is silicic acid, $\text{Si}(\text{OH})_4$ [11], seen in Figure 2.2, which is the monomer present in solution below pH 7 [3]. It is one of the soluble forms of silica and exists in equilibrium with the solid phase [1]. The other forms are silicate ions, which are the forms silica take when dissolving at higher pH [3]. The silicates are, however, transformed into silicic acid in the presence of hydrogen ions, as silicic acid is a weak acid and, therefore, the silicate ions are strong bases, see Reaction 2.1 [3]. Silicic acid can be found in much of our drinking water, it passes through the body without affecting it and is considered inert [3].



Silicic acid can be obtained in different ways, one of which is through ion exchange of sodium silicate (one form of which is seen in Figure 2.3), as discussed further in Section 2.4. Another method is to dissolve amorphous silicon dioxide in hot water over time in the presence of a catalyst such as a hydroxide ion that weakens the bond between a silicon atom closest to the surface and the oxygens bonded to it, see Reaction 2.2 [3]. In pH below 2, the reaction mechanisms are different, and the dissolution is instead catalysed by hydrogen ions.

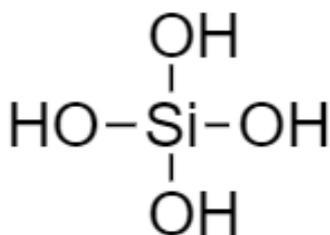


Figure 2.2. Orthosilicic acid

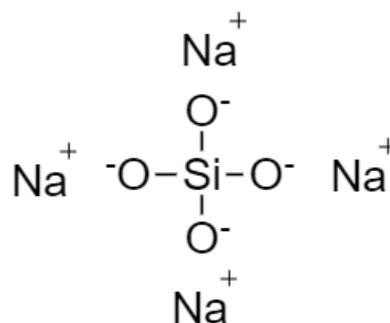


Figure 2.3. Sodium orthosilicate

The dissolving of silica is reversible, and the silicic acid will start to polymerise on its own unless kept somewhat stable, by e.g. changing the pH to 2 [3]. Another way is to keep it highly diluted [1]. In concentrations greater than the solubility of silica (100-200 ppm) the silicic acid will either polymerise into particles or, in the presence of solid phase, deposit on the surface. Beyond the dissolution, the polymerisation is also catalysed by either hydroxide or hydrogen ions, depending on pH [3].

The solubility of silica increases with decreasing particle size, meaning that smaller particles will dissolve faster than larger ones. The opposite reaction will make them polymerise on the surface of other particles. This will result in comparatively larger particles to grow in a phenomenon called Ostwald ripening [1, 3]. That means there are two ways of particle growth, either by using up silicic acid or by Ostwald ripening [1]. Since small, more soluble particles will dissolve and redeposit on the surface of larger, less soluble particles, Ostwald ripening will affect the size distribution, which typically can be kept quite narrow.

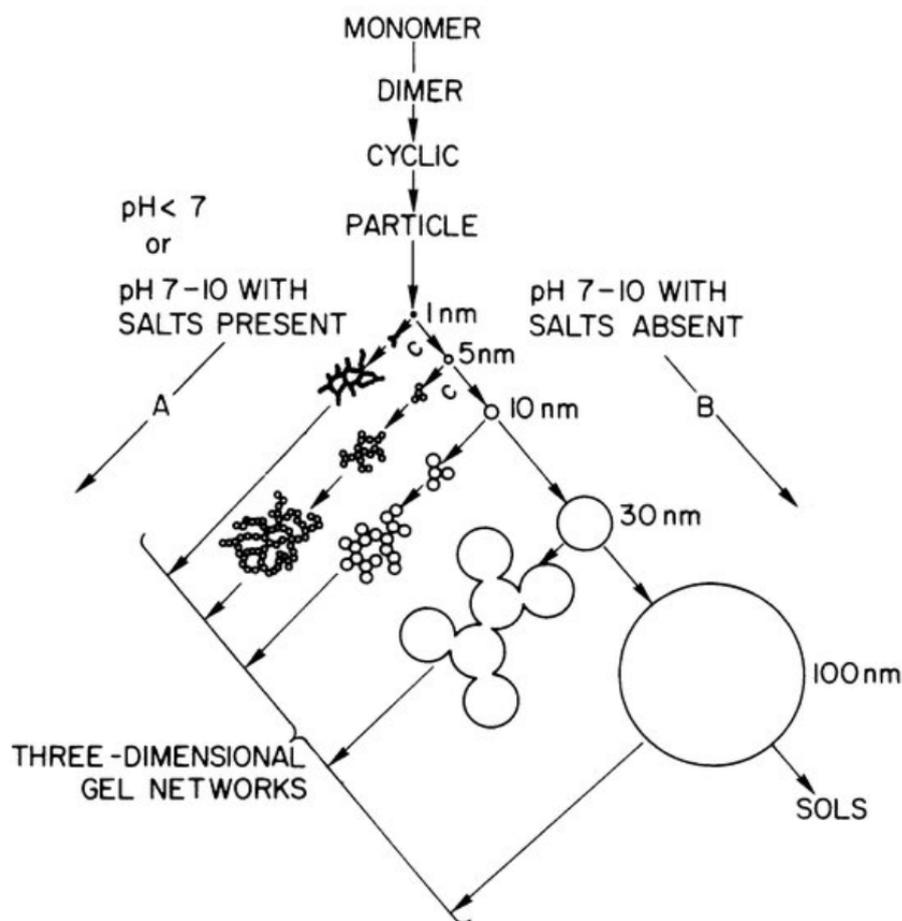
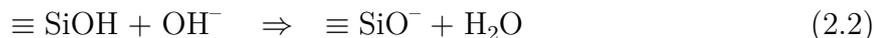


Figure 2.4. Polymerisation of silica at high and low pH values, respectively, and in the presence of salt. [1]

The polymerisation rate of silicic acid increases with both pH and temperature [3]. Polymerisation of silicic acid is a condensation reaction [1, 12] where silanol groups are converted into siloxane bonds. See Reactions 2.2 and 2.3 for polymerisation above pH 2, where in the first reaction step the silanol group is ionised by reaction with a hydroxide ion [1]. The condensation is maximised so that the particle ends up at its most compact state, with a majority of the hydroxyl groups on the surface

[3].



If left on its own, a solution of silicic acid will start to aggregate and eventually gel and then dry as the water in the network will start to leave. The aggregation steps of silicic acid are:

1. Polymerisation of the monomers into round particles, i.e. nuclei, built up of mostly siloxane linkages with hydroxyl groups on the surface.
2. Particle growth on the surface causing volume expansion.
3. Several particles link together into strands and three-dimensional networks.
4. The network extends to the entire solution, forming a gel.

The different steps can be controlled and completely avoided by various factors. In step 2, the size of the particles can be controlled by terminating the reaction after a certain time. Another way is to regulate the pH. At lower pH the polymerisation and reverse dissolving reaction is slow, meaning the particles will stop growing at around 2-4 nm and not be very affected by Ostwald ripening [1]. At pH above 7, however, the growth rate is very fast, and the particles can grow to be very big. The primary mechanism of particle growth in this region, after the initial particles of a couple of nanometres are formed, is Ostwald ripening [3]. The rate is therefore affected by particle size distribution and temperature. At pH above 7, the particles will also be highly charged. This results in high electrostatic repulsion, making the particles unlikely to aggregate and thus avoiding steps 3 and 4 [3].

If porous particles are wanted, however, the polymerisation path can be changed so that several particles start linking together into aggregates, thus continuing past aggregation step 2. This can be achieved by lowering the pH or by addition of salt, as seen in Figure 2.4. Low pH results in lower surface charge, allowing the particles to approach and link together. By the addition of salt to the solution, the ions can shield the surface charges and have a similar effect. The aggregation can be stopped by raising the pH to 8 or 9 as seen in Figure 2.1 [3].

If a gel is desired, the aggregation reaction is allowed to continue until the entire solution is affected. A gel is a colloid of solids in a fluid, and it has properties similar to a solid [13]. It is a solid phase network holding a lot of water. If subjected to mechanical impact, the silica gel will separate into many small, shard-like pieces, resembling the breaking of glass, which is another type of amorphous silicon oxide. The shards will have what looks like sharp edges but will be soft and exhibit plastic deformation when gently prodded. An uncontrolled reaction can result in different degrees of unwanted gelling, which can mean a complete blockage of reactors, pipes, etc.

2.4 Production of colloidal silica

The production of colloidal silica through polymerisation of silicon dioxide is done in a series of steps with water glass, solvated sodium silicate, as the raw material [3]. The production of colloidal silica consists of three main steps: ion exchanging of sodium silicate to silicic acid, polymerisation of silicic acid into particles, and concentration of particles. Before the silica monomers can start polymerising, the counter ion, in this case, sodium, must be removed through ion exchange. The ion exchange and the following polymerisation can either be done in the same reactor, such as in the consol process described in Section 2.4.4, or carried out separately in the column process, see Section 2.4.3.

2.4.1 Water glass

Water glass, commonly written as $(\text{Na}_2\text{O})_x \cdot (\text{SiO}_2)_y$ and also known as sodium silicate, is a water-soluble mixture of silica and sodium oxide, Na_2O . It exists in such forms as sodium metasilicate, Na_2SiO_3 , sodium orthosilicate, Na_4SiO_4 (seen in Figure 2.3), and sodium pyrosilicate, $\text{Na}_6\text{Si}_2\text{O}_7$ [14]. It is a glasslike material that is a common source of sodium in different industries but is used as an economic silica source in the production of colloidal silica [5]. Water glass is produced by heating pure silica sand and sodium carbonate in a furnace to over 1000°C , resulting in the salt and carbon dioxide as seen in Reaction 2.4 [15, 16]. The reaction depicts one common way of presenting the product [17]. The salt, called lump glass, can then be dissolved in water forming the viscous fluid water glass.



The important property of water glass as a raw material is the weight per cent ratio of silica to sodium oxide [18]. A common ratio is 3.3 [3]. The sodium ion left over after the ion exchange can be used to stabilise the finished particles, and by changing the sodium silicate for some other alkali silicate, such as the one containing potassium, counter ion stabilisation will be achieved with potassium instead.

2.4.2 General ion exchanger

In the ion exchanger, sodium silicate is ion-exchanged resulting in silicic acid. In the process, the alkaline pH of water glass around 12.5 is lowered to a level of around 2.5 because of the acidic product [5]. Ion exchange can also be used in a later step to remove unwanted ions from the product.

An ion exchange resin is made up of a matrix of polymer or copolymers with functional groups, the so-called active sites [19]. The functional groups have different ions attached to them that can be exchanged for other ions, hence the name ion exchange. After the ion exchange of sodium silicate, the active sites of the ion exchange resin have been partly filled with sodium ions and the bed is exhausted. In order to be used again, the bed must be regenerated, using some source of hydrogen ions, for example, acid. The level of regeneration of the bed is called the regeneration degree or capacity and can be calculated by indirectly measuring the number of

hydrogen ions that are bonded to active sites and compare it to the total capacity. Total capacity is the total number of active sites per volume [19].

There are many different ion exchange resins, and these are divided into categories depending on their properties, starting with whether the resin ion exchanges anions or cations, i.e. anion or cation exchange resin respectively. Cation exchange resins have acidic functional groups as active sites, and anionic exchange resins have basic functional groups [19]. Further, depending on if the functional group is strongly or weakly acidic respectively basic, four types of exchange resins can be distinguished. These are presented in Table 2.1 along with the functional group of the active sites and typical resin matrices.

One common resin matrix is cross-linked polystyrene [20]. It is produced by copolymerisation of styrene and divinylbenzene (DVB). The ratio of DVB determines the amount of cross-linking as the molecule contains one extra vinyl group compared to styrene, readily creating a bond to the backbone of other copolymer chains.

Table 2.1. Typical active groups and matrices for the four types of exchange resins

Type of exchange resin	Active sites	Typical polymer matrix
Strongly acidic cation	Sulfonic groups	Cross-linked polystyrene
Weakly acidic cation	Carboxylic groups	Cross-linked acrylic
Strongly based anion	Quaternary ammonium groups	Cross-linked polystyrene
Weakly based anion	Tertiary ammonium groups	Cross-linked polystyrene

For the ion exchange of water glass, a weakly acidic cation (WAC) or strongly acidic cation (SAC) resin is used. The affinity for different ions varies greatly between types of resin. For a SAC resin, the affinity for ions increases with ion charge and ion size, while WAC resins show the opposite affinity [20]. As the ion exchange in the production of silicic acid is done between just two different ions, sodium and hydrogen, there are two different forms of the resin; the regenerated H-form and the exhausted Na-form.

Since the affinity is higher for one of the ions, that means the resin can be completely ion-exchanged into this form [20]. The other form, however, is sometimes not possible to completely achieve. For the resin to ion exchange to the ion, it has lower affinity for, the ion must be present in excess in order to move the equilibrium. This is part of the reason why it is easier to ion exchange to H-form at lower pH.

Different types of resins have different properties [19]. During ion exchange, the resin can for example change size, and the different types of resin swell/shrink to different degrees. Another example is that some resins withstand deformation better than others, determining how suitable they are e.g. the stirring in a reactor or the pressure of a tall column. Properties can also vary among the same resin type. The size distribution of the beads and their size are two important qualities, where smaller and less uniformly sized resins will pack tighter, resulting in the column having a greater pressure drop over it. The size distribution of the beads depends on production method and can be measured by the so-called uniformity coefficient,

where a value closer to one indicates a more narrow distribution. Uniform bead size is often desired as this allows for the use of smaller beads without having a large pressure drop. Smaller beads have a higher specific surface area, resulting in a higher capacity of the ion exchanger and therefore give more exchanged ions per time unit. This can, in turn, mean that the flow rate can be increased. Increased flows, however, increase the pressure drop, but this can be partly counteracted by using coarse beads.

The resins are cross-linked to a degree that makes them insoluble [20]. A young resin can for a time, however, lose short chains from the resin, but it stops after the resin has been used more [20]. SAC resins are somewhat sensitive to chlorine that breaks up the cross-linking, but a resin with 8% DVB can be used for several years in chlorine concentrations up to 1 mg/kg. SAC resins are, unlike basic resins, very temperature stable. SAC resins are more mechanically stable than basic resins, that have especially poor compression stability.

2.4.3 Column process

In the column process, the ion exchange step and the polymerisation step are separated. The ion exchange is done in an ion exchanger column. In the column ion exchanger, sodium silicate is added to the top of the column by pumping. It goes through the column using gravity and the volume of liquid above the bed is regulated using a combination of pressurised air and controlled in- and outflows of the column.

As mentioned, a SAC resin is typically used for the ion exchange of sodium silicate. SAC resins have a higher affinity for the ions in the reactant than in the product [20], assuring that complete conversion to products in Reaction 2.5 can be achieved. By knowing the total capacity of the resin, the amount of cross-linking can be approximated [19], which in turn gives an estimate of the resin's relative affinity for the two ions [20].



The higher affinity for the sodium ion means the resin can be fully made into exhausted form, but getting it fully regenerated is not practically possible [20]. In order to regenerate the resin, an excess of hydrogen ions is needed to move the equilibrium toward the regenerated side. In order to approach 100% regeneration degree, this excess of acid will rapidly become too large to be economically practical [21]. Instead, a set regeneration limit is usually decided based on a trade-off between a high regeneration degree and the cost associated with adding acid in excess along with the additional time the regeneration step will take the more acid is added.

The steps of a column ion exchanger are exhaustion, backwashing, regeneration and rinsing [19]. The rinsing is done to displace the acid or water glass. It is also done to remove free ions from the column before the next reaction stage can begin. The ion exchange column is typically operating in co-flow, meaning the regeneration step and the exhaustion step are done in the same direction (top-down).

Backwashing the column means washing the bed with water in the opposite direction (bottom-up) [19]. This is done to remove any channelling in the bed and for decompaction. It is also done in order to remove unwanted particles and resin fines from the top of the column. During the backwashing, the resin is fluidised and therefore take up an increased amount of space in the column.

After the ion exchange is done, the silicic acid is transferred to a reactor where the polymerisation step takes place. The reactor is typically a stirred tank reactor. For the theory of polymerisation, see Section 2.3.

2.4.4 Consol process

In the consol process, both ion exchange and polymerisation take place in the same vessel. The name comes from “concentrated sol” since both the water glass and the particles are of high concentration compared to e.g. the column process [2]. Sol is an alternative name for a solid dispersed in fluid, and colloidal silica can alternatively be called silica sol. As can be seen in Figure 2.5, the water glass is added to the reactor together with the ion exchange resin, typically a WAC resin. The sodium ions are ion-exchanged to a lower degree than for the column process, leaving some amount of sodium in the finished product. As the ion exchange proceeds, the silicic acid can start to polymerise, and the constant production of more silicic acid results in colloidal silica of small size distribution [2].

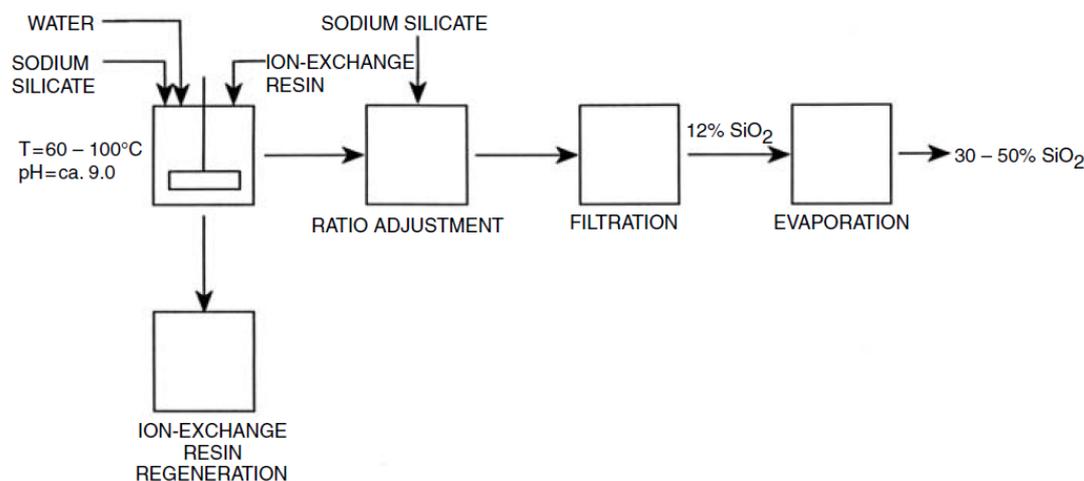


Figure 2.5. Schematic image of the consol process. [2]

After the polymerisation is finished, the product must be separated from the resin. The resin can then either be regenerated in the same vessel or moved and regenerated in a column [20]. The product is stabilised by the addition of sodium ions and concentrated using evaporation or ultrafiltration. The higher level of sodium ions still present after the reaction, reduces the needed sodium addition compared to a colloid manufactured through the column process. Also, because of the high concentration of particles when exiting the reactor, compared to the product from the column process, less evaporation or ultrafiltration is required.

The stirring of the reactor gives very good contact between resin and water glass [2]. The same is true for the contact between resin and hydrogen ions if the resin is regenerated in the reactor. One advantage of the column ion exchange, however, is that each part of the bed interacts with fresh reactant [19], as the highly concentrated front moves down the column, case in the consol ion exchanger. Since a WAC resin typically is used, the resin favours the regeneration, thus reducing the need of the high concentration of hydrogen ions that are so crucial in the column ion exchanger. The lower affinity for the sodium is counteracted by having a high concentration of water glass entering the combined ion exchange reactor.

2.4.5 Concentration of product

In order to concentrate the silica particles, evaporation or ultrafiltration is used. Types of evaporators that can be used are forced circulation evaporators [1, 5] or even atmospheric evaporators. Great care should be taken as to not concentrate the suspension too much, as this will result in silica scales on the equipment walls [1, 5]. Because of the additional heat in the evaporation step, silica particles can grow additionally through Ostwald ripening [1, 5]. Due to large energy consumption, evaporation has over the years often been substituted for ultrafiltration (UF) [1].

UF concentrates the colloid without forming a filter cake, making it different from other types of filtration [1]. The technique uses a membrane with a set mesh that retains anything above its size while smaller particles are removed together with some solution [2]. The membrane pores are very small, on the scale of a few to 15 nm. By stirring or by using high flow rate, too thick build-up is effectively prevented through the entailing turbulent flow, and the desired concentration of colloidal silica is maintained in the retentate [1, 2]. The concentration can be done either before or after the formation of the finished particles, depending on which product is made.

2.4.6 Surface modifications

After silica particles have formed, their surfaces can be modified by the addition of different compounds to the system [5]. By adding aluminate ions, the surface will contain aluminosilicate that will increase the colloid system's stability and prevent gelling even at lower pH levels of 4-6 or after addition of salts [5]. The properties of silica particles are to a large extent governed by their surface properties, and by coating a particle in a different material, the characteristics of that particle and the whole system changes to behave more similarly to a particle and particle system of the coating material [5]. Cationic particles can be produced by bonding the oxygen of two silanol groups with aluminate and stabilising the colloid with chloride. Silane can be attached to the particle through a condensation reaction with silanol groups.

2.5 Theory specific to the optimisation project

As this project included IP, the text has been written using non-confidential terminology. A general theory will now be given in order to understand the terminology used.

The process step that was optimised is called the process unit or the unit, for short. During the process step, Chemical A is added continuously for a certain time to the inflow of the unit. The process flow exiting the production unit was collected and studied. Four different quality parameters, A, B, C and D, were studied. The measurements were either done in the collected solution or in the flow itself. These types of measurement techniques are called sample measurements and continuous measurements, respectively.

The three parameters studied in the effluent via these methods were Parameter A, B and C. These are called effluent parameters, describing the properties of the liquid. They are presented as percentages of the maximum value exhibited in this project for each parameter. For the studies of Parameter C, results from previous work were used.

The chemical of interest to reuse in this project is Chemical A. The quality parameter values of pure Chemical A at 25°C are seen in Table 2.2. These also represent the optimal parameter values for reuse of Chemical A.

Table 2.2. Optimal values for the effluent parameters for reuse of Chemical A.

Parameter	Optimal value
A	100%
B	0%
C	0%

If Parameters A to C are affluent parameters, Parameter D is a process parameter, describing a property of the process step. Parameter D is, as is the case with the other parameters, expressed as a per cent of a common level reached. In the full-scale process unit, Parameter D is kept at 80%. This level is required for proper productivity and quality of the process. It is therefore a parameter value that must be kept similar even after the implementation of the optimisation. That means that a Parameter D level of 80% was a requirement during the experiments. Two different levels of Parameter D have been given specific names in this report, due to the frequent use and need to describe them. These are:

- *Target level of Parameter D*, meaning the level of 80%.
- *Combined level of Parameter D*, meaning the level reached when using both reused and fresh Chemical A.

2.6 Economics

The cost estimations in this project were made for the fixed capital cost. It was done by calculating inside battery limit investment and including engineering costs. Added to this cost was also 15% due to contingency. The outside battery limit investments were considered low, and not included in this estimation.

There are many methods for predicting capital costs of an investment [22]. They range in accuracy based on factors such as level of known design information. In the earlier stages of a project, less is known about the design and other specifications needed for a detailed cost estimate. At this stage, simpler versions of estimation models can be used. When, as in this case, simply investigating an idea, the estimations and methods will be rough, with an accuracy of around 50% [22]. At the later stages of a project, the methods that are used increases in sophistication and detail level along with the level of known information about the final plan.

Open literature can be used for finding cost information for different types of equipment, and there is cost estimation software such as Aspen ICARUS™ Technology and Aspen Process Economic Analyzer [22]. The real prices are, however, often kept secret from the public. Companies then heavily rely on previous knowledge about investments made and expertise within the company. In the later stages of the project, detailed offers can be made from the suppliers of equipment.

On top of all equipment costs, must be added the costs of planning, drawing and calculating what equipment should be used and its placement [22]. Then comes costs e.g. installation, heavily dependent on the conditions of the area of the placement, and costs of infrastructure for utilities, heavily dependent on the location of the equipment with respect to other infrastructure. Below are described two typical methods for basic cost estimations of equipment and a method used to calculate the capital cost, based on these figures. Lastly, a method of checking any capital cost estimates and calculating alternative numbers is presented.

2.6.1 Estimation using cost curves

If equipment costs are unknown, they can be estimated by using different cost curves. In this case, the estimations are based on the assumption that the price of a certain type of equipment increases with a size parameter, S , according to Equation 2.6 [22].

$$C_e = a + b \cdot S^n \tag{2.6}$$

In the equation, C_e is the purchased equipment cost, while a , b and n are cost constants specific to the type of equipment. The size parameter has a different unit depending on the equipment that is estimated.

2.6.2 Order of magnitude estimates

Another method of estimating equipment cost is to use known prices of similar equipment and scale it based on capacity, S, as seen in Equation 2.7 [22].

$$C_2 = C_1 \cdot \left(\frac{S_2}{S_1}\right)^n \quad (2.7)$$

In this equation, C is either the capital costs of the planned equipment (2) or the known capital cost of a similar piece of equipment (1). The exponent, n, is specific to different types of industries. For the chemical industry, the common exponent is 0.6, resulting in the method being commonly called the six-tenths rule.

2.6.3 Factorial method of cost estimation

The factorial method is used to calculate the installed costs of different pieces of equipment after calculating the equipment cost in one of the methods described above [22]. It uses an installation factor, sometimes called Lang factor, to determine the fixed capital cost based on equipment cost, as seen in Equation 2.8.

$$C = \sum_i (C_{e,i} \cdot F_i) \quad (2.8)$$

C is the capital cost including engineering, Ce is the delivered equipment cost for each equipment, and F is the installation factor based on what type of equipment is installed.

2.6.4 Reverse engineering methods

A reverse engineering method is a type of rough estimate of capital cost [22]. In the method, commonly appearing connections between factors are utilised. These can be connections frequently displayed in projects across several industries and that are widely known, or connections based on the practices within a certain company. One example is to use the payback method to reverse engineer the plant cost. This would be done by knowing the gross profit, taxes and a common relation between these and plant cost.

If, for example, there is a trend (on large scale across industries, or within a company, alike) that a certain percent of the capital cost is spent on engineering, this connection can be reverse engineered to calculate a reasonable capital cost, solely based on the probable amount of engineering hours for a project. An example of this is shown in Equation 2.9. A common percent used in literature is between 10 and 30% [22].

$$\text{Capital cost} \cdot x\% = \text{Engineering cost} \cdot \text{Engineering time} \quad (2.9)$$

Thus, the capital cost can be approximated by Equation 2.10.

$$\text{Capital cost} = \frac{\text{Engineering cost}}{x\%} \quad (2.10)$$

2. Theory

This relationship can also be use in reverse order, to see if a calculated capital cost corresponds to a reasonable amount of engineering hours, based on previous experiences.

3

Materials and methods

The following chapter presents the materials and methods used in the optimisation project. As experimental work has been done both on lab and pilot scale, Section 3.1 and 3.2 are divided up accordingly. Section 3.1 details the materials and chemicals used. In Section 3.2, the different preparation steps needed before the experiments could start and the final setups used, are presented, ending with the calculations that are the basis of the downscaling. All experiments performed are described in Section 3.3, divided based on what the experiments were designed to investigate.

3.1 Materials and chemicals

Listed below are the materials and chemicals used in the different experiments, starting with the lab-scale experiments and lastly for the pilot-scale experiment.

3.1.1 Lab scale

The different chemicals and the concentrations used for the experiments on lab-scale are found in Table 3.1.

Table 3.1. Chemicals and concentrations used in lab scale experiments.

Chemicals	Relative concentrations used [a]
Chemical A	14 or 1
Deionised water	-

[a] Concentrations presented are relative concentrations compared to the lowest concentration used.

The materials used for the lab scale experiments presented in Section 3.3 are described in Table 3.2, together with short comments on why and how they were used. See Figure 3.1 for an idea of how the material setup was done.

3. Materials and methods

Table 3.2. Materials including machines used in lab scale experiments.

Materials	Type	Comments
Process unit on lab scale		For dimensions, see Table 3.4
Sample bottles for collecting liquid with Chemical A exiting the unit		With known empty weights
Small funnel for aiding in collection of solution		
Buckets for spillage and capturing exiting fluid	1 l	
Buckets for holding liquids before and after the unit	1-5 l	
Masking tape		Used for everything
Timer for timing the steps		
Meter for Parameter A		Accuracy $\pm 0.5\%$
Meter for Parameter B		Accuracy $\pm 0.02\%$
Meter for Parameter C		Accuracy $\pm 0.001\%$

3.1.2 Pilot scale

The chemicals used in the pilot-scale experiment were the same as for the lab scale. The materials used are presented in Table 3.3. For the experiment, two meters for Parameter A and two meters for Parameter B were used. They were placed at different points of the end stream from the unit, see Section 3.2 for the full setup.

Table 3.3. Materials used in pilot scale experiment.

Materials	Type	Comments
Pilot scale unit		For dimensions, see Table 3.4
Buckets for holding liquids before and after the unit		
Sample bottles for collecting liquid exiting the unit	1 l to 10 l depending on need	With known empty weights
Timer for timing the steps		
Meter 1 for Parameter B		Right after the unit, minimum detection limit 12%
Meter 2 for Parameter B		Downstream from the first meter, accuracy $\pm 0.06\%$
Meter 1 for Parameter A		Right after the unit, maximum detection limit 0.02%
Meter 2 for Parameter A		Downstream from the 1st meter, accuracy $\pm 0.5\%$

3.2 Setup and preparation

In this section, the initial work to be able to start the experiments, followed by the final setups are presented. In Section 3.2.1, the lab-scale unit is presented, and in Section 3.2.2 same is shown for the pilot-scale unit. See Figures 3.1 and 3.2 for schematic images of the process unit on the two scales. The background to and basic descriptions of the calculations of different setup parameters for lab and pilot scale, based on downscaling of the full-scale process, are presented in Section 3.2.3.

3.2.1 Lab scale

The lab-scale unit used can be seen in Figure 3.1. The unit dimensions are presented in Table 3.4. At the end of the unit, measurements of different parameters were made, and liquid could be collected.

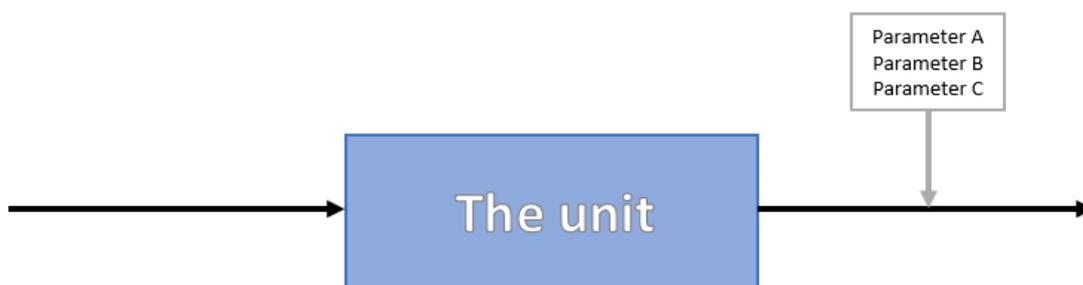


Figure 3.1. Schematic image of the lab scale process step. In the outflow of the unit, measurements of different parameters can be taken.

The flow of the unit was determined by downscaling the flow of the full-scale unit. See Section 3.2.2 for more exact calculations.

3.2.2 Pilot scale

For the pilot experiment, a bigger version of the lab-scale unit was used. Figure 3.2 shows a schematic picture over the setup used. Shortly after the outflow of the process unit, Parameter A and Parameter B were measured the first time, see meters 1 and 1 respectively in Table 3.3. Further downstream, the parameters were measured again using meters 2 and 2 respectively in Table 3.3. The second measurements were done at the same point as the collection of liquid.



Figure 3.2. Schematic image of the pilot scale process unit. The properties of the effluent can be measured at two points, marked out on the image.

The pilot unit step was scaled so it would be approximately 20 times bigger than the lab scale. The flow was also adjusted to this ratio, but when comparing the relative feed rates between different scales, the flow rates were tried to be kept close to unity.

3.2.3 Calculations for downscaling

In Table 3.4, different parameters for the units of each scale are presented. The parameters that needed scaling were the amounts of Chemical A to be used in the unit on different scales and the flow rates. The Chemical A amount for the lab unit was determined by calculating how much that was required to reach 80% of Parameter D. For the pilot-scale unit, the Chemical A amount was calculated by multiplying the amount for the lab unit with the volume ratio between the pilot and the lab volume. The used amounts for lab and pilot scale are presented in Table 3.4.

Table 3.4. Dimensions of the process units at different scales.

	Lab scale	Pilot scale	Full scale
Relative volume [a]	1	21.32	3100
Relative feed rate [a]	1	0.95	1.04
Relative feed concentration of Chemical A [b]	14	14	14
Time unit step (min)	20.78 [c]	20.00	16.80

[a] Calculated relative to the lab unit.

[b] Concentrations are presented as relative concentrations compared to the lowest concentration used in the experiments.

[c] Mean residence time.

The lab-scale and pilot-scale flow rates were determined by having the same equivalent rate as is used in the full-scale process. They are presented as relative flow rates compared to the lab-scale unit. The same flow rate was used for all experiments on lab-scale, except when the experiment consisted of trying different flow rates.

The concentrations used for the lab and pilot scales was the same concentration as used in the full-scale unit. The concentrations are presented in Table 3.4 as relative concentrations to the lowest concentration used in one of the experiments. When testing the effect of concentration of Chemical A on Parameters A, B and D, in one of the repeats of Experiment 1, the relative concentration 14, was instead used.

3.3 Experiments

The optimisation project was divided into several experiments that were repeated and/or varied. The main experiments conducted were:

Experiment 1. Lab-scale; using the same equivalent amount of fresh Chemical A as in full-scale

- To simulate the full-scale unit.
- To determine if Parameter D values of 80% are possible to reach with this setup.
- To examine the quality parameter profiles and compare to the process unit on other scales.
- To examine the quality parameter profiles and establish baselines for Experiment 2 and 3.
- To collect Chemical A and study its properties.

Experiment 2. Lab-scale; using only reused Chemical A

- To determine what level of Parameter D can be reached by just using reused Chemical A.
- To determine what range of Parameter A and B collect Chemical A in.
- To compare quality parameter profiles to baselines.

Experiment 3. Lab-scale; using a combination of reused and fresh Chemical A

- To determine if target level of Parameter D (80%) is possible when substituting some of the fresh Chemical A for reused, i.e. to see if target level can be reached by the combined level of Parameter D.
- To test the calculation method for determining how much fresh Chemical A is needed in combination with reused Chemical A to reach the target level of Parameter A.

Experiment 4. Pilot-scale; using the same equivalent amount of fresh Chemical A as in full-scale

- To simulate the full-scale unit.
- To examine the quality parameter profiles and compare to the process unit on other scales.
- To collect Chemical A and study its properties.

3.3.1 Experiment 1. Using only fresh Chemical A

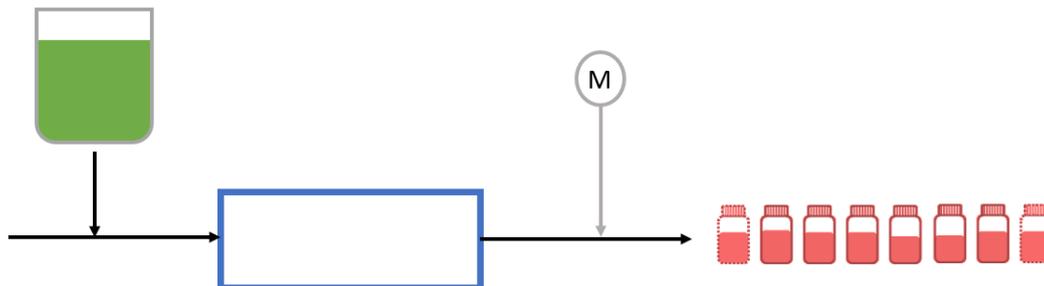


Figure 3.3. Schematic image of Experiment 1. Fresh Chemical A (green) is added to the inflow of the process unit (blue), and the outflow is collected in a varying number of sample bottles containing old Chemical A (red). Measurements can be taken in the effluent.

Experiment 1 was done for several reasons and was repeated 6 times. One reason was to investigate how the current case looked on lab-scale, both to establish baselines for Parameter A and B, and to determine if the target level of Parameter D could be reached. Another reason was to collect the effluent containing Chemical A for reuse in future experiments, see Figure 3.3, and to measure Parameter A and B of the collections at different intervals. Parameter C was not measured, and analysis was instead based on results from previous studies. The quality parameter curves obtained in Experiment 1 were used as baselines when comparing with Experiments 2 and 3, and also for comparison between process units of different scales (pilot scale in Experiment 4 and full-scale).

3.3.1.1 Procedure

All effluent from the process step was collected, by retrieving it in sample bottles over three-minute intervals. Parameter A was continuously measured, at the measurement point indicated in Figure 3.3. Parameter B was measured in every sample bottle. Parameter C was not measured, and results from previous studies were instead used. The general steps of the experiment are the following.

1. The inflow to the process unit was started.
2. After a certain time, an equivalent amount of Chemical A as is used in the full-scale unit was added. The same relative speed and concentration were used. These correspond to the relative speed 1 and relative concentration 14, seen in Table 3.4. The chemical was added at the same time for each experiment.
3. After three minutes, the collection of effluent was started. One collection was done for three minutes and then a second collection was started. This was

repeated until the Parameter A values were close to 0%.

4. The addition of Chemical A continued until all the chemical had been added.
5. The inflow was stopped when the value of Parameter A was 0%.
6. The sample bottles were labelled and the level of Parameter B in each bottle was measured.

3.3.1.2 Altering concentration

Experiment 1 was conducted a seventh time with a lower concentration, corresponding to the relative concentration 1 in Table 3.4. The same number of moles was added to the process unit, but the concentration was 14 times lower than for the other repeats of Experiment 1. The same relative flow rate of 1 was maintained, however. This part of the experiment was done in order to investigate if the concentration of Chemical A influences the level of Parameter D.

3.3.2 Experiment 2. Using only reused Chemical A

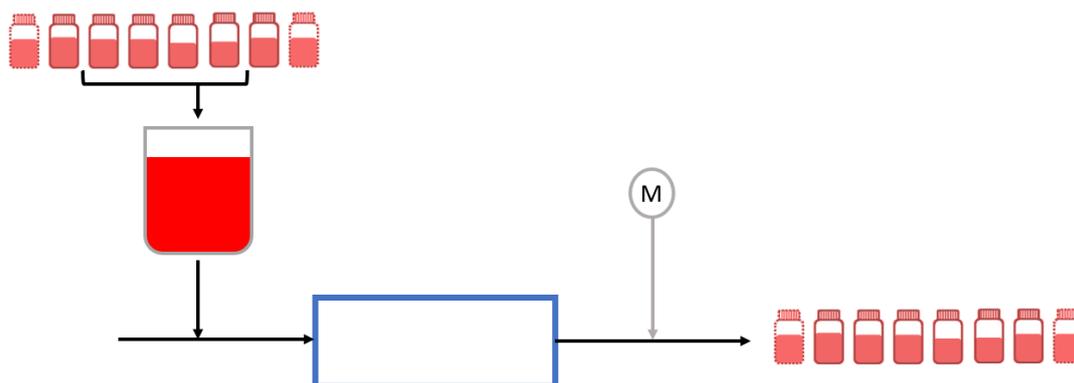


Figure 3.4. Schematic image of Experiment 2. On the left of the process unit (blue), sample bottles containing old Chemical A (red) from Experiment 1 are selected for a subset and mixed into a reused Chemical A mixture. Parameter A and B are measured in the outflow and the effluent is collected in a varying number of sample bottles containing old Chemical A (red). Measurements can be taken in the effluent.

In the second part of the lab work, collected Chemical A from Experiment 1 was reused in the process unit. The experiment was devised so that Chemical A from one repeat of Experiment 1 was used in one repeat of Experiment 2. This was done four times. Since the objective of Experiment 2 was to investigate which parts of the collected Chemical A that could be used, a subset of the collection was selected.

3.3.2.1 Subset selection

From each repeat of Experiment 1, a collection of Chemical A in sequential sample bottles was obtained. In Figure 3.6, the different sample bottles containing varying

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amounts of Chemical A solution can be seen. Each bottle had a known level of Parameter B. For each of the four Chemical A collections respectively, a subset of samples was selected for further use. The selection was based on Parameter B values, where sample bottles with a value below a certain level were chosen, see Figure 3.5. The Parameter B level, marked x , was varied for each repeat. This was done to test if different cut-off limits of Parameter B would have an effect on the levels of Parameter D for the process unit. The subset was then mixed into one single container forming the reused Chemical A mixture, see Figure 3.6. The levels of Parameter A and B, along with the weights were determined for the four separate reused Chemical A mixtures.

The reused Chemical A mixtures varied in quantity for reasons beyond which level of Parameter B they were collected below. The level of Parameter B of the sample bottles varied between repeats of Experiment 1, making the selection of bottles unique each time. Also, the amount of Chemical A in each sample bottle varied.

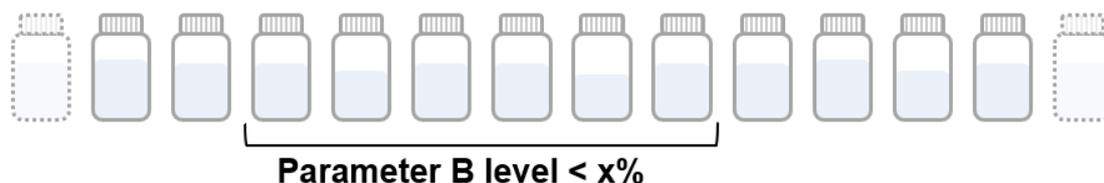


Figure 3.5. A varying number of sample bottles with a solution containing Chemical A were obtained in each repeat of Experiment 1. For the samples of each repeat, a subset was selected based on Parameter B level. The cut-off level was varied between repeats and is depicted here as $x\%$. The number of bottles in the subset would vary in each repeat.

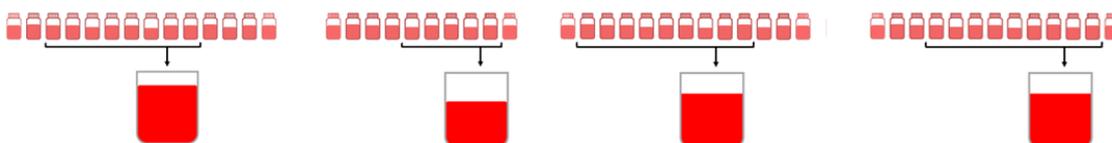


Figure 3.6. The sample bottles from four repeats of Experiment 1 are shown. Red represents old Chemical A. The number of sample bottles varied between repeats. Parameter B levels were measured for each sample bottle and bottles beneath a certain level were selected for a subset. The cut-off level was varied between differed subsets. Each subset was then mixed into a container, resulting in four so-called reused Chemical A mixtures.

The different mixtures of reused Chemical A were distributed between experiments, based on the quality of the mixtures. The quality was determined by the results in Experiment 1 and 4, and the distribution of mixtures is therefore described further in Section 4.1.5.

3.3.2.2 Procedure

Using the same lab-scale process unit as in Experiment 1, Experiment 2 was conducted similarly to Experiment 1. The only exception from the procedure list in Section 3.3.1.1 is step 2, where the addition of Chemical A was done solely by adding a reused Chemical A mixture described in Section 3.3.2.1.

3.3.3 Experiment 3. Using a combination of reused and fresh Chemical A

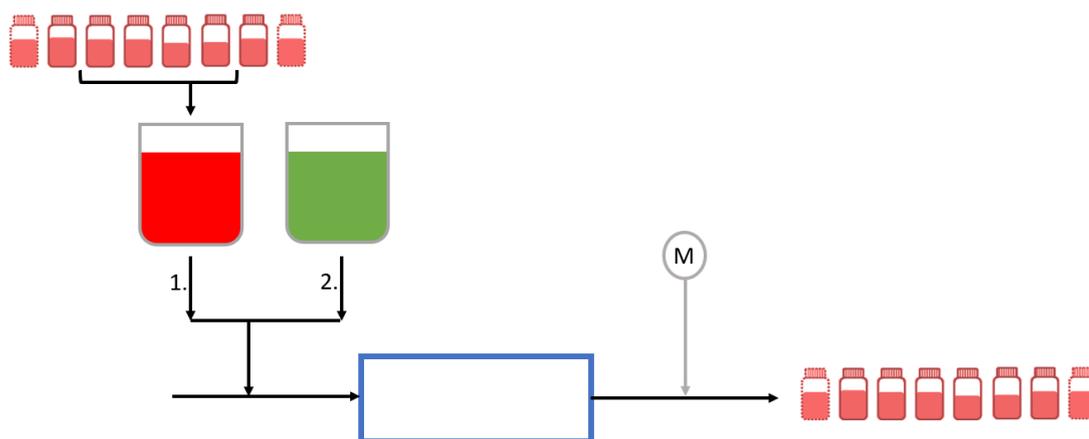


Figure 3.7. Schematic image of Experiment 3. On the left of the process unit (blue), sample bottles containing old Chemical A from Experiment 1 are selected for a subset and mixed into a reused Chemical A mixture (red). The reused Chemical A mixture is added to the process unit in step 1. In step 2, the fresh Chemical A (green) is added. On the right side of the process unit, Parameters A and B are measured, and the outflow is collected in a varying number of sample bottles containing old Chemical A (red). The separation of the addition of chemical into two different steps, step 1 and 2, was only done when using methods B and C, described in Section 3.3.3

In Experiment 3, a combination of reused and fresh Chemical A used in the production step. The goal was to reach a combined level of Parameter D of 80%. The experiment was done three times, using three different methods that are presented in 3.3.3.2.

The old Chemical A that was reused had been collected in Experiment 1. Similarly to Experiment 2, a subset of the old Chemical A samples was selected and mixed into a reused Chemical A mixture, of which three in total were used in Experiment 2. For the subset selection process, see Section 3.3.2.1.

In order to do Experiment 3, the amount of fresh Chemical A had to be decided. This was done by calculations based on the level of Parameter D when only using old Chemical A in Experiment 2, as discussed in Chapter 2. The calculations are presented in Section 3.3.3.1. The level of Parameter D that theoretically would be reached when using a reused Chemical A mixture was either determined by testing

in Experiment 2 or by testing similar reused Chemical A mixtures and making assumptions and approximations. The testing was done in Experiment 2, and the knowledge from those repeats was used to decide the fresh Chemical A amounts in Experiment 3.

To make the results from Experiment 2 useful for the calculations and carrying out of Experiment 3, the reused Chemical A mixtures should be as similar as possible. This was solved by using “the same” mixture in both Experiment 2 and 3. It was done by mixing two reused Chemical A mixtures and separating them into two identical ones. One mixture was then used in Experiment 2 and one in Experiment 3. This was done twice.

For two of the reused Chemical A mixtures, the level of Parameter D of the process unit after use was known since the reused Chemical A mixtures had been duplicated and one batch of each pair had been tested in Experiment 2. For the last reused Chemical A mixture, however, the entailing Parameter D level of the process unit was unknown. For this reused Chemical A mixture, the assumption was instead made that it was similar to other reused Chemical A mixtures that were tested in Experiment 2.

3.3.3.1 Fresh Chemical A amount calculations for combination with reused Chemical A

The level of Parameter D of the process unit during usage with reused Chemical A, $x\%$, was determined in Experiment 2. By calculating the difference between the target level and $x\%$, as seen in Equation 3.1, the needed amount of fresh Chemical A was determined by a relationship shown in Equation 3.2.

$$80\% - x\% = z\% \quad (3.1)$$

$$m(\text{fresh Chemical A}) = f(z\%) \quad (3.2)$$

3.3.3.2 Procedure

With knowledge about the amount of fresh Chemical A, the experiment could be conducted. The process unit was the same as was used in Experiment 1. Experiment 3 was conducted similarly to the list of steps seen in Section 3.3.1 for Experiment 1, except for step 2. Here, the addition of Chemical A, to the inflow was a combination of old and fresh Chemical A.

There were three different methods used for the addition of Chemical A. The methods were the following.

- (i) The reused and fresh Chemical A containers were mixed and added to the process unit in a single step.
- (ii) The reused Chemical A was added (see step 1. in Figure 3.7) first, followed by the addition of fresh Chemical A (see step 2.).
- (iii) Method B was used, but the residence time for Chemical A (for the reused and fresh Chemical A) was adjusted to be the same as in Experiment 1, by increasing the flow to the relative flow rate of 1.56.

The combined level of Parameter D was calculated and could be compared both to the target level of 80% and between different methods.

3.3.4 Experiment 4. Pilot-scale

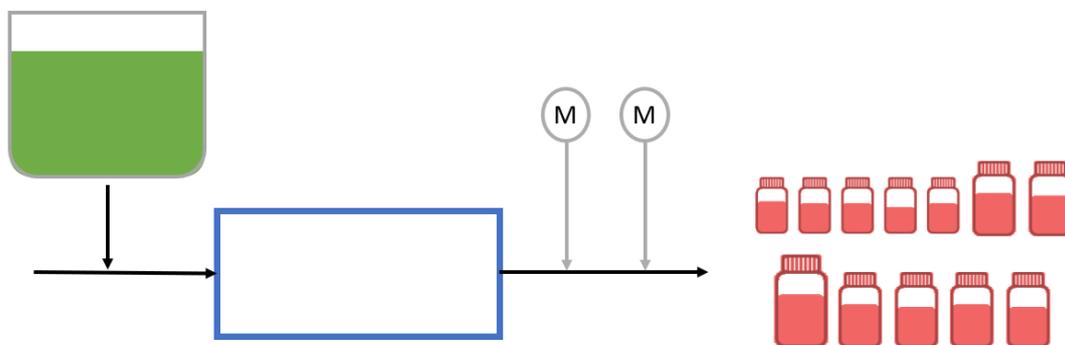


Figure 3.8. Schematic image of Experiment 4. On the left of the pilot-scale process unit (blue), fresh Chemical A (green) is added to the inflow to the process unit. Parameters A and B are measured at two different points of the outflow from the process unit and the effluent is collected in several sample bottles containing old Chemical A (red).

Experiment 4 was conducted similarly to Experiment 1 but on pilot-scale and was only done once. It was conducted for several reasons. One reason was to investigate how the current process step looked on pilot-scale. By studying the profiles of Parameters A and B, the pilot process could be compared to the full-scale and the lab-scale processes. Another reason was to collect large amounts of old Chemical A to be used in Experiments 2 and 3. The Parameter C curve was not studied, and the analysis was instead based on results from previous studies. The level of Parameter D for the process unit was not studied.

3.3.4.1 Procedure

The values of Parameters A and B for the four meters were continuously noted. During the experiment, the following steps were conducted.

1. The inflow to the pilot unit was started.
2. After a certain time, an equivalent amount of Chemical A as is used in the full-scale unit was added. Approximately the same relative speed and concentration were used. These correspond to the relative speed 0.95 and relative concentration 14, seen in Table 3.4. Chemical A was added at the same time for each experiment.
3. The collection of effluent was started when Parameter B reached a value of 28%. The collection in each sample bottle was done until the sample bottle was full or until Parameter B reached any of the levels 25%, 22%, 19% when decreasing.

4. When the level of Parameter B started increasing, the sample bottles were changed when the levels reached 19%, 22%, 25% and 27%.
5. The addition of Chemical A ended when the chemical ran out.
6. When Parameter B reached 28%, the collection of effluent was stopped, and so was the flow to the process unit.
7. The sample bottles were labelled and the level of Parameter B in each bottle was measured.

The collection of Chemical A from Experiment 4 was used similarly as the collections from Experiment 1, to form reused Chemical A mixtures for further use in Experiment 2 and 3. Before the subset selection step, described in Section 3.3.2.1, could be performed, however, the collected Chemical A sample bottles had to be scaled down. They were scaled down to sizes equivalent to a lab-scale unit by dividing each sample bottle size by 21.32, as is the relative size between the units, see Table 3.4.

3.4 Economics

The economic evaluation of the process optimisation was done by comparing the fixed capital investment to the cost savings attained through the optimisation. The cost estimations in this project were made for the fixed capital cost inside battery limits, including engineering costs. Added to this cost was also a contingency of 15%. The outside battery limit investments were considered low, and not included in this estimation.

The capital costs were calculated using a combination of the factorial method developed by Lang in 1948, described in Section 2.6.3, and different methods of calculating equipment costs described in Sections 2.6.1 and 2.6.2. Both these methods are basic estimation methods that are commonly used on the idea-stage of this type of work, to get an initial idea of what the equipment costs can be.

For the optimisation studied in this project to become a reality, however, several more economic studies will have to be performed. Each one will be on a more advanced, detailed and, hopefully, accurate level. A sensible next step after the idea-stage, and a level above the estimates made in this report, could be to use cost estimation software such as Aspen ICARUS™ Technology and Aspen Process Economic Analyzer [M31].

For the capital cost estimation, the costs of equipment had to be calculated. A preliminary list of possible equipment was made, and the equipment costs were estimated using one of the two methods mentioned. One of these methods, the order of magnitude estimate described in Section 2.6.2, was used for scaling equipment costs similarly to the scaling of capital costs described in Chapter 2. The costs of equipment were used to do a capital cost estimation, by using Equation 2.8 and looking up constants for the different pieces of equipment. In this estimation, the costs of engineering and installation are included. The capital cost was then assumed to be increased by 15% as a contingency.

After the final sum was presented, it was reverse calculated to determine how many engineering hours this figure would mean. Since the number of engineering hours seemed to be on the lower side, a second capital cost calculation was instead done to determine an upper cap of the capital investment. This was done by using Equation 2.9 and 2.10 and determining, based on the number of probable engineering hours for this type of project, the corresponding capital investment assumed in the equation. Overall, the calculations described in this section resulted in the upper and lower capital investment.

The cost savings for the investigated process optimisation were calculated for a year of operations and were based on raw material costs and the saving potentials found in the laboratory work. They were calculated separately for the cost savings attained through a reduction in chemicals usage and for the cost savings in the subsequent wastewater treatment steps. The possible yearly savings were added up and compared to the two possible capital investments. The different options were compared by looking at simple payback period.

4

Results

The results of the optimisation project are presented in this chapter.

4.1 Experiment 1. Using only fresh Chemical A

In this section, the results from the lab-scale unit runs are presented. In Section 4.1.1, the measurements of Parameters A and B are presented for each of the six repeats of Experiment 1 with similar feed concentrations of Chemical A, i.e. Experiments 1.1 to 1.6, along with the subsequent baseline selections. The values of Parameter D for all repeats of Experiment 1 are presented in Section 4.1.2, and results from concentration variation of Chemical A are shown in Section 4.1.4. In Section 4.1.3, Parameter C values from two studies are compiled.

The Chemical A collections were divided into subsets based on the results from Experiment 1, and the subsets and subset properties are presented in Section 4.1.5. Since the collections of Chemical A from Experiment 1 were to be used in Experiment 2 and 3, a plan for how to distribute the collections between different experiments had to be done. This distribution was based on the results in Sections 4.1.1 and 4.1.2 and is presented in 4.1.6.

4.1.1 Results and establishing baselines

In Figure 4.1, the summarised results of the repeats of Experiment 1 with the same feed concentration of Chemical A, are shown. The detailed results and means are shown in Figure 4.3 to 4.2. In Figure 1, curves of Parameter A (measurements taken every 3 minutes) and B (measurements taken of sample bottles collected over three-minute intervals) from Experiment 1.4 are compared to mean curves based on the values in Figure 4.4 and 4.2 respectively. These four curves were picked out as so-called baselines for future comparisons between experiments and unit scales.

Since measurements of Parameter A sometimes were taken more frequently than every three minutes, Figure 4.1 also displays some additional measurements of repeat 1.4, called “all values”, for comparison. This curve reaches a similar maximum value of Parameter A as is the value of pure Chemical A. The Parameter B curves reach values close to pure Chemical A at approximately the same time.

4. Results

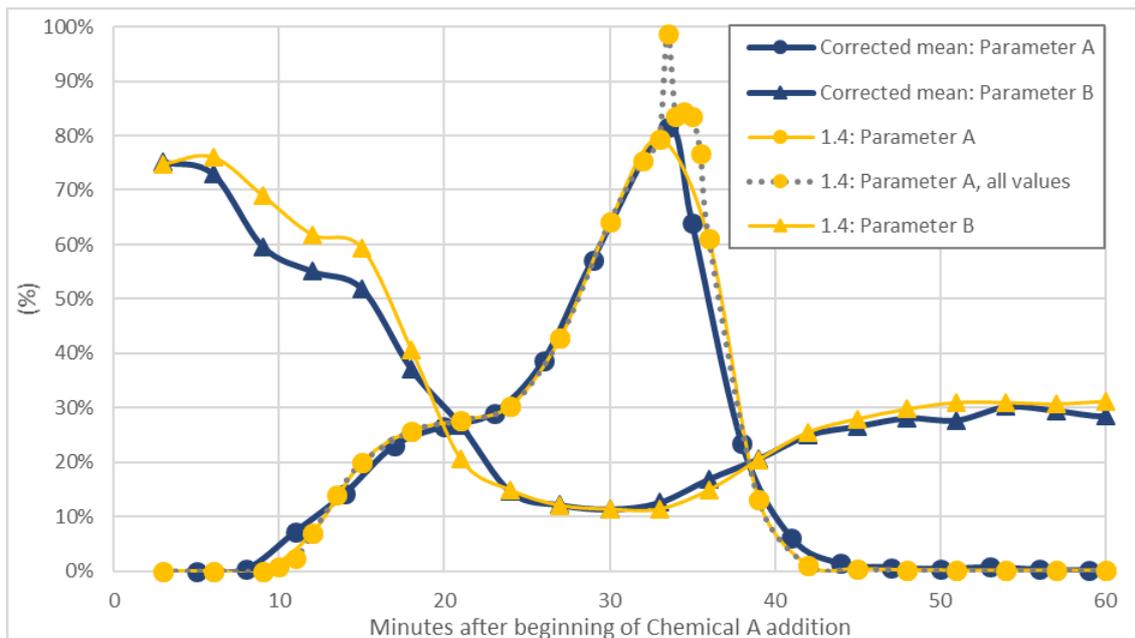


Figure 4.1. The collected results of Experiment 1, showing the curves later used as baselines. The corrected means are based on values in Figure 4.4 and 4.2 respectively. Remaining curves are of Experiment 1.4 and shows the values for Parameter A (both measurements taken every 3 minutes, and additional measurements) and Parameter B.

The reason why the mean curves of Parameter A and B were made is because of the differences displayed between repeats of experiments and, for Parameter A, between measurement techniques. Establishing a connection between the curves in Figures 4.3 and 4.4 was key to determining a common behaviour of Parameter A, and the same was true for the Parameter B curves in Figure 4.2.

As can be seen in Figure 4.1, the measurements from Experiment 1.4 and the mean curves overlap. This was achieved by a combination of excluding outliers as well as pushing the mean curve of Parameter A by two minutes. The peak of the same curve was also adjusted in order to get a more representative height. For the process of the choice of mean Parameter A curve, see Appendix A.

Parameter B

Figure 4.2 shows the measurements of Parameter B in the sample bottles collected over three-minute intervals. As the samples are a collection over three minutes, the values are not representative of the minute the collection started (i.e. the value marked on the x-axis) but can instead be seen as a mean over the three-minute interval. That would explain why a push by about two minutes would better align the mean of these curves to a curve of measurements taken every three minutes, as was the case in Figure 4.1.

In Figure 4.2, Experiment 1.1 and 1.3 are partly considered outliers. Since the measurements are from sample bottles, they have been rechecked. Experiment 1.1 was the first experiment performed in the process unit. After 18 minutes, the values started to mimic the values of the other experiments, but the values in sample bottles

collected before this time were excluded from the mean curve calculations. Because of inconsistent measuring and collecting during Experiment 1.3, due to time issues, the samples with collection start at 9 to 15 minutes were considered outliers, and not included in the calculated mean curves of neither Parameter A nor B.

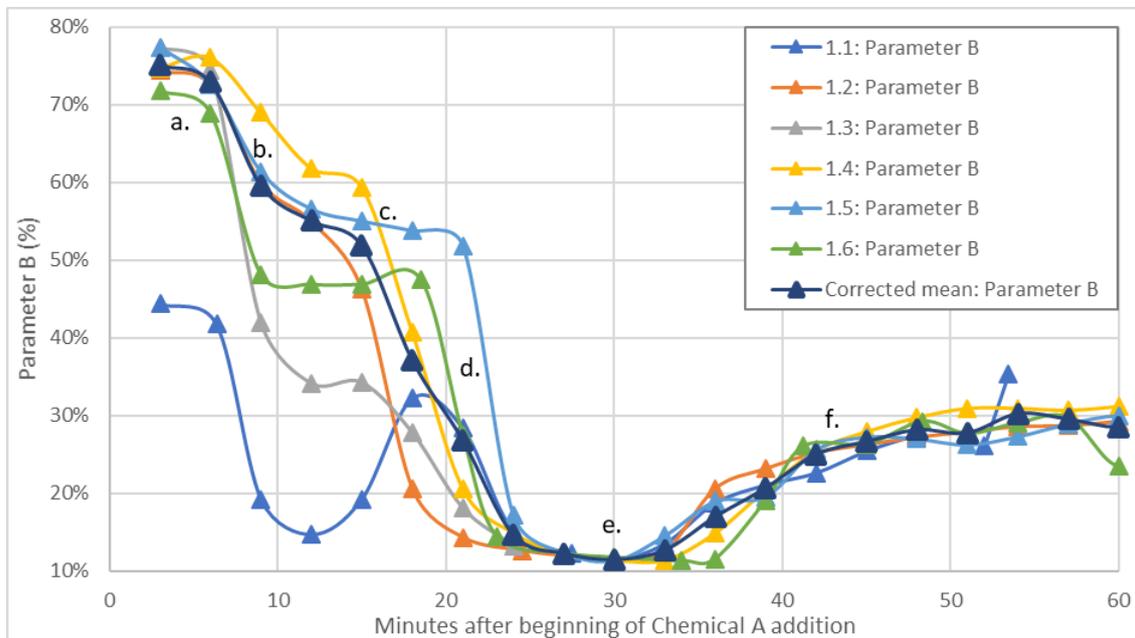


Figure 4.2. Measurements of Parameter B for Experiment 1.1 to 1.6 taken of sample bottles collected for three minutes. Observe that the y-axis is of different scale than previous figures. The curves display similar behaviours: a. start values between 70 to 80%, b. decrease after 6 minutes, c. the curves flatten out, d. rapid decrease, e. reaching minima of about 10%, f. slow increase again until values are stable around 30%.

A general behaviour can be seen for Parameter B when looking in Figure 4.2. The curves mostly exhibit the same behaviour by starting at between 70 to 80% (point a.), followed by a fast decrease (b.). The slope flattens out, however, at a value between 45 to 60% (c.) before decreasing rapidly once again (d.). The curves reach minima within the same time interval (e.), and the minimum value is the same for all curves, at around 10%. After the minimum, the curves slowly increase to a value of around 30% after 1 hour (f.) and, if continued for another 30 minutes, some reach approximately 40%.

Parameter A

When comparing the curves in Figures 4.3 and 4.4, the behaviours of Parameter A measured at the same intervals but with different techniques can be studied. The strange initial behaviour of Experiment 1.1 in Figure 4.3 is attested by a similar behaviour seen for the experiment in Figure 4.4. After 24 minutes, the curve in Figure 4.3 start to once again approaching the values of the other experiments. In Figure 4.4, however, the only measurement considered an outlier was the sample with collection start at 12 minutes, and this one was excluded from the mean curve calculation.

4. Results

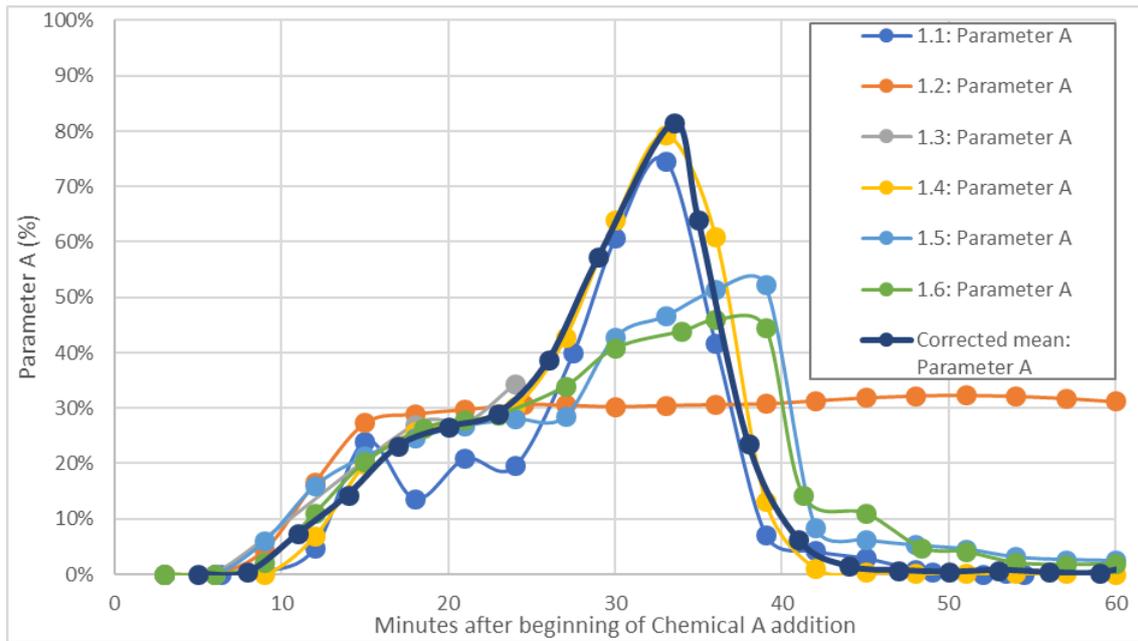


Figure 4.3. Measurements of Parameter A for Experiment 1.1 to 1.6, taken every 3 minutes.

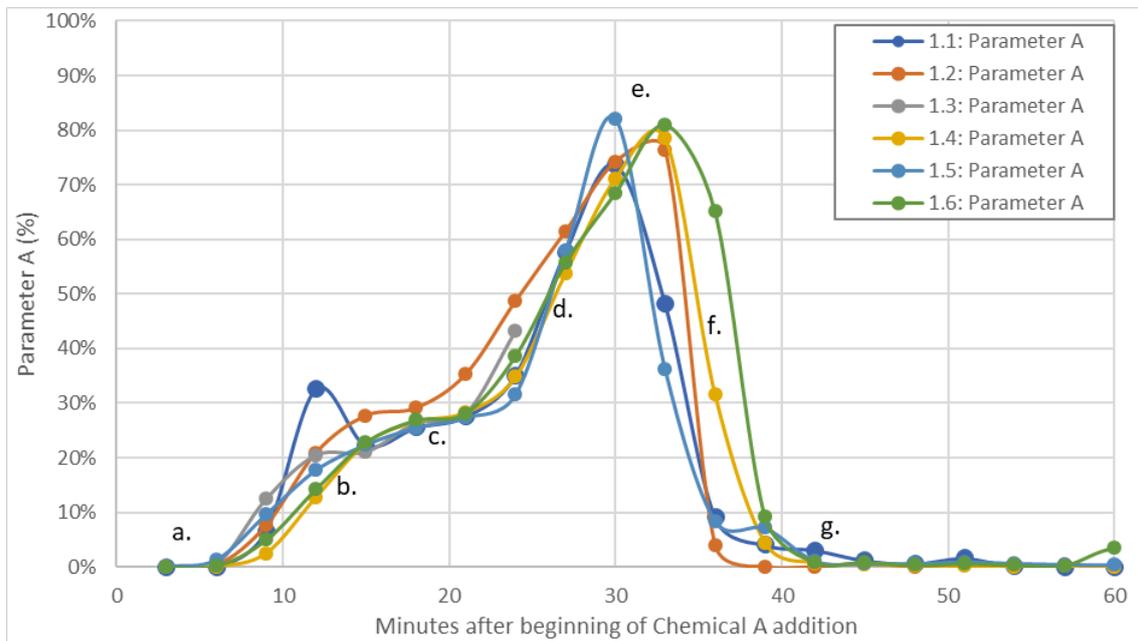


Figure 4.4. Measurements of Parameter A for Experiments 1.1 to 1.6, taken of sample bottles collected for three minutes. Values are shown at the start time for each collection. The curves show similar behaviour: a. start value at 0%; b. after 8 minutes an increase is observed; c. the curve flattens out after about 18 minutes; d. second increase; e. reaches a maximum after about 35 minutes; f. fast decrease, and; g. the curves flatten out and slowly approach 0%.

Figure 4.3 shows the Parameter A measurements for all six similarly conducted repeats of Experiment 1, as taken every 3 minutes, and also the mean curve of the sample bottle measurements in Figure 4.4. As can be seen, only Experiment 1.4 follows the mean curve well, while Experiment 1.1 follows the curve except between minute 15 and 24. That shows that all repeats of Experiment 1 except these two, differed greatly from the curves and behaviours so uniformly exhibited when using the measurement technique used to gather the results seen in Figure 4.4. In Figure 4.3, Experiment 1.4 and 1.1 are similar and Experiment 1.4 and 1.5 are similar. Experiment 1.3 was stopped prematurely due to errors in the process run. As can be seen for Experiment 1.2, the curve completely flattens out after the initial increase.

Although the curves in Figure 4.3 differ, a general behaviour for Parameter A in the outflow of the process unit can be observed, especially with the help of the curves in Figure 4.4. The curves have an initial value of 0% (point a. in Figure 4.4) and then start to increase after about 9 minutes (b.). A flattening of the curve after about 18 minutes can be observed for all experiments (c.) followed by an increase again (d.). For the curves that have maxima (e.), these occur at roughly the same time, around 35 minutes, and then the parameter value rapidly falls (f.) and eventually flattens out and approaches 0% (g.). The maximum values of the curves in Figure 4.3 are just below 80%. Compare this to the maximum value reached for the additional measurements of Experiment 1.4, seen in Figure 4.1. There, the Parameter A value approached 100%, i.e. the parameter value of pure Chemical A.

Concentration dependence of time steps

The time until Chemical A ran out in the bucket for each experiment is presented in Table 4.1 together with the times until Parameter A maxima were reached along with mean values. As can be seen for Experiment 1.1 to 1.6, the values are quite uniform. These, as can be expected, stand out from the values for Experiment 1.7. When comparing the difference between the time of depletion of Chemical A and the time until the maximum is reached, however, there is little difference between Experiments 1.1 to 1.6 and Experiment 1.7. Indicating that the difference is not concentration-dependent.

Table 4.1. Times for different steps in each repeat of Experiment 1.

Experiment	Time until depletion of Chemical A (min)	Time until Parameter A maximum reached (min)	Difference (min)
1.1	<i>20.83</i>	<i>33.00</i>	12.17
1.2	22.00 [a]	33.00 [b]	11.00
1.3	<i>20.83</i>	-	-
1.4	<i>20.83</i>	<i>33.00 / 34.00</i> [c]	12.17
1.5	<i>20.75</i>	33.00 [b]	9.25
1.6	<i>20.75</i>	33.00 [b]	12.25
1.7	295.73	304.00	8.27
Mean (based on italic numbers)	20.80	33.00	12.20

[a] Considered an outlier.

[b] Measured in sample bottle.

[c] Second value is from the maximum reached in the additional values in Figure 4.1.

4.1.2 Comparing Parameter D

In Table 4.2, the values of Parameter D are presented. The measurement of Parameter D was only done for Experiment 1.1, 1.4, 1.5, 1.6 and 1.7.

Table 4.2. Parameter D values for repeats of Experiment 1.

Experiment	Parameter D (%)	Difference from target value (percentages)
1.1	66%	14
1.4	78%	2
1.5	76%	4
1.6	79%	1
1.7	83%	-3

The results have an approximate margin of error of 2 percentages, due to possible measurement errors. The values are based on a minimum of 3 measurements. The theoretical value of Parameter D for pure Chemical A is 80%. A difference of 5 percentages from the target value is considered to be within reasonable proximity and therefore seen as equally good. Observe that Experiment 1.1 has a much lower value and that this was the first experiment conducted. Also, observe that Experiment 1.7 has a higher value than was considered probable. Compared to the other repeats of Experiment 1, the concentration was 14 times lower, and therefore the residence time was 14 times longer for Experiment 1.7.

4.1.3 Comparing Parameter C

Measurements from two previous studies of Parameter C levels in the effluent from lab-scale and full-scale units were put side by side for comparison in Figure 4.5. They were compared to the Parameter A curves chosen as baselines in this project. Table 3.4 shows that an average residence time of Chemical A in the full-scale unit is 16.8 minutes. The residence time of the lab-scale unit studied in Figure 4.5 is assumed to be similar to the mean residence time, 20.78 minutes, presented in Table 3.4.

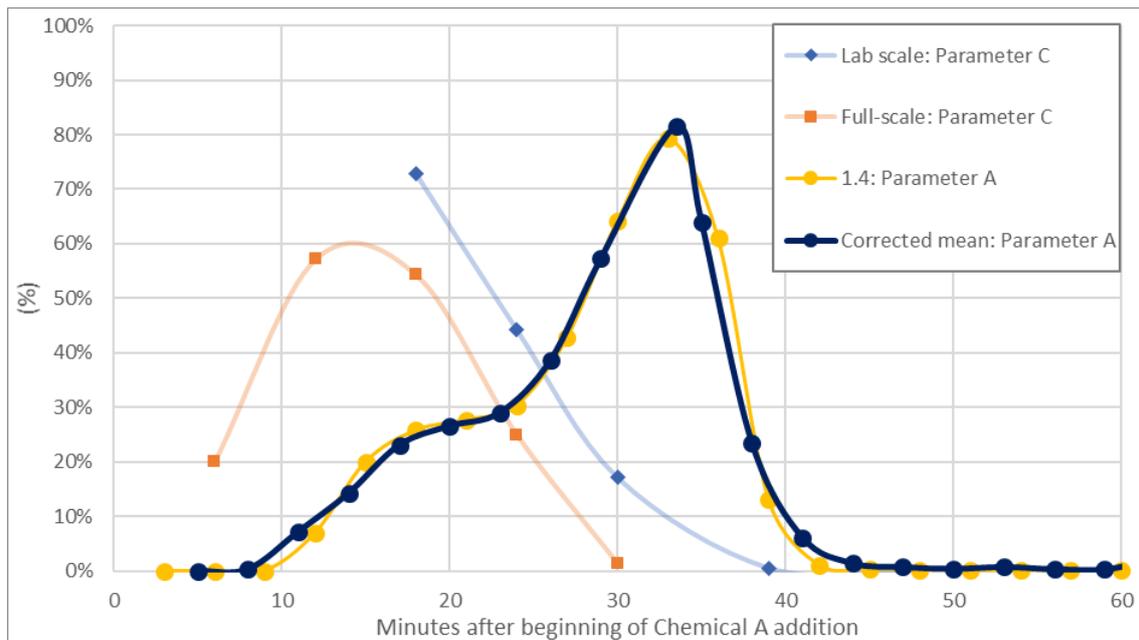


Figure 4.5. Levels of Parameter C in the effluent from a unit on lab scale and one from full-scale compared to two baselines of Parameter A. Parameter C values are from two separate reports.

The levels of Parameter C appear quite similar between the two unit scales. So does the decrease in values, that can be seen for both unit scales. For the full-scale unit, more measurement points are taken in the beginning, showing an increase and therefore a peak of Parameter C. Since the lab-scale unit lacks measurement points in the beginning after the addition of Chemical A, the behaviour of the full-scale curve cannot be corroborated. It is assumed, however, that the lab-scale values of Parameter C follow a similar trend as the full-scale process.

The peak in Parameter C occurs around the time that the addition of Chemical A is stopped in the inflow. However, since the residence time means the effect that the inflow has on the outflow is shifted over time, the mentioned connection would appear to be coincident. A more interesting connection, however, is that the difference in residence time between the two units is the same as the lag time between the declines of Parameter C for the two scales. The lag for the decline is approximately four minutes. It was determined by calculating and comparing the approximate slopes of the decline of Parameter C of the two units.

When looking at the lab scale behaviours of Parameter A compared to Parameter C, in Figure 4.5, it is apparent that the flattened-out part of the Parameter A curve (corresponding to point c. in Figure 4.4) occurs at the same time as the highest values of Parameter C. It is not possible to say if the behaviours are linked or not. The behaviours could either be reactions to the same thing, or Parameter A is affecting Parameter C or Parameter C is affecting the Parameter A curve.

4.1.4 Altering concentration

When comparing experiment repeats with different feed concentrations, i.e. Experiments 1.1 to 1.6 with Experiment 1.7, the difference in the total amount of liquid means the experiment work was done within widely different time frames. This can be observed in Table 4.1 as well as in Figures 4.6 to 4.8.

In Figure 4.6, the values of Parameter B for Experiment 1.7 are compared to Experiment 1.4. In Experiment 1.7, Chemical A took 14.2 times longer to deplete than in Experiment 1.4, and 14.22 times longer compared to the mean depletion time seen in Table 4.1. As the concentration was 14 times lower for Experiment 1.7 compared to the other experiments, the curve in Figure 4.6 was adjusted by this factor on the time-axis. The new curve for the adjustment with factor 14 did not, however, align well with Experiment 1.4 when comparing the rapid decreases (corresponding to point d. in Figure 4.2). The adjustment that fitted best with Experiment 1.4, for this type of alignment of Parameter B, was a reduced time of factor nine. The number was determined by trying different factors and had no known connection to any other factors in the experiment.

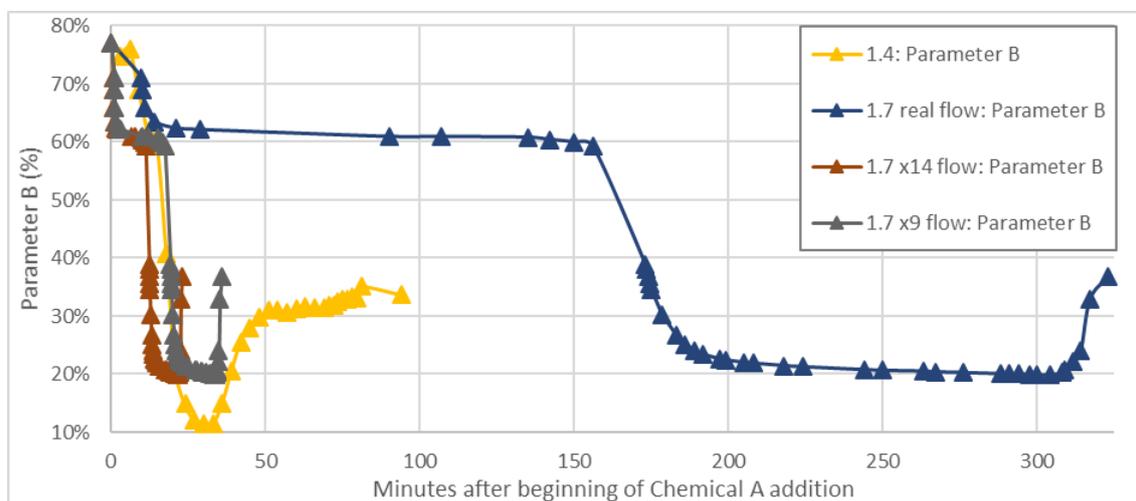


Figure 4.6. Parameter B measurements of Experiment 1.7, using the relative concentration 1 of Chemical A, compared to Experiment 1.4, using the relative concentration 14 of Chemical A. Additionally, the curve of Experiment 1.7 is adjusted by dividing the time with two different factors, 14 times and 9 times, to simulate a higher concentration and less total volume or a higher flow rate.

In Figure 4.7, Parameter A is compared between the three curves of Experiment 1.7 of different adjustments and Experiment 1.4. Since the time difference between de-

pletion of Chemical A and when Parameter A reaches maximum value is almost independent of how long the addition of Chemical A takes, as seen in Table 4.1, the abrupt decrease seen for the curves of Experiment 1.7 in Figure 4.7 could be expected. Within 8 minutes of depletion of Chemical A (or 12 minutes as is the mean-time for Experiment 1), the curve would reach maximum and after the maximum is reached, the decrease has been rapid for each previous repeat of Experiment 1.

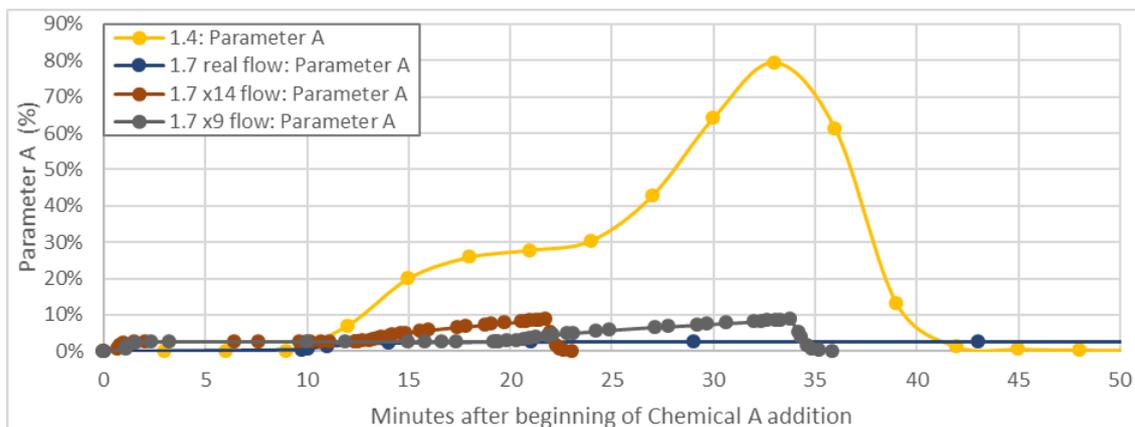


Figure 4.7. Parameter A measurements of Experiment 1.4, using relative concentration 12 of Chemical A, compared to three curves of Experiment 1.7, using relative concentration 1 of Chemical A. One of the curves of Experiment 1.7 is of the real flow, while two are compressed on the time-axis by division with two different factors, 14 and 9.

The adjusted curve that fits best with Experiment 1.4 for Parameter A is the one adjusted with factor 14. Since this differs from the curve best aligned when studying Parameter B, it is not obvious how to best fit the curves of Experiment 1.7 to other experiments.

By once again studying Parameter B and comparing with more experiments, as seen in Figure 4.8, only the curve adjusted by factor 9 align with the rapid drop (point d. in Figure 4.2). The only curve, however that show similar behaviour in the initial drop (point b.) and the flattening of the curve (point c.) is Experiment 1.7 with the real flow. This indicates that point a., b. and c. could be independent of the concentration difference.

4. Results

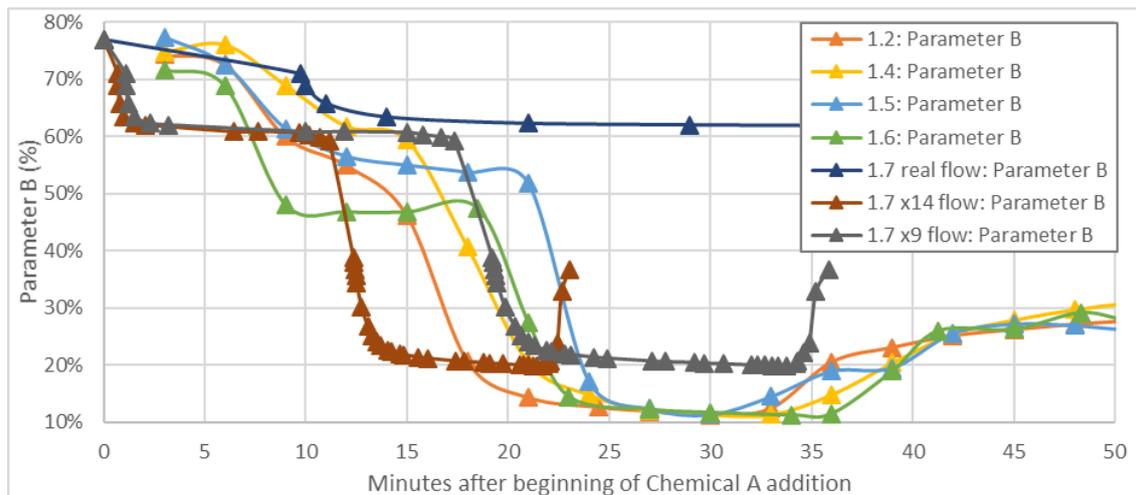


Figure 4.8. Parameter B measurements of Experiment 1.2, 1.4, 1.5 and 1.6, all using the relative concentration 14 of Chemical A, compared to Experiment 1.7, using the relative concentration 1 of Chemical A. Besides the curve of Experiment 1.7 with the real flow, two adjusted curves are shown, where the original curve has been compressed on the time-axis to simulate a higher concentration and lower total amount of Chemical A, or a higher flow rate.

4.1.5 Subset selection

As the subsets were chosen based on Parameter B, these values were measured for each sample bottle. The values are seen in Figure 4.4. Two different approaches for what selection of Chemical A to reuse were developed. Either, the goal was to collect as much as would reasonably be possible, and therefore include samples in the subset that were of lower quality. Or, the focus would be on only choosing high-quality samples in a narrow subset interval. Which level of Parameter B that would be considered high or low, was based on the level in pure Chemical A. The cut-off level decided for the first approach was between 30 or 40%, and the level for the second approach was set to 19%. The levels were called the cut-off levels and can be seen in Table 4.3 for each sample subset.

Table 4.3 shows in which experiment the chemical was collected for each reused Chemical A mixture. It shows the magnitude of each reused Chemical A mixture by how many sample bottles that fit into the interval below the cut-off level of Parameter B, together with the total amount of Chemical A in the mixture. Levels of Parameter A and B in the reused Chemical A mixtures are also shown. Further, the experiment in which the reused Chemical A mixture was reused is presented, along with information about residence time and the relative flow rate of the experiment. The table includes the subsets collected from Experiment 4.1, that is the experiment done on pilot-scale.

Table 4.3. Cut-off levels and information about the sample subsets, i.e. reused Chemical A mixtures, used in Experiments 2 and 3.

Experiment, used in	2.1	2.2	3.1	2.3	3.2	2.4	3.3
Experiment, collected during	1.4	1.5	1.6	1.1 mixed with 1.2		4.1	
Cut-off level of Parameter B	33%	34%	30%	32% [a] and 31% [b]		19%	
Number of sample bottles in subset	24	23	15	15 [a] and 19 [b]		3 [c]	
Total amount of liquid in subset [d] (g)	3772	3330	1881	2172 [a] and 2553 [b]		795	795
Parameter A in subset	11%	13%	22%	19%		52%	
Parameter B in subset	18%	18%	16%	17%		13%	
Contact time (min)	79.08	69.83	- [e]	51.25	48.83	16.22	20.47
Flow rate	1	1	1	1	1	1	1.56

[a] Properties of the reused Chemical A mixture from Experiment 1.1.

[b] Properties of the reused Chemical A mixture from Experiment 1.2.

[c] Large sample bottles used.

[d] The amount corresponds to the reused Chemical A mixture and does not include the amount of fresh Chemical A added in Experiment 3.

[e] The fresh and reused Chemical A mixtures were mixed together before addition (Method A), resulting in a combined time of 55.83 minutes.

As can be seen, the reused Chemical A mixtures varied in size and therefore residence time. The residence time for Experiment 3.3 was adjusted to be similar to the average residence time in Experiment 1, seen in Table 4.1, by increasing the relative flow to 1.56. Notice how Parameters A and B varied in the reused Chemical A mixtures for the different cut-off levels of Parameter B used. Large reused Chemical A mixtures meant lower Parameter A and higher Parameter B values.

4.1.6 Distribution of reused Chemical A mixtures

The distribution of chemical collected during Experiments 1 and 4 to different experiments for reuse, was based on the results from Experiments 1 and 4. A flowchart over the distribution is shown in Figure 4.9.

Based on a combination of looking at Parameters A, B and D, the reused Chemical A mixtures were rated how good they were thought to be for reuse. Experiment 1.3 was excluded due to too little liquid being collected. Mixtures 1.4 to 1.6 were rated as good and mixtures 1.1 and 1.2 were rated as OK. The collected chemical from

Experiment 4 was also studied and rated as good. Considering all five reused Chemical A mixtures mentioned from Experiment 1 had similar curves of Parameter A, seen in Figure 4.4, none of the five repeats were rated as bad. Parameter D was a determining factor in deciding Experiment 1.1, with low value, and Experiment 1.2, with no value calculated, were just rated as OK. Experiment 1.1 also displayed strange behaviour during the measuring of Parameter B.

Due to the collected liquids from Experiment 1.1 and 1.2 being considered less good, they were mixed and separated into two identical solutions. The same technique was used for two batches of chemical from Experiment 4, that were mixed and divided. One solution from each pair was used in Experiment 2 and the others in Experiment 3, as can be seen in Figure 4.9.

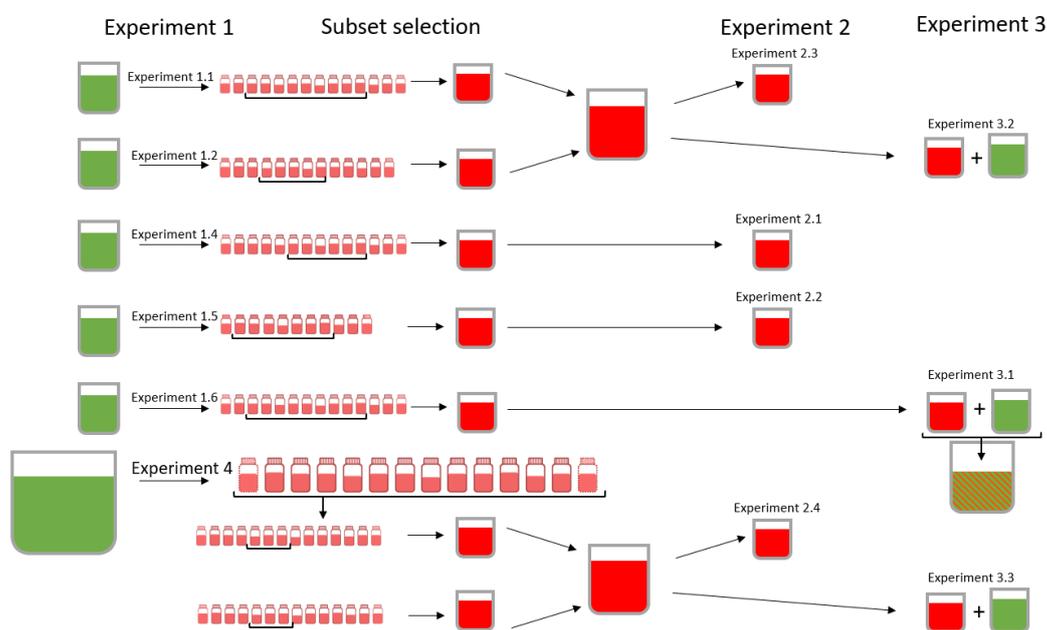


Figure 4.9. A schematic image of how sample bottles of old Chemical A from Experiments 1 and 4 were selected for subsets called reused Chemical A mixtures. These were, in turn, distributed between repeats of Experiments 2 and 3. Red indicates old Chemical A and green indicates fresh Chemical A.

4.2 Experiment 2. Using only reused Chemical A

In this section, the results from the process unit run with only reused Chemical A are presented. In Figure 4.10, the Parameter B values are presented for Experiment 2 compared to some baselines from Experiment 1. The points a. to f., originally seen in Figure 4.2 are marked out for the mean curve to indicate the different stages of the Parameter B curves. The figure shows that the initial values (a.) are the same for Experiments 1 and 2, and that the timing of the initial decrease (b.) is similar. The curves also flatten out around the same level (c.). The flat part continues much longer, however, for the experiments using old Chemical A. Also, when those curves reach minima (e.) it is not the same low values as the experiments using

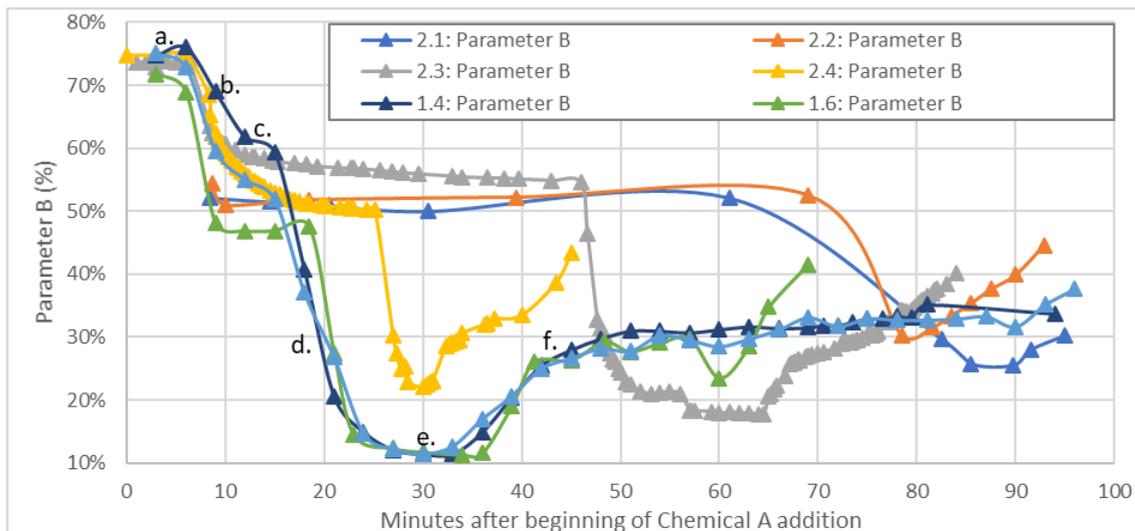


Figure 4.10. Comparison of Parameter B curves between Experiment 2 and the baselines from Experiment 1. The points a. to f., originally seen in Figure 4.2, are marked out for the mean curve of Experiment 1, indicating the different stages for all the curves. .

fresh Chemical A. The old Chemical A curves also rise much quicker (f.) after the minima, and end on much higher values at the end of the experiment.

Another thing that differed between the experiments using old and fresh Chemical A, was that the fast decrease (point d.) happened at different times. This decrease is probably connected to a combination of total liquid amount and quality. It is reasonable to assume that the concentration is lower for the reused Chemical A mixtures than for fresh Chemical A, and as seen in Figure 4.10, so was the Parameter A level. That, together with the higher level of Parameter B, confirmed that the reused Chemical A mixtures were of lower quality than fresh Chemical A solutions used in Experiment 1. This information indicates a quality order between the reused Chemical A mixtures, where the quality was highest for mixture 2.4, followed by 2.3, then 2.2 and lastly 2.1.

This was not, however, reflected in the levels of Parameter D, seen in Table 4.4. The Parameter D value is highest for mixture 2.1, and mixture 2.2 has a higher level than 2.3, all indicating that something else affects the results of Parameter D. The differences might have to do with measuring techniques, and the results are after all similar if the error of margin is taken into account. But the large differences in quality trends when looking at Parameter D versus Parameters A and B is still of interest to look further into.

When looking at the results from Experiment 1.7, using much lower concentration than normal fresh Chemical A, and during a longer time, the answer might be made clear. The concentration in Experiment 1.7 was tailored to be similar to the concentration in reused Chemical A mixtures 2.1 and 2.2. While the low concentration used did not have a negative effect on Parameter D, the long residence time instead had a positive effect. The longer residence time, as seen in Table 4.3, might explain why Experiment 2.1 has the best Parameter D level but lowest quality when looking

4. Results

at Parameter A and B in Table 4.4. The long residence times make up for the low qualities of the reused Chemical A mixtures of Experiment 2.1 and 2.2.

Table 4.4. Parameters A and B in reused Chemical A mixtures and the subsequent Parameter D values.

	2.1	2.2	2.3	2.4
Parameter A	11%	13%	19%	52%
Parameter B	18%	18%	17%	13%
Parameter D	24.4%	21.5%	18.7%	23.3%

As with Experiment 1, the values of Parameter A increase as Parameter B decreases. This is seen in Figure 4.11.

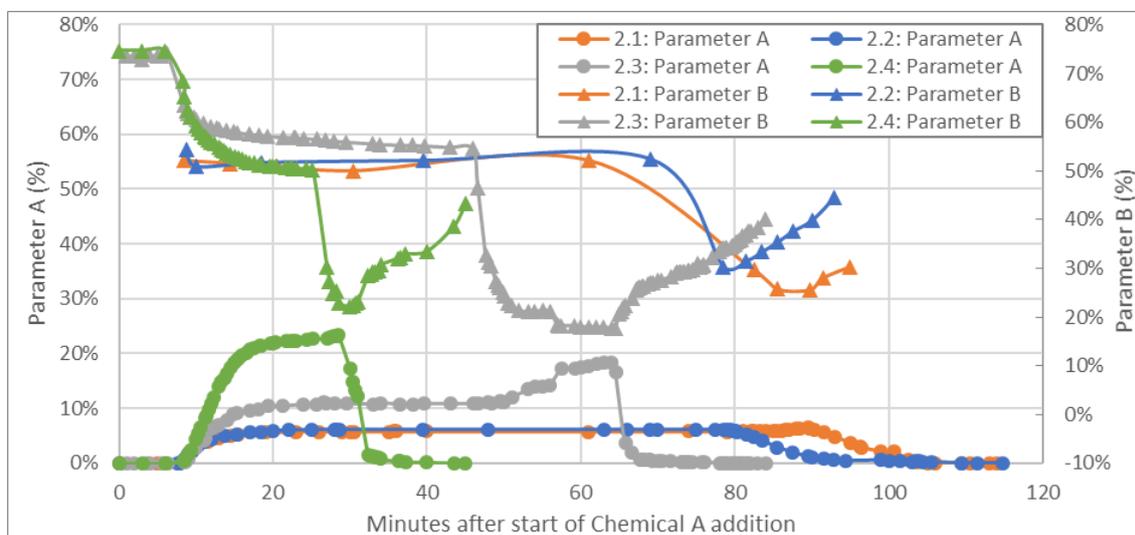


Figure 4.11. Parameter A and B for all repeats of Experiment 2. The connection between Parameter A and B for each experiment is visible.

4.3 Experiment 3. Using a combination of reused and fresh Chemical A

Parameters A and C

In Figure 4.12, the Parameter A values for the three repeats of Experiment 3 are shown. For Experiment 3.3, three different curves, representing the real flow and two adjusted flows are seen. The points a. to g., originally seen in Figure 4.4, are marked out on the curve of Experiment 3.3 with the real flow. The points, though placed on this one curve, are meant to indicate the different stages of all the curves seen in the figure.

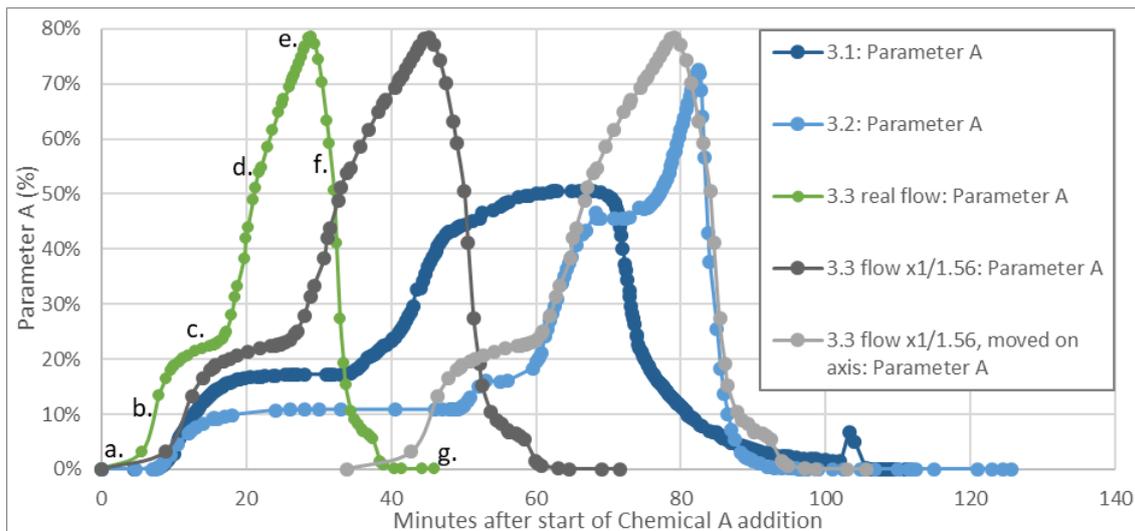


Figure 4.12. Parameter A curves for the repeats of Experiment 3. For Experiment 3.3, three different curves made by different adjustments along the x-axis are shown.

When looking at the curves in Figure 4.12, the three different methods of Chemical A addition described in Section 3.3.3.2, can be compared. Method A, i.e. Experiment 3.1 where the old and fresh Chemical A were mixed, has the lowest levels of Parameter A. Method A also has a very low Parameter D value compared to the other methods, seen in Table 4.5.

Table 4.5. Parameter D level for the three methods used in each respective repeat of Experiment 3.

Experiment	3.1	3.2	3.3
Method	A	B	C
Parameter D level	52.9%	76.6%	77.1%

When comparing Methods B and C, i.e. Experiment 3.2 and 3.3, they have very similar Parameter D values. The methods also have similar Parameter A curves, seen in Figure 4.12. This is not apparent at first but becomes clearer when making adjustments to the Experiment 3.3 curve with the real flow. Since the experiment had a relative flow rate of 1.56, the curve was adjusted on the x-axis by dividing with this factor. This made the curve equally wide as Experiment 3.2 when comparing the increase (point d.) before the maximum to the decrease thereafter (point f.). If the Experiment 3.3 curve was further adjusted by moving it along the x-axis by 34 minutes, the similarities in the curves became extra apparent. 34 minutes corresponds to the time difference that the reused Chemical A mixture for Experiment 3.2 took to deplete compared to the flow-adjusted Experiment 3.3, i.e. the time difference between when the fresh Chemical A addition was started for the experiments.

4. Results

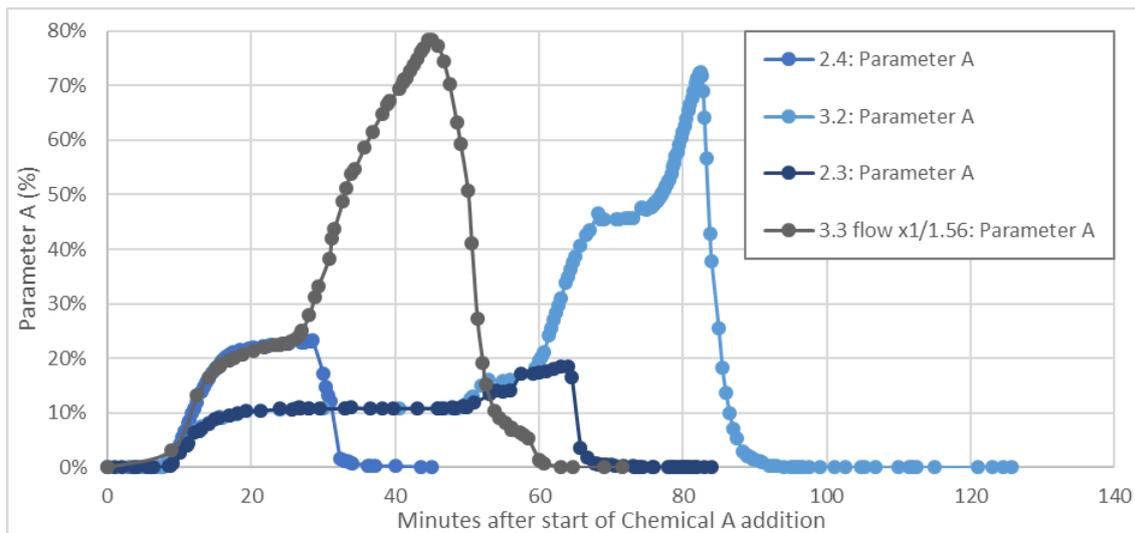


Figure 4.13. Comparison of Parameter A curves between experiments with identical reused Chemical A mixtures, i.e. between Experiment 2.3 and 3.2 as well as between Experiment 2.4 and the flow-adjusted curve of Experiment 3.3.

The flow-adjusted curve of Experiment 3.3 (before the move by 34 minutes), can be compared to the curve of Experiment 2.4, seen in Figure 4.13. These two experiments had identical reused Chemical A mixtures. The apparent overlap between the two curves is an indication that the flow-adjustment of the Experiment 3.3 curve by factor 1.56 was correct.

In Figure 4.13, the same overlap between curves from Experiment 2 and 3 can be observed for Experiment 2.3 and 3.2. These experiments also had identical reused Chemical A mixtures. The mimicking of the Experiment 2 curves in the initial phase of Experiment 3, when using identical batches of old Chemical A, should be expected.

This mimicking also helps explain the time difference between the main peak of Experiment 3.2 compared to 3.3. The reused Chemical A mixture in Experiment 3.2 was much larger than in Experiment 3.3. That made the addition of fresh Chemical A happen about 34 minutes later for Experiment 3.2, thus pushing the main peak by approximately this time. This was the reason why the flow-adjusted Experiment 3.3 curve was moved by 34 minutes in Figure 4.12. After the move along the x-axis, the main peaks of the curves of Experiment 3.3 and 3.2 aligned very well.

Parameter B

The striking similarity between Experiment 2 and 3 when using identical reused Chemical A mixtures, that was observed for Parameter A, is also visible when comparing the Parameter B curves in Figure 4.14. The curves of Experiment 2.3 and 3.2 (both grey) are very similar. For Experiment 2.4 and the flow-adjusted 3.3 (both green), the curves flatten out (point c.) on different values, but the drop (point d.) is similar for the two curves.

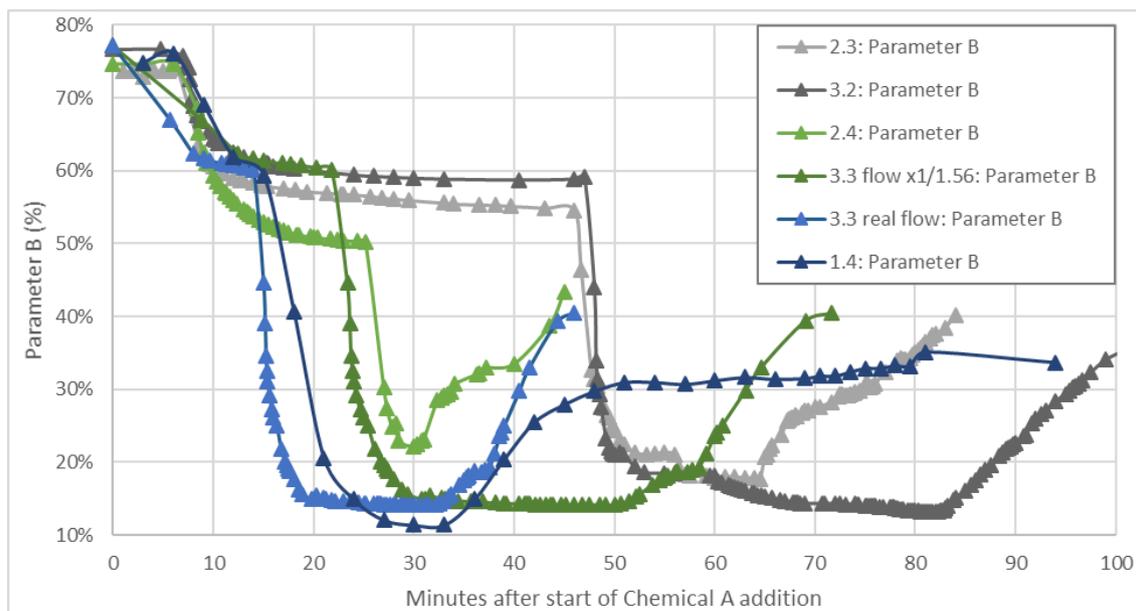


Figure 4.14. Parameter B curves for the repeats of Experiments 2 and 3 that uses identical reused Chemical A mixtures, i.e. between Experiment 2.3 and 3.2 as well as between Experiment 2.4 and the flow-adjusted curve of Experiment 3.3. The curves of Experiment 3 are compared with the baseline from Experiment 1.4.

When comparing Experiments 3.2 and 3.3 for Parameter B, the flow-adjusted curve of Experiment 3.3 can be used. When comparing the curves, the time difference is once again apparent. Though the minima occur at different times, the curves reach the same low values. These values almost correspond to the levels seen for the baseline from Experiment 1. This indicates that the method of using a combination of old and fresh Chemical A works. It also shows that it is unnecessary to, as is the case in Experiment 3.2, use a reused Chemical A mixture of such large quantity. Instead, the reused Chemical A mixture amount in Experiment 3.3 should be used. The curve for Experiment 3.3 without any adjustments, representing the used flow of 1.56, overlaps well time-wise with the baseline curve from Experiment 1.4.

Since the Parameter B values of Experiments 3.2 and 3.3 are comparable to the values in Experiment 1, it means that Chemical A collection for reuse should be possible in the effluent of Experiment 3 as well. This would open up the possibility to use reused Chemical A in every run of the process unit and to collect the effluent of each run for use in the next.

The comparisons between Experiment 3.2 and 3.3 show that the increased flow in Experiment 3.3 did not have a negative effect on the Parameters A and B, or for Parameter D. Therefore, adjusting the flow to achieve the same residence time as in Experiment 1, is a good way of combating the otherwise increased process time associated with using both old and fresh Chemical A.

In Table 4.6, the levels of Parameter D reached in Experiment 2 are compared to the levels reached in Experiment 3, when using the identical reused Chemical A mixtures as in Experiment 2, along with fresh Chemical A.

Table 4.6. The Parameter D levels reached when using the reused Chemical A mixtures alone in Experiment 2 and in combination in Experiment 3.

Experiment 2	2.3	2.4
Experiment 3	3.2	3.3
Parameter D:		
In Experiment 2 (x%)	18.7%	23.3%
Difference to target level (z%)	61.3%	56.7%
Combined level (%)	76.6%	77.1%

The difference to the target level, $z\%$, is the difference between the level of Parameter D in Experiment 2 and the target Parameter D level, and it was calculated according to Equation 3.1. Equation 3.2 was used to correlate the difference, $z\%$, to the actual amount of fresh Chemical A needed in order for the combined level of Parameter D to reach the target level. The amount was calculated for Experiment 3.3 to 795 g. The amount of reused Chemical A mixture used in Experiment 3.3, as seen in Table 4.3, was also 795 g.

Table 4.6 shows the combined level of Parameter D reached for Experiment 3.2 and 3.3. This level can be compared to the theoretical target level. None of the experiments reached the target level but was considered close enough as they were almost within the margin of error. They were, more importantly, on a similar level to the level of Parameter D reached in Experiment 1 (excluding 1.7). This level can be considered the actual target level of the process on lab-scale.

The method of tailoring the amount of fresh Chemical A to be used on top of the reused Chemical A mixture has been proven to work by the results of Experiments 3.2 and 3.3.

4.4 Experiment 4. Pilot-scale

In this section, the results from the pilot-scale experiment are presented. The levels of Parameter A and B were measured in the effluent at two different points and the curves are presented in Figure 4.15. Meter 1 for Parameter A had such low detection limit, below 0.02% as seen in Table 3.3, that the results are excluded from Figure 4.15.

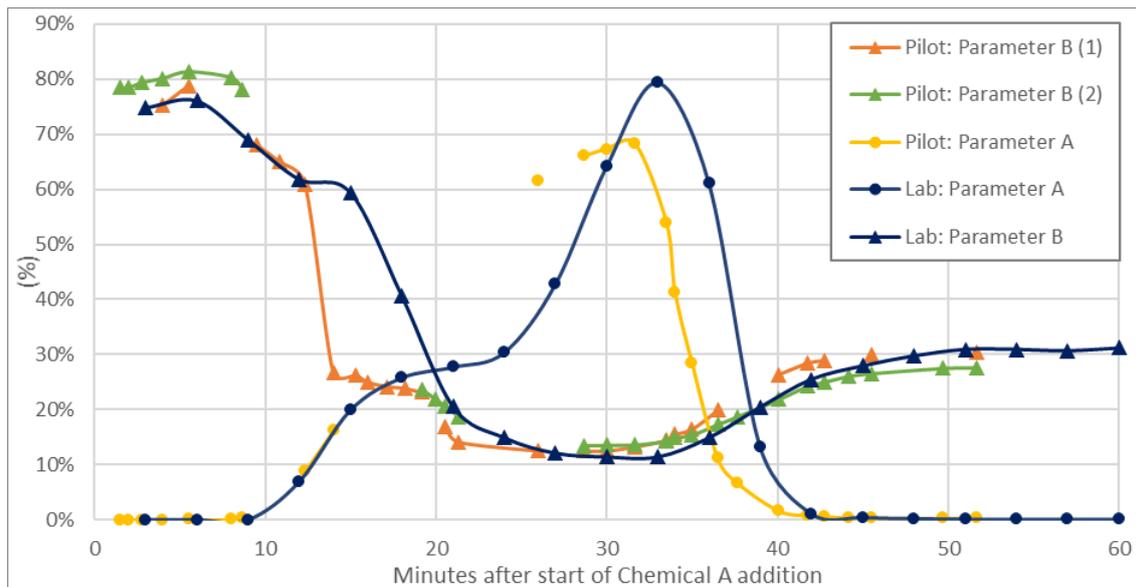


Figure 4.15. Parameters A and B compared between the unit on lab scale and pilot scale, when only using fresh Chemical A. Both units are downscaled versions of the full-scale unit. The lab scale curves are from Experiment 1.4.

The curves in Figure 4.15 are the results from Experiment 4 compared to curves from Experiment 1.4. As can be seen, the curves of the different scales are similar, both for Parameter A and B. The height difference between the Parameter A curves can be due to measurement techniques, as has been the case in several experiments. The difference in the location on the x-axis of the Parameter A maxima can be due to the difference in residence time for the two experiments as seen in Table 3.4. The residence time for the pilot-scale unit was approximately 4 minutes shorter than the mean residence time in Experiment 1. This corresponds to the time difference between the Parameter A curves both at and after the maxima.

The reused Chemical A mixtures generated from Experiment 4.1 were selected by using a cut-off level of Parameter B of 19% as seen in Table 4.3. As the curves of Experiment 4 overlapped so well with the curves of Experiment 1.4, the reused Chemical A mixtures were considered to be of high quality. The two reused Chemical A mixtures from Experiment 4 were prepared in the same batch, as seen in Figure 4.9 and were therefore considered identical.

4.5 Economics

Savings

The reduction of fresh Chemical A used in Experiment 3.3 compared to the original case was approximately 20%. This level was assumed to be similar on full-scale and the amount of saved Chemical A in a full-scale unit run was calculated.

$$20\% \cdot m(A, normal) = m(A, saved) \quad (4.1)$$

The cost saving was calculated by using the cost of Chemical A.

$$m(A, \textit{saved}) \cdot C(A, \textit{kg}) = C(A, \textit{saved}) \quad (4.2)$$

The reduction in the wastewater treatment step after one unit run was calculated by comparing the normal case to the case for Experiment 3.3. The reduction in wastewater treatment was assumed to be 80%. The level was assumed to be similar to the full-scale unit and the total cost saving was calculated for one unit run.

$$80\% \cdot C(WWT, \textit{total}) = C(WWT, \textit{saved}) \quad (4.3)$$

The total cost saving for one year was calculated by using the approximate number of times the unit was used per year.

$$\frac{t(\textit{operation})}{\textit{year}} \cdot \sum C(A, \textit{saved}) + C(WWT, \textit{saved}) = \frac{C(\textit{total, saved})}{\textit{year}} \quad (4.4)$$

Costs

The lower limit of the fixed capital cost was calculated by a combination of Equations 2.6 and 2.7, and the addition of contingency of 15%.

$$C(\textit{fixed capital, low}) = 115\% \cdot \sum_i C_{e,i} \cdot F_i \quad (4.5)$$

The upper limit of the fixed capital cost was calculated by Equations 2.9 and 2.10. A comparison between the high and low fixed capital costs is seen below.

$$C(\textit{fixed capital, high}) = 2.8 \cdot C(\textit{fixed capital, low}) \quad (4.6)$$

Payback period

The simple payback period was calculated for the two fixed capital costs. They were decided to be 0.4 and 1 year, respectively.

5

Discussion

In this chapter, the results in the previous chapter are discussed further.

5.1 Parameter behaviours

The Parameter A and B curves showed distinct behaviours in the effluent of both the lab and pilot-scale and these parameters will be key for knowing what parts of the effluent to collect. When comparing Parameters A and B, the measurements for Parameter B seemed much more reliable, however. It is important to be able to trust the real-time measurements and not have to do analysis on samples while running a process and time is a factor. Parameter B was therefore seen as a good parameter to use for the cut-off, both on lab and pilot scale, and later when continuing to full-scale. The levels of Parameter C should be studied further. This would help determine the parameter behaviour in the effluent, so that the level can be minimised in the collected effluent.

5.1.1 General behaviours of the curves

The different stages of the Parameter A and B curves would be interesting to study, as this will provide a guide both for explaining of strange behaviours, as well as predicting behaviours by knowing a few details about the Chemical A mixture that will be added.

By studying the effects of lower concentration in combination with higher volume, without changing the flow rate, the parameter behaviours could be investigated. As mentioned in Section 4.1.3, the timing of points a. b. and c. seem to be independent of concentration. No connections between which Parameter B level the curves flatten out on in point c. was found, however, as this value differed a lot between repeats.

Since the changes in parameter levels sometimes happen very fast and the sharp changes even out, it is possible that the differences in how point b. transitions to point c. for Parameter B, is more or less similar between experiments. As it is now, however, the transition seems to happen at different rates, i.e., slopes of the curve. But no connection between rate and type of experiment or concentration level has been found. It would appear that the end stages of the Parameter A and B curves don't differ much between experiments. The timing is usually similar, making it probable that the end stage is not dependant on concentration or quality.

5.1.2 Effect of concentration

When studying Parameters A and B in Experiment 1.7 with low concentration, a few effects were visible compared to experiments with high concentration. Parameter A didn't reach a fraction of the height exhibited in the other repeats of Experiment 1, showing a clear negative effect of the low concentration. This low level of Parameter A would mean that any reused Chemical A mixtures collected in the effluent would be of low quality.

When looking at Parameter B, the level was higher than for experiments using higher inlet concentration, but the difference wasn't as big as for Parameter A. Considering, however, that the collection would have to be done for 14 times longer time, the Chemical A concentration would probably be low, and the collected solution would, therefore, be of poor quality.

The low concentration used in the experiment doesn't seem to have a negative effect on Parameter D. Since the concentration was so low, the total amount of liquid was large and the time that the chemical spent in the unit was much longer than normal. This was probably the reason why Parameter D was higher for the experiment with low concentration. For future tests of concentration, the flow rate should be adjusted so that the residence time would be equal for all experiments. However, the concentration can be said to have no apparent negative effect on Parameter D within this concentration level as long as the total number of moles is the same. Longer residence time can be said to have a positive effect on Parameter D. This would explain the apparent high quality of the reused Chemical A mixture used in Experiment 2.1 when looking at Parameter D, while Parameters A and B indicated lower quality.

The concentration tested in Experiment 1.7, i.e. the relative concentration 1, was the same as was calculated to be a reasonable concentration in some of the repeats in Experiments 2 and 3. The test was done in order to be able to exclude low concentration as a factor negatively affecting Parameter D, which was done. The low concentration does, however, negatively affect other parameters, as discussed above.

5.1.3 Measurement techniques

As levels close to 100% for Parameter A were observed only when measuring more frequently than every three minutes, the measurements should always increase in frequency when key points of the process step are reached, such as around the maximum. The changes in Parameter A and B are sometimes very rapid, and the testing was continuously adapted to better capture a good representation of the behaviours and levels.

The use of different measuring techniques strongly affected the appearance of the Parameter A curves. The measuring of individual sample bottles, although giving a possible delay on the x-axis among other drawbacks, is to be preferred during the studying of Parameter A and B curves due to the possibility of otherwise missing the overall behaviours. A combination of sample bottle measurements and real-time

ones is always preferable, however, especially around maxima and minima where changes occur fast. The sample bottles are a mixture over three minutes of collecting and are therefore not representative of any specific minute. They should instead be seen as mean values over the sample time interval and notice should be taken when comparing results between different measuring techniques. In the full-scale unit, real-time measurements must be used as they indicate important changes as they occur.

5.1.4 Deviating values

The first experiment conducted in the lab unit had an uncharacteristically low Parameter D value as well as initially strange curves of both Parameter A and B. The strange results probably had something to do with it being the first experiment, and that the unit had not been properly prepared at that stage. The strange values of Parameter A and B in real-time were corroborated by the sample bottle measurements, and these were tested several times, with similar results. This means the measurements captured a strange behaviour, rather than that the measuring techniques were wrong.

In Experiment 1.2, the values of Parameter A stayed constant after flattening out (corresponding to point b. in Figure 4.4) after the initial increase (point c.). These values were not accredited to problems in the unit, despite the problems during the previously conducted Experiment 1.1. This was decided since the appearance of the Parameter A curve measured in real-time was not corroborated by the measurements taken from the sample bottles. Meaning that it most likely was due to measuring technique errors.

The Parameter A curves in Experiments 1.5 and 1.6 show similar behaviours of never reaching the high maxima as in Experiment 1.1 and 1.4. As with Experiment 1.2, however, the behaviours were not apparent when looking at the sample measurements, meaning the difference probably was due to faulting measuring technique.

5.2 Collection of reused Chemical A mixture

When considering an optimisation based on collection of chemical, the parameter profiles connected to the concentration of the chemical should first be studied. Figure 4.1 clearly shows the presence of unused Chemical A in the outflow of the process unit on lab-scale. Figure 4.15 shows the same for the process unit on pilot-scale. Parameter A values close to 100% were observed in the effluent from the lab-scale, and Parameter B levels close to 10% were noted. This is promising for the possibility of reusing Chemical A after one unit.

5.2.1 Interval

The method of first studying the reused Chemical A mixtures on their own in the unit turned out to be a good approach. The results of reused Chemical A mixtures

collected below different levels of Parameter B were compared, and a few different connections became apparent.

The more effluent that was collected for the subset, the higher amount of liquid was in the reused Chemical A mixture, as can be seen in Table 4.3. Since reused Chemical A mixtures of large size were showing signs of low quality, the assumption that the mixtures were of low concentration was made. This would indicate that the subset selections done with wide cut-off interval, capture more Chemical A but at the expense of a higher dilution. Low concentration is unwanted, as previously discussed in the experiment testing the effects of concentration. A low concentration in combination with the high total amount takes too long and results in poor levels of Parameter A and B, that ensure that the effluent cannot be collected again. The high levels of Parameter D are probably just an effect of the high residence time and not an indication of high-quality mixtures.

Comparing reused Chemical A mixtures collected below different values of Parameter B, resulted in approximately the same levels of Parameter D. This is important as it would allow for a more narrow collection interval while maintaining productivity. Reused Chemical A mixtures collected within more narrow intervals had better, i.e. lower, amounts of liquid and resulted in better levels of Parameter A and B. Therefore, the amounts used in Experiment 3.3 were used as the guide for how the collection should be done. In this interval, the levels of Parameter C appear to be below maximum levels but are still possibly high. This is solely based on the levels of Parameter A in the interval, and the connection seen between these two parameters. Measurements need to be taken of the effluent of an experiment similar to 3.3 to find out the exact levels.

The results in Experiment 3.3 weren't repeated as it was considered that the multiple tests done both in Experiments 2 and 3 were enough to determine a good enough cut-off interval. The interval should, however, be optimised further, both in regard to Chemical A concentration, Parameter C levels and total amount of liquid.

5.3 Reuse of Chemical A mixture

The comparisons between Experiments 3.2 and 3.3 show that Method B and C give the same results. This is especially striking when looking at Parameter D, where the levels are the same. This indicates two things. First, the collection of old Chemical A should be reduced to low amounts of high-quality chemical. The lack of difference between the Parameter D values for the mentioned experiments along with the increased Parameter D values when collecting less effluent (as seen in Experiment 2.4 compared to Experiment 2.3 in Table 4.6), indicates that the smaller collection was better than the larger collection. Secondly, the results show that an increase in flow rate by a factor of 1.56, did not have a negative effect on Parameter A, B or D. As using reused Chemical A in combination with fresh chemical increases the total amount of liquid, it is an important finding that the prolonged process time can be combated by increased flow rate on lab-scale.

The results only show, however, that old Chemical A can be reused from one unit.

Not that the reuse can be done after every unit, in a row. The good levels of Parameter A and B in the effluent after one reuse, is promising though. This was the basis for the assumption that the reuse and collection of Chemical A can be done in every unit run.

5.4 Comparing units on different scales

The target level of Parameter D was not reached when simulating the full-scale process on lab-scale. The values reached were close to 80%, however, and were therefore deemed good experiments. The similarities in Parameter D level between scales is one indication that results are comparable and therefore translatable between scales.

The mean level of Parameter D reached in Experiment 1 can be seen as a sort of new target level, as it shows the actually possible target values for this setup. In future studies, it would be interesting to study if the target level of Parameter D could be reached on pilot-scale.

The results from Experiment 4 show that the pilot-scale curves of Parameter A and B are very similar to the lab-scale curves. As the pilot-scale unit is closer to the full-scale unit in proportions, this means that the results from the lab and pilot-scale units are probably comparable to the full-scale unit.

5.5 Economics

Since the results of Parameter A and B are comparable between different scales, the assumption that the economics can be compared between scales is deemed valid. This means that the amount of Chemical A saved when reusing chemical in Experiment 3 can be directly extrapolated to the equivalent amount this would mean for the full-scale unit. This amount is the basis of the savings calculations in the economics evaluation. For further work on the optimisation project, this assumption must be tested, first by doing Experiment 3.3 on pilot-scale, and then possibly on full-scale.

Another basis of the economic evaluation is that the reuse of Chemical A will be possible to do in cascade in an indefinite number of units. This assumption too must be validated by experiments on lab-scale, and later pilot-scale. If the assumption was to be incorrect and for example, the reuse of chemical can only be done between three units in a row before the quality becomes too low, the case would have to be studied additionally in order to find optimum parameter values, collection intervals and number of reuses in a row.

5.6 Future work

Beyond finding optimal settings for the reuse by further experiments, the use of modelling and simulation tools such as Aspen HYSYS could be of great assistance.

Such a simulation could also be useful for determining how the unit behaviour on different scales vary.

More tests of the values of Parameter C in the effluent have to be done. The mutual effect of Parameter C on the other parameters, and thereby the quality of the reused Chemical A mixtures, have to be studied.

The economics report would benefit from an expansion that included different scenarios in raw material prices and the costs of implementing the optimisation on different sites. Depending on regional raw material prices, the investigated optimisation step could be even more promising.

Since the payback period was determined to be quite short, no consideration has been given to the effects of interest rates or index changes over the years. Further economic studies will have to include such factors.

Beyond the mentioned possible work that can be done, the techniques used in this project could also be developed. One such example is during the testing of concentration effects. In order for the residence time not to interfere with the test, the flow rate should be increased with the same factor as Chemical A is diluted in the inlet.

6

Conclusion

The concentration of Chemical A in the inlet does not have a negative effect on Parameter D, within the concentration span tested. Low concentration does, however, affect Parameters A and B negatively. Parameter D increases with increasing residence time, but as time is a factor in the process, the residence time must be limited for productivity reasons.

Collecting Chemical A in the effluent interval that yields high concentration ensures good parameter values for A and B. The level of Parameter C is assumed to be rather high, however, and has to be investigated further. The collection interval should be decided by Parameter B. Narrowing the collection interval ensures a high concentration of Chemical A. It also reduces the total liquid amount without affecting productivity due to the higher quality of the collected solution.

Concluded is that low volume, high-quality Chemical A solutions are preferred. The overall residence time was possible to decrease to fit within the current time frame without affecting Parameter D.

It should be possible to collect Chemical A in the effluent after Experiment 3, and reuse this a second time, and so on. The cascade reuse of Chemical A would ensure maximum profitability. However, more studies on the exact properties of the effluent depending on what quality of Chemical A is added to the inflow, with respect to Parameters A, B, C and D, should be done. Deeper knowledge about how and why the parameter curves vary should be strived for to aid in these studies.

The striking similarities in parameter values between the units of different scales were the basis for assuming that Chemical A savings on lab-scale are comparable to the savings on full-scale.

The saved cost of the optimisation studied, compared to the total investment cost, results in a payback period of between 0.4 and 1 year. That indicates that the optimisation of the process step is profitable.

Acknowledgements

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All joking aside, the warm atmosphere and basic nature of your welcome have made me grow. Like a silica particle.

Maria Livrell Klingberg, Gothenburg, June 2020

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A

Appendix A

As can be seen in Figure 4.1, the measurements from Experiment 1.4 and the mean curves overlap. This was achieved by a combination of excluding outliers as well as pushing the mean curve of Parameter A by two minutes. The peak of the same curve was also adjusted in order to get a more representative height.

Moving of peak

This was done since the curves of the repeats, seen in Figure 4.4, reach their maxima at two different time points, making the real mean maximum only 74% at 32 minutes. The mean value was instead calculated between the two highest values, in Experiment 1.5 and 1.6, and placed between minute 32 and 35.

If instead the mean was to be calculated of all experiment maxima, it would be 78%, instead of 82% (the current value). Since a maximum value of close to 100% had been measured (Experiment 1.4, all values, seen in Figure 4.1), it was decided that 82% would make a more accurate representation of the results, although it is not a proper value mean.

The mean curve after only removing outliers is shown in Figure A.1.

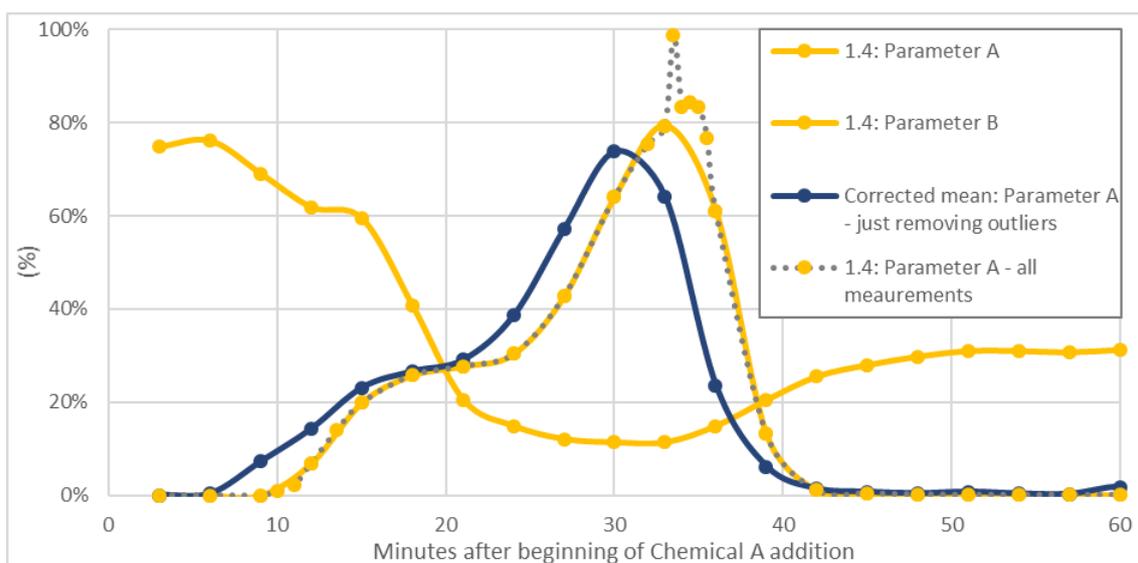


Figure A.1. The Parameter A mean curve after only removing outliers is shown in blue.