CHALMERS
UNIVERSITY OF TECHNOLOGY

Assessment of enhanced carbon dioxide absorption in water

The impact of carbonic anhydrase and pH regulation

Master's thesis in Sustainable Energy Systems

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Department of Energy and Environment
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Cover: A coral reef surrounded by marine life.
Image credit Brian Zgliczynski.

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Preface

The road towards a civil engineering degree stretches over five long years of learning and has now come to a close with this thesis. The project has been an excellent opportunity to summarize the education; knowledge and skills acquired in several, if not all, of the topics I have studied throughout the years, have come in handy and been a vital part of the completion of the thesis. Carrying out the work has been a great learning in itself too, I have gained a deeper understanding of engineering as a craft, and the immense challenge that is posed by climate change mitigation.

Although I stand as the sole author of this report, there are others who have helped me on the way and deserve a word of acknowledgement. First of all, I want to thank my supervisor Fredrik Normann for taking me on with short notice, giving positive and encouraging feedback and letting me work in my own bubble. Your solution oriented mindset has been an asset when facing problems, and appreciation for word play never hurts!

Furthermore, my examiner Filip Johnsson along with visionaries and project starters Lars Strömberg and Lars Kristoferson, have contributed with valuable input, enthusiasm and inspiration that helped propel the project forward. Listening to your discussions around the dinner table has been an interesting and entertaining learning experience in itself!

In retrospect, I send my respect and warmest wishes to my high school English teacher Marianne Borsch Reniers, who taught me the art of writing and structuring a text, and to learn for life. Last, but definitely not least, my final words of gratitude are for Stefania Òsk Gardarsdòttir and Max Biermann who always kept their doors open and offered to help whether obliged to or not. Your assistance with simulations, input in discussions and evaluation of my thoughts and ideas have been invaluable! Þakka þer fyrir! Vielen Dank!

Johanna Beiron, Göteborg, May 2017

Abstract

The world is faced with an enormous challenge in the form of climate change. As a part of mitigation strategies, the industrial scale feasibility of a carbon capture process is determined, where CO_2 is absorbed in water and reacted to ${HCO_3}^-$ that could possibly be stored in oceans or in solid form. The focus is on the absorption and reaction stages, and the effects on capture rate of the enzyme catalyst carbonic anhydrase, and addition of base for pH regulation are evaluated.

The main methodology consists of simulations performed with the software Aspen Plus. Sensitivity analyses and case studies on plants where the process could be implemented are carried out. Material and energy balances are given attention, as well as operating conditions. Three possible reaction paths are compared based on required liquid phase residence time and column height to reach equilibrium. Two process alternatives are considered with differing strategies for pH control.

The results indicate that the carbon capture process is technically feasible to use, with regard to residence time and equipment size. However, pH regulation is critical for adequate performance, and the material flows required, especially the large quantities of base, are limiting due to high production costs. Moreover, the storage of ${HCO_3}^-$ needs further research before a suitable option can be decided on; the impact on marine life of oceanic storage is unknown, and the energy consumption of salt precipitation is grand. The use of carbonic anhydrase is not a necessity although it can reduce equipment size; a base with OH^- anions will yield fast enough reaction rates for realistic column heights without a catalyst.

Keywords: carbon dioxide, bicarbonate ion, absorption, water, pH, carbonic anhydrase, CCS

Contents

Abbreviations and symbols

Abbreviations

BECCS	Bio Energy Carbon Capture and Storage
CA	Carbonic Anhydrase
CCS	Carbon Capture and Storage
CHP	Combined Heat and Power
DIC	Dissolved Inorganic Carbon
DH	District Heating
MEA	Monoethanolamine
NJV	Nordjyllandsværket
PCCC	Post Combustion Carbon Capture

Chemical compounds

Ca^{2+}	Calcium ion
$CaCO_3$	Calcium carbonate or limestone
$Ca(HCO_3)_2$	Calcium bicarbonate
CH_4	Methane
Cl^-	Chloride ion
CO_2	Carbon dioxide
${CO_3}^{2-}$	Carbonate ion
H_2	Hydrogen
H^+	Hydrogen ion
H_2O	Water
H_2S	Hydrogen Sulfide
${HCO_3}^-$	Bicarbonate ion
$KHCO_3$	Potassium bicarbonate
N_2	Nitrogen
Na^+	Sodium ion
$NaCl$	Sodium chloride
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
$NaOH$	Sodium hydroxide
O_2	Oxygen
OH^-	Hydroxide ion
${Zn_2}^+$	Zinc ion

Latin letters

A	Pre-exponential factor
c	Concentration of a species
E_a	Activation energy
k	Rate constant
K_H	Henry's law constant
P	Pressure
P_{CO_2}	Partial pressure of CO_2
R	Ideal gas constant
r	Reaction rate
T	Temperature
y_{CO_2}	Mole fraction of CO_2 in a gas

State symbols

aq	aqueous
g	gaseous
l	liquid
s	solid

1 Introduction

In the light of global warming, efforts to limit the CO_2 concentration in the atmosphere by reduced emissions of CO_2 must urgently be employed in order to minimize irreversible impacts for people and ecosystems [1]. There are two distinct ways to achieve this: decreasing the use of fossil fuels that form CO_2 when burned, or capture and storage of these CO_2 emissions before they reach the atmosphere. Although investments in renewable and carbon neutral technologies are made, this development is slow and there is a reluctance towards phasing out fossil fuels, especially from countries that are heavily dependent on domestic resources of coal, oil and gas for energy supply. Carbon capture and storage (CCS) is therefore likely to play a vital role in accomplishing the necessary reduction of CO_2 emissions [1].

CO_2 capture can be carried out in several ways, and depending on the context different solutions may be appropriate. Presently, the most discussed option for CO_2 storage is to inject the gas into deep lying geological formations, for example aquifers. However, to utilize this storage method a large infrastructure network for gas transport must be constructed, and there has also been some issues with public acceptance of the concept. Together with the fact that current capture processes are presently not cost-competitive given the low price of CO_2 emissions, other CCS options should be considered to initiate widespread application.

An alternative storage suggestion is to absorb CO_2 in water and let it react to the bicarbonate ion, ${HCO_3}^-$, followed by injection into seawater. ${HCO_3}^-$ is a stable ion at pH around 8 and is naturally present in large quantities in the ocean. There is also a chance that ocean injection of additional ${HCO_3}^-$ could help counteract ocean acidification [2], which has become a widespread problem. In addition, by absorbing CO_2 in water the use of environmentally harmful amine based solutions, commonly present in other absorption processes, can be avoided. The only chemical that is needed other than water and CO_2 is a base that can neutralize the H^+ ions resulting from the ${HCO_3}^-$ producing reaction:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons {HCO_3}^-\,(aq) + H^+\,(aq) \tag{1}$$

For instance, the common mineral $CaCO_3$, limestone, could be used:

$$CaCO_3\,(s) + CO_2\,(aq) + H_2O\,(l) \rightleftharpoons Ca^{2+}\,(aq) + 2\ {HCO_3}^-\,(aq) \tag{2}$$

To make these reactions industrially feasible the reaction rates can be increased by the use of carbonic anhydrase, an enzyme that catalyses the CO_2 hydration (Reaction 1). Several studies have confirmed the catalytic effects of the enzyme [3, 4].

This CCS method has been discussed in theory, and some lab scale experiments has verified the chemistry [2, 5]. However, thermodynamic consideration of the process is lacking. Without an estimation of the mass and energy flows that would potentially be required in such a process, progress towards industrialization is hindered. Of course, not all point emitters of CO_2 are located in coastal proximity so other storage options than ocean injection can also be of interest, for instance precipitation of solid material. Hence, examination of balances and flows, and an investigation of possible forms of permanent storage of the carbonate are needed.

1.1 Aim

The purpose of this thesis is to determine the feasibility of carbon capture and storage by absorption of CO_2 in water, followed by conversion to ${HCO_3}^-$ for storage in oceans or as solid material. To fulfill the aim, heat and material balances are made with a simulation software for integration of the capture technology with five industrial cases. The possibility to incorporate use of the biocatalyst carbonic anhydrase will also be evaluated, as well as the importance of pH control for process performance. Furthermore, the relevant literature is consulted to provide theoretical background and evaluate the process potential and suitability. A discussion of the overall process is held, from capture of CO_2 to final storage.

This thesis consists of three main parts. First, the theory and chemistry of the suggested CCS method is reviewed. Secondly, kinetics, sensitivity analyses and flowsheets of potential process configurations are developed and simulated with software to estimate material and energy flows. In relation to potential cases of application, the industrial feasibility of the process is considered. Lastly, long-term storage options are discussed, focusing on ocean injection and conversion to solids.

2 Background

To gain an overall understanding of the concept of CO_2 capture in water and storage as HCO_3^-, many factors must be considered and several topics studied. First of all in the CCS process, absorption of CO_2 is carried out. As the CO_2 dissolves in water, the relevant chemical reactions must be included and used to produce the desired HCO_3^- product. Furthermore, the consequences of oceanic storage should be given some attention, with regard to environmental impact of large scale HCO_3^- ocean injection. As an option, final storage in solid form is evaluated. The more conventional option gaseous storage could of course also be considered, but is merely briefly discussed in this work. This section will give some background information on CCS, CO_2 absorption in water, the chemistry of CO_2 dissolved in water, and precipitation reactions.

2.1 Carbon capture and storage

Carbon capture and storage (CCS) is a technique that can be used to reduce emissions of CO_2 from power plants and industry that burn carbon-containing fuels. The concept entails separation of carbon from fuel or flue gases, followed by transportation to a long-term storage site. The most considered storage option presently is underground aquifers and depleted oil/gas reserves, on- or offshore, but utilizing these sites requires a substantial infrastructure network for transportation of CO_2 from source to storage site.

There are three types of carbon separation processes: pre-combustion, post-combustion and oxyfuel combustion. Pre-combustion means that CO_2 is separated from the combustible fuel before it is burned. This is achieved by gasification processes. Post-combustion is separation of CO_2 from flue gases after combustion. In the oxyfuel case, the fuel is combusted in a mixture of pure oxygen and recycled flue gases without nitrogen. In this way, only carbon dioxide and water are present in the flue gases, where the water can easily be condensed, leaving a stream of pure CO_2.

Post combustion carbon capture (PCCC) is the method considered in this thesis. It is a suitable option for large point emitting sources, for instance stacks that emit several hundred thousand or million tons of CO_2 per year. It can be retrofitted to existing plants by placing the separation equipment last in the flue gas cleaning process.

The IPCC enhance that CCS technologies are likely to be a key part of climate change mitigating strategies, and that mitigation costs are estimated to be 1.5-4 times greater if CCS is not employed [6]. CCS furthermore allows negative emissions of CO_2 if applied to biomass combustion, so called (BECCS)[1], that may be required to limit temperature

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[1] BECCS stands for bio energy carbon capture and storage and refers to capture of CO_2 from combustion of biomass. Since growing plants consume CO_2 the net CO_2 emissions from combustion of biomass is zero, but if the emissions are captured and stored net negative emissions are possible.

increase. The importance of developing and utilizing CCS methods is thus paramount.

If CCS is not used the only option to reduce CO_2 emissions is to stop using fossil fuels and leave them in the ground. Many countries are likely to protest against this option, as their development, economy and energy production are dependent on fossil fuels. CCS will allow countries with vast fossil fuel reserves to take part in climate change mitigation while still using their resources. Otherwise developing economies are likely to oppose raised carbon taxes and other strategies to replace coal, gas and oil by renewable alternatives, as this will require significant investments. Having the ability to utilize domestic fuel resources enhances security of supply [7].

Even for countries that are not dependent on fossil fuels for energy supply, CCS will still be an important part of strategies to reduce CO_2 emissions. For instance, Sweden has set a goal to be carbon-neutral by 2050 (zero net emissions of CO_2). The electricity production in Sweden is 97% CO_2 free, leaving little room for emissions reductions in this sector. However, the industrial sector emits CO_2 (about 23% of national CO_2 emissions), that is difficult to reduce without employment of CCS [8].

2.2 Separation of CO_2 by absorption in water

Absorption of CO_2 from flue gases or process streams in water is categorized as a Post combustion carbon capture technology (PCCC), which means that the capture process is part of the flue gas cleaning, located after the combustion process. The basic design of an absorption column is that flue gases containing CO_2 are introduced at the bottom of the column and an absorber liquid, in this case water, is added at the top of the absorber in a counter-current fashion. In the absorber, the CO_2 is absorbed in the water stream, so that treated flue gas containing little CO_2 leaves the column at the top, and a water stream rich in CO_2 leaves the column from the bottom.

Conventionally, a stripper column is also used in PCCC to regenerate the absorber liquid and extract the captured, gaseous, CO_2 for permanent storage in underground aquifers. Since the idea with water absorption is to keep the CO_2 in the liquid stream the stripper section will not be necessary in this case. This could potentially reduce operational costs of capture a great deal, as the heat required in the stripper for absorber regeneration is the largest operating cost by far, about 80% [9]. This is part of the reason why CCS is not cost-competitive at present. Common absorber liquids, for instance MEA (monoethanolamine), also bring other problems. MEA is highly corrosive which causes damage to equipment, it emits environmentally harmful volatile organic compounds, and requires frequent replenishment due to high volatility [9]. Water is an environmentally benign substitute to such solvents.

However, there are challenges associated with using water instead of MEA. Water does not absorb CO_2 as well as MEA, so the amounts of water required for adequate separation can become large. The amount of gaseous CO_2 that can be absorbed in water is given by Henry's law (Equation 3), which states that the concentration of a gas dissolved in a liquid is proportional to the partial pressure of the gas in contact with the liquid. The constant of proportionality, K_H, is called Henry's constant and its value depends on the gas, solvent and temperature [10].

$$c_{CO_2} = K_H * P_{CO_2} \tag{3}$$

For CO_2 the solubility increases with decreasing water temperature. Based on this and Henry's law, high pressure and low temperature will increase the amount of CO_2 absorbed by water. However, if the absorbed CO_2 is reacted to aqueous ${HCO_3}^-$, see Equation 4, the problem with low solubility can be largely eliminated or decreased. Water can hold much larger amounts of ${HCO_3}^-$ than CO_2, so for every mole of dissolved CO_2 converted to ${HCO_3}^-$, another mole of CO_2 can be absorbed. More information about this conversion reaction is given in Section 2.3.

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons {HCO_3}^-\,(aq) + H^+\,(aq)} \tag{4}$$

The absorption rate of Reaction 4 can be sped up with the addition of the enzyme carbonic anhydrase, that catalyses the reaction. A catalyst is a substance that provides an alternative reaction path with lower activation energy, without being consumed in the reaction. A lower activation energy means that the likelihood of a reaction happening is increased, so the higher reaction frequency enables equilibrium to be reached in shorter time. For industrial purposes, the reaction time is an important parameter to consider when dimensioning reactors, and faster reactions can allow for smaller equipment sizes, and reduced costs.

2.2.1 Carbonic anhydrase as an industrial catalyst

Carbonic anhydrase (CA) is an enzyme present in living organisms, ranging from humans and plants to microorganisms. In human bodies, CA helps with transport of CO_2 from muscles to the lungs. CA catalyses the CO_2 uptake in the blood in the muscles by hydrating CO_2 to HCO_3^- in water. HCO_3^- is then transported by the blood to the lungs, where CO_2 is reformed, again with the actions of CA. In plants CA is used in the photosynthesis, also involving CO_2 related chemistry.

CA exists in five classes (α, β, γ, δ and ζ), where the exact configuration depends on the type of organism it operates in. The catalytic function of CA comes from a metal ion in its molecular structure, located in the active site. In most cases this metal ion is Zn^{2+}. The CA hydration mechanism of interest is shown in Equations 5 and 6. First, the zinc ion reacts with water and forms a complex binding a hydroxide ion ($Zn^{2+} - OH^-$) and one hydrogen ion (H^+). Secondly, the zinc-hydroxide complex reacts with carbon dioxide (CO_2) and returns the zinc ion and a hydrogen carbonate ion (${HCO_3}^-$).

$$Zn^{2+} + H_2O \rightleftharpoons H^+ + Zn^{2+} - OH^- \tag{5}$$

$$Zn^{2+} - OH^- + CO_2 \rightleftharpoons Zn^{2+} + HCO_3{}^- \tag{6}$$

Given the natural functions of CA with mechanisms involving CO_2 hydration, research has been carried out on whether CA could be used for industrial purposes in CCS processes, with promising results. Russo et. al. [3, 11, 12] have conducted several studies on amine-based CCS with CA. The chemistry of the absorption itself has been confirmed in lab scale experiments in many studies, for instance Gundersen et. al. [4], and Kunze et. al. [13] got promising results at pilot scale, but further development is needed before industrial application is possible. Especially the process configuration must be given attention: how to place or use CA for the best performance, and what other process requirements and operating conditions are the most suitable. Identification of CA forms that can be used, and manufactured at industrial scale at affordable price is also important.

In order to be a competitive option, the CA enzyme must be able to maintain a high catalytic activity for long periods of time, since it is not economically favorable to replace or replenish too often, which also may require production stops. Exposing CA to high temperatures will cause denaturing, loss of structure and activity. However, progress is made with research on thermostable forms of CA, for example [14].

To increase the lifespan of CA, the enzyme can be immobilized in the reactive zone. Immobilization entails fixation of CA on some type of structure in the column, it could be packing material, nanostructures or other. Migliardini et. al. [15] performed experiments with immobilized CA and their results showed that the activity of immobilized CA remained at the same level after one month, compared to "free" CA that lost some of its activity. The problem with immobilizing CA is that CO_2 must be transported in the liquid phase to the place where CA is fixed in order to benefit from the catalytic effect. This mass transport rate tends to be rather slow, so it will be important to place the immobilized CA in the gas-liquid interface for this technique to be successful.

2.3 The chemistry of CO_2 dissolved in water

Absorption, or dissolution, of CO_2 in water occurs spontaneously in nature. CO_2 is present in the atmosphere and exerts a partial pressure above the sea. Given Henry's law (Equation 3), this implies that some of the atmospherical CO_2 is absorbed by the ocean. As the concentration of CO_2 in the atmosphere is increased, due to anthropogenic emissions, more CO_2 is absorbed by the ocean, which has started to cause problems with ocean acidification. CO_2 is a sour gas that causes a lowering of pH when dissolved in water.

As mentioned in Section 2.2, aqueous CO_2 can react to ionic ${HCO_3}^-$ according to Equation 4, but ${HCO_3}^-$ can react further to ${CO_3}^{2-}$:

$$ {HCO_3}^- \,(aq) \rightleftharpoons {CO_3}^{2-}\,(aq) + H^+\,(aq) \tag{7}$$

Both Reactions 4 and 7 are equilibrium reactions that can go both forward and backwards. The equilibrium, and the distribution of CO_2, ${HCO_3}^-$ and ${CO_3}^{2-}$, is largely dependent on pH. Figure 1 illustrates how the pH value affects the distribution of the dissolved inorganic carbon (DIC).

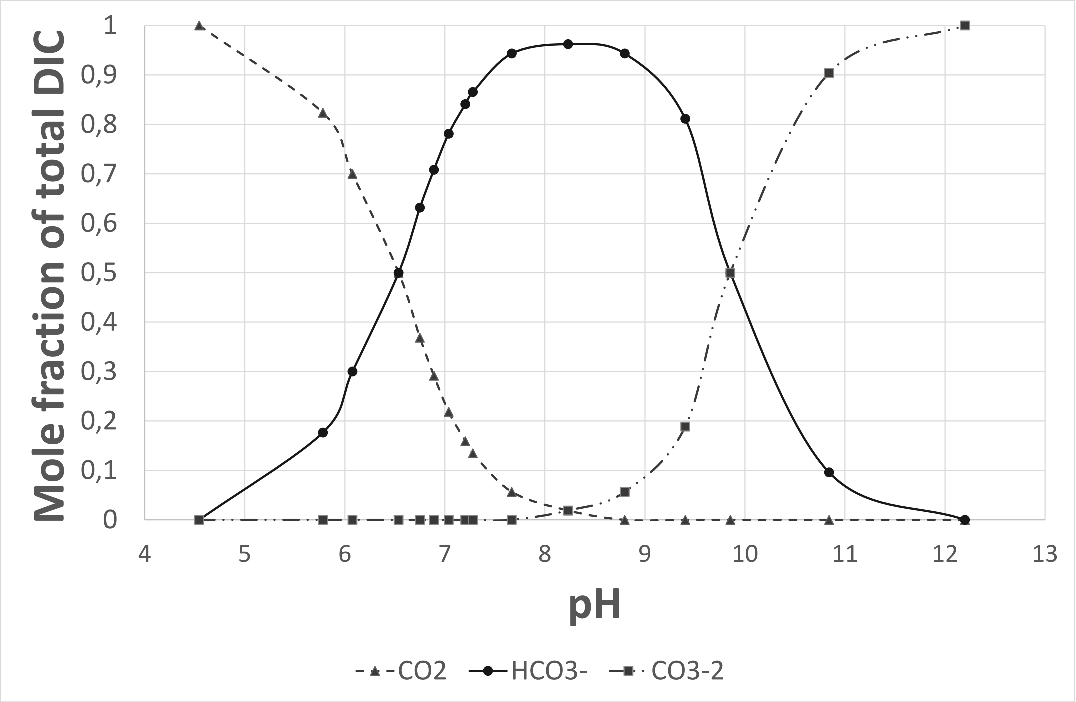

Figure 1: The composition of DIC - dissolved inorganic carbon (CO_2, ${HCO_3}^-$ and ${CO_3}^{2-}$) at different pH levels in water. Based on simulations in Aspen Plus.

Since acidic hydrogen ions are produced when ${HCO_3}^-$ and ${CO_3}^{2-}$ are formed, pH is lowered. In water that has a low pH value (i.e. a large concentration of H^+), it will not be favourable to produce more H^+, therefore the most abundant species will be CO_2. On the other hand, in very basic conditions, hydroxide ions (OH^-) are available to neutralize any H^+ generated, so now the least protonated form ${CO_3}^{2-}$ will be in majority.

Ocean pH is slightly above 8, and at this mid-range pH HCO_3^- is in abundance.

Reaction 4 is not the only route from CO_2 to HCO_3^- though. In basic solution, with high availability of OH^-, Reaction 8 is faster than Reaction 4.

$$CO_2\,(aq) + OH^-\,(aq) \rightleftharpoons HCO_3^-\,(aq) \tag{8}$$

On the other hand, in acidic solution Reaction 4 is faster than Reaction 8, due to lower OH^- concentration. It is Reaction 4 that may be catalyzed by the enzyme carbonic anhydrase to increase the reaction rate, as mentioned in Section 2.2. For equilibrium composition and yield considerations, it is not important which of Reactions 4, 8 or catalyzed that is used. On the other hand, for dimensioning equipment the different reaction rates should be considered.

As stated above, controlling the pH, in this case to around 8, is crucial for keeping the CO_2 in the stable HCO_3^- form. Literature suggests addition of the mineral $CaCO_3$ for pH adjustment [2, 16], but other basic substances are also possible, such as NaOH or Na_2CO_3. However, for ocean storage the choice of base might need more careful attention, so that natural balances are not disturbed. In seawater $CaCO_3$ is formed by shell-producing organisms:

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightleftharpoons CaCO_3\,(s) \tag{9}$$

Due to acidification of ocean waters, the calcium carbonate dissolves more readily, causing problems for coral reefs and shell formation. There is also a lack of CO_3^{2-} as the extra H^+ generated by more dissolved CO_2 are neutralized by reaction with CO_3^{2-}:

$$CO_3^{2-}\,(aq) + H^+\,(aq) \rightleftharpoons HCO_3^-\,(aq) \tag{10}$$

The oceans contain roughly 38 000 gigatons of carbon dioxide [17], of which more than 90% is in the form of HCO_3^-, and most of the remainder is CO_3^{2-}. Carbon in the hydrosphere (oceans) interact with the atmosphere and lithosphere (rocks) according to Figure 2. CCS is also included for completeness, where captured CO_2 is injected into deep lying aquifers for storage. On a large time scale, captured CO_2 reacts with minerals in the aquifer and is converted to solid material, for example $CaCO_3$.

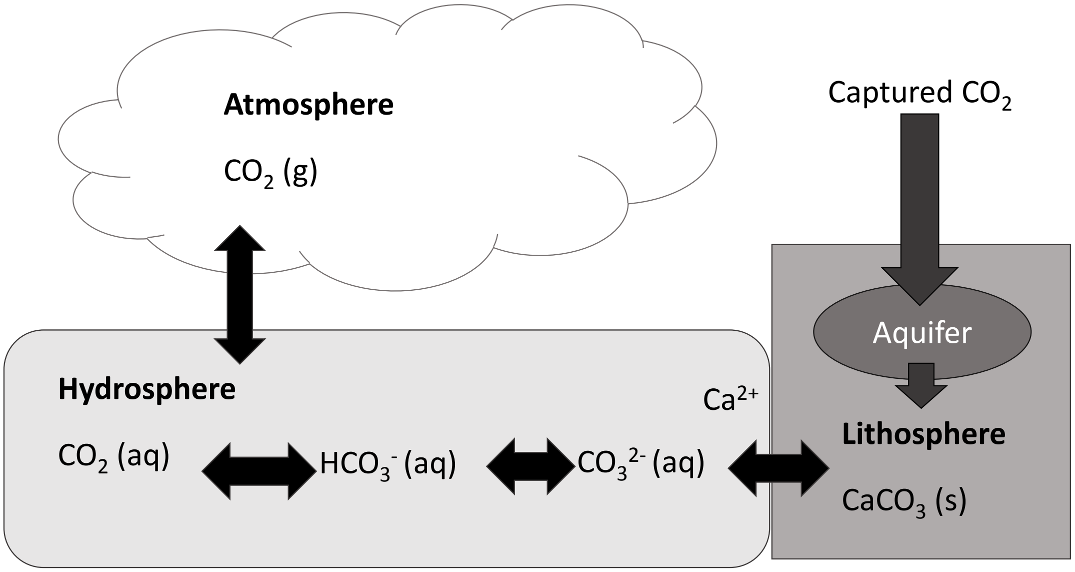

Figure 2: Figure illustrating the global carbon cycle, where carbon is interchanged between the atmosphere, hydrosphere and lithosphere; and CCS where captured CO_2 is stored in aquifers and after a long time becomes solid material.

2.4 Mass transport and kinetics

The chemical, or rather thermodynamic, equilibrium of CO_2 described in the previous sections limit the theoretical capacity to capture CO_2, but in reality the time taken to reach equilibrium will make or break a process. The amount of CO_2 absorbed and reacted depends on times associated with mass transport phenomena and chemical reaction kinetics.

The absorption of CO_2 essentially means that CO_2 molecules are transported from the gaseous bulk phase, through the gas-liquid interface consisting on two contacting gas and liquid films, and finally transfer into the liquid bulk. Figure 3 illustrates this mass transport pathway, known as the two-film theory, where the driving force for transport is a concentration gradient.

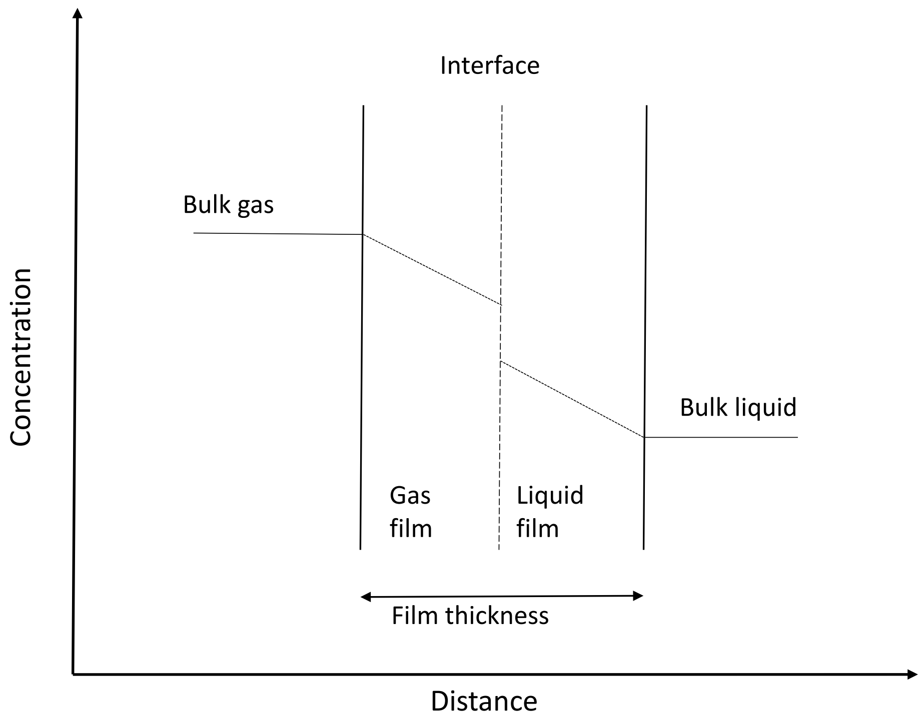

Figure 3: Illustration of the two-film theory. The horizontal lines represent the concentration profile that govern mass transport of a species.

The conversion of CO_2 to $HCO_3{}^-$ starts once the CO_2 has reached the liquid phase. The rate of conversion is given by reaction kinetics, which is described in Appendix A, but the rate is mainly affected by species concentration and temperature. The overall absorption rate is the sum of mass transfer and reaction rates. If the rates are of differing magnitudes, two extreme cases are established: if the mass transfer is significantly faster than the reaction, the reaction rate will be limiting to the absorption and the process is said to be reaction controlled; the opposite case is fast reaction and slow mass transfer which makes the absorption diffusion controlled and limited by mass transfer.

Aspen Plus, the simulation software used, has built-in methods that can be used to include mass transport and kinetics into calculations. The model can either assume that equilibrium is reached, independent of the time taken, or it can take into account rate limitations. For mass transport, or phase equilibrium, rate based calculations are provided that does not assume establishment of equilibrium. Similarly, kinetics can be specified for reactions that calculate reaction rates depending on temperature.

Thus, kinetics and mass transfer from gas to liquid phase can be calculated by Aspen.

However, for enzyme applications, there is yet another element of mass transport to consider: transfer of CO_2 through the liquid bulk and liquid film surrounding the immobilized carbonic anhydrase. Literature reports that this liquid phase mass transport resistance is the rate limiting step for the use of immobilized catalytic enzyme [9].

2.5 Salt solutions and precipitation

It is not only CO_2, ${HCO_3}^-$ and ${CO_3}^{2-}$ that are dissolved in the ocean, large amounts of salts are also present in seawater. The most abundant salt ions in seawater are Na^+ and Cl^-, with concentrations of 10.53 and 19.33 g/kg water respectively[18]. A salt is an ionic compound that consists of a cation and an anion. When in aqueous solution, all salts dissociate into their constituent ions to some extent, depending on the solubility of the salt. Solubility is a measure of how much salt that can be dissolved in the liquid until the saturation limit is reached, and is commonly given in g/kg solvent. The solubility depends on how well the ions interact with the solvent, and differs for various liquids. When the saturation limit is reached the opposite of dissociation occurs - precipitation - where the ions combine and form the salt again. Equations 11 and 12 exemplify these phenomena with Na^+ and Cl^-.

Dissociation of NaCl:

$$\mathrm{NaCl\,(s) \rightarrow Na^+\,(aq) + Cl^-\,(aq)} \tag{11}$$

Precipitation of NaCl:

$$\mathrm{Na^+\,(aq) + Cl^-\,(aq) \rightarrow NaCl\,(s)} \tag{12}$$

The solubility of salts, that is the tendency to dissociate into ionic form in water, varies to a great extent. Some salts are almost insoluble in water while others completely dissociate into their constituent ions. For example, the solubility of the salt NaOH in water is 1 110 g/l at 20°C, while for $CaCO_3$ the solubility is 0.013 g/l at 25°C. If an amount of salt, larger than the solubility limit, is added to the liquid solution the solution is said to be supersaturated and the aqueous ions will start to combine to the solid salt, a precipitate is formed.

The solubility of the salt varies with temperature, commonly the solubility increases with temperature. This implies that if the temperature of a saturated solution is lowered, a precipitate will form until the saturation point at the new temperature is reached. Temperature manipulation is not the only way to cause precipitation. Concentrating the solution, that is decreasing the water content, will also do the job. Concentration can be achieved by evaporation, filtration or other separation processes. Commonly, dilute solutions are first evaporated in one or more effects, followed by centrifugation, filtration or cooling to separate the solid from the resulting slurry [19]. However, cooling is only attractive for compounds whose solubility is strongly affected by temperature. Table 1 gives the solubility at various temperatures for sodium salts.

Table 1: Solubility in water of some sodium salts at various temperatures, given in g/100 ml [18].

Salt	0°C	20°C	40°C
$NaHCO_3$	6.48	8.73	11.13
NaCl	26.28	26.41	26.67
Na_2CO_3	6.44	17.9	32.8
NaOH	30	46	58

Since the main objective of this thesis is to form ${HCO_3}^-$, salts containing this ion is of particular interest. Several cations form salts with ${HCO_3}^-$, such as $Ca(HCO_3)_2$, $KHCO_3$ or $NaHCO_3$. However, the solubility of the various salts differ greatly, where salts including cations with valence 2+ (for example ${Ca_2}^+$) are practically only existent in aqueous form and not as a solid, while cations with valence 1+ (for instance Na^+) can be precipitated:

$$Na^+\,(aq) + {HCO_3}^-\,(aq) \;\rightarrow\; NaHCO_3\,(aq) \tag{13}$$

3 Method

The overall aim of the work is to determine the industrial scale feasibility of the CO_2 separation through absorption in water. Both literature and simulations were consulted to arrive at a suitable process design that could be applied and tested in industrial case studies. The process itself consists of three main parts: absorption, reaction and storage, that were combined in the process design. Figure 4 illustrates how these parts are related and their role in the overall project structure.

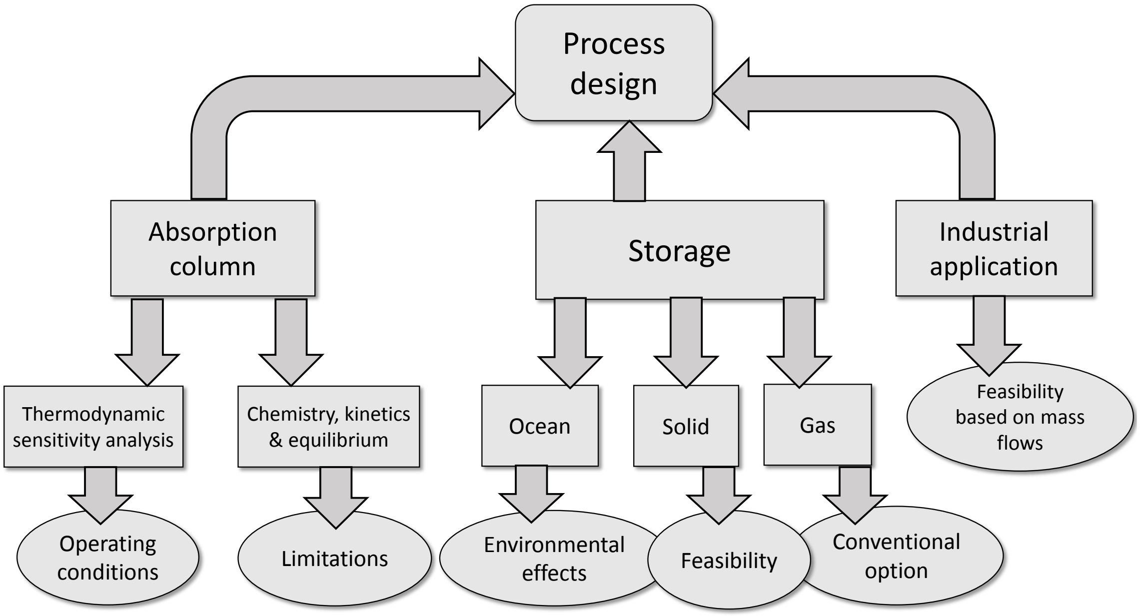

Figure 4: Illustration of the arrangement of the major parts of the methodology.

Both absorption and reaction were assumed to take place in an absorption column. Absorber operating conditions were varied in a sensitivity analysis to find suitable parameter intervals, and rates for mass transport and chemical equilibria were calculated to estimate equipment dimensions and residence times that could be limiting to the process. The next part, storage, was divided into three options: solid, gas and oceanic storage. Gas and oceanic storage was not simulated, but is discussed in Section 5.2. Simple simulations of conversion of ${HCO_3}^-$ to solid salt were carried out to determine the process potential for plants where oceanic storage is not an option. Finally, these parts were combined into an overall process design that was applied to industrial cases where the process could be of use. Based on the case studies the feasibility of the process was evaluated with regard to mass and energy flows.

3.1 Model set up in Aspen Plus

The simulation software was Aspen Plus V8.8. Aspen provides specially designed modules for unit operations commonly encountered in the chemical industry that calculates mass and energy balances based on user input. The program also includes databases to acquire default values for unit parameters and properties that are required for calculations. In the present models, the physical property parameters were estimated with the ELECNRTL method, which is suitable for electrolytes and ionic liquids, and it is used in Aspen's own CO_2 absorption models. The electrolyte wizard was used to specify electrolyte reactions for global chemistry. Standard data provided by the program were used for necessary parameter inputs, only values for equilibrium reaction and kinetic constants were specified in the reactive distillation reaction scheme.

For the absorber, the unit RadFrac was selected because it handles absorption and reaction simultaneously in one unit. RadFrac has two calculation options for phase equilibrium: equilibrium, assuming that vapor and liquid are in equilibrium with their respective segments before and after a stage; or rate based, where phases are not assumed to be in equilibrium. There are also two ways to model reactions: equilibrium, or kinetic that takes into account reaction rates according to the Arrhenius power law with temperature dependency. The calculation modes were varied depending on the aim of the specific simulation.

The RadFrac column had no reboiler or condenser, and 20 stages were used. A packed column was chosen with standard Sulzer Mellapak 250Y as packing material. Column dimensions (diameter and height) were varied and adapted to flow conditions. The pressure drop was assumed to be zero. Reactive distillation (REACT-DIST) sets of reactions were specified for use in the column, on all stages. The reaction sets are described in detail in Section 3.2.1.

A Gibbs reactor was used when two streams were mixed. The Gibbs reactor provides a simple estimation of products based on thermodynamic equilibrium. No consideration is given to reaction times or reactor volume, it merely assumes that equilibrium is reached, similarly to the equilibrium calculation options in RadFrac. No heat duty was selected, as well as no pressure drop. The vapour phase was not included in calculations, since the relevant reactions occur in the liquid phase only.

In models were heating or cooling was used, a standard heater/cooler that assumes zero pressure drop was employed. Unless otherwise specified, the gas composition used in the models was according to Table 2. This gas composition is an approximate representation of typical flue gas compositions in power plants. It is assumed that such flue gases have been cleaned of substances like nitrous oxides, sulphates and particles.

Table 2: Flue gas composition used in absorber model.

Compound	Mole%
N_2	80
CO_2	16
H_2O	2
O_2	2

3.2 Reaction and absorption modeling

The absorption consists of transfer of CO_2 from gas to liquid phase followed by reaction of aqueous CO_2 to HCO_3^-. The study of phase equilibrium, kinetics and sensitivity analyses of operating conditions are described in the next two sections.

3.2.1 Reaction kinetics and phase equilibrium in absorber

As described in Section 2.4, mass transfer and kinetics are important to consider for determination of process feasibility. A theoretical thermodynamic equilibrium might seem promising, but the time taken to reach the equilibrium could be limiting. Therefore, the time to reach chemical and phase equilibria in the absorber was simulated. The absorption chemistry was specified in sets with three reactions in liquid phase, as shown in Table 3. Reaction 2 was varied to account for all the reaction paths that produce HCO_3^- from CO_2.

Table 3: The general reaction set used in modeling of reactive distillation. The various reactions for conversion of CO_2 to HCO_3^- are shown in Table 4.

Number	Reaction formula	Type
1	$H_2O \rightleftharpoons H^+ + OH^-$	Equilibrium
2	Reaction converting CO_2 to HCO_3^-	Equilibrium or kinetic
3	$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H^+$	Equilibrium

Equilibrium constants were specified for Reactions 1 and 3, and kinetic constants were used for kinetic type Reaction 2. Reaction 3 was set to equilibrium type because it is a fast reaction compared to Reaction 2, meaning that the resulting composition will be limited by Reaction 2 rather than 3. Four variations of Reaction 2 were studied, given in Table 4.

Table 4: The four CO_2 reactions modeled.

Number	Reaction formula	Reaction type	Base anion
2a	$CO_2 + OH^- \rightleftharpoons HCO_3^-$	Equilibrium	OH^-
2b	$CO_2 + OH^- \rightleftharpoons HCO_3^-$	Kinetic, non-catalyzed	OH^-
2c	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	Kinetic, non-catalyzed	CO_3^{2-}
2d	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	Kinetic, catalyzed	CO_3^{2-}

The reactions were selected based on the background given in Section 2.3, where the three reaction paths from CO_2 to HCO_3^- are presented: with OH^-, H_2O or enzyme catalyzed. The kinetics differ between the reactions, but the equilibrium composition will not depend on which reaction path is taken, so only Reaction 2a with OH^- as reactant was used to simulate the equilibrium case. The base anion column gives an indication of when each reaction will be important, depending on the type of base added to manage pH levels. An important fact is that only the reaction with H_2O can be catalyzed by carbonic anhydrase (see Section 2.2.1).

Kinetic parameter values for reaction 2b were available in example simulations provided by Aspen and used in the model as they correlated well with literature values. However, for reactions 2c-d kinetic constants had to be estimated based on literature and correlations, mainly because the reaction kinetics were not of the form applied in Aspen. For a detailed description of the parameter estimation, see Appendix A. The final values of the kinetic parameters for forward and reverse reactions are shown in Table 5.

Table 5: Kinetic input parameters for reactions that convert CO_2 to HCO_3^-. The Arrhenius equation for the rate constant is used, $k = A * e^{(-E_a/RT)}$, where A is the pre-exponential factor and E_a is the activation energy.

Reaction	A	E_a [kJ/mol]
2b forward	$4.32*10^{13}$	55.47
2b reverse	$2.38*10^{17}$	123.3
2c forward	$2.01*10^{9}$	61.40
2c reverse	$2.65*10^{12}$	45.86
2d forward	$2.01*10^{9}$	37
2d reverse	$2.65*10^{12}$	27

As well as simulating the conversion rate from the four reactions 2a-d, the two modes of gas-liquid mass transfer calculations were also used (equilibrium or rate based), resulting in a matrix of 8 models as displayed in Table 6. Each scenario was run in Aspen with the same input data. For reactions 2b-d, in the phase equilibrium cases the residence time was varied in a sensitivity analysis, and in rate based cases the column packed height was varied (as a representation of residence time, since increased volume leads to longer time given constant volumetric flow). The goal was to determine and compare the time taken to reach chemical and phase equilibrium for the different models, and to see if the corresponding column height was realistic. Models with 2a were used as a reference for the equilibrium composition. The results are presented in section 4.1.

Table 6: 8 models for simulation of kinetics and mass transfer.

Number	Phase equilibrium	Rate based
2a		
2b		
2c		
2d		

3.2.2 Thermodynamic sensitivity analyses of absorption

A sensitivity analysis was performed. The parameters that were included are given in Table 7 along with the intervals considered. Partial pressure, temperature and pH are discussed in the background section, but salt content of the water was also included to compare use of fresh and salt water.

Table 7: Parameters varied in sensitivity analyses and their respective intervals.

Parameter	Interval
CO_2 partial pressure	0.16 - 0.80 bar
Water inlet temperature	0 - 50°C
Gas inlet temperature	50 - 100°C
Amount of NaOH added (pH value)	0 - 9.3 kg NaOH/s
Salt content of water	0 - 30 g/kg water

For the variation of CO_2 partial pressure, CO_2 concentration in the gas was kept constant and the total pressure was varied. Three pressure levels were used: 1, 2 and 5 bar total pressure, resulting in partial pressures of 0.16, 0.32 and 0.8 bar respectively, with 16 mol-% CO_2.

The simulation model used consisted of a Gibbs reactor where water and base was mixed to allow for manual pH adjustment, followed by an absorption column with equilibrium reactions and phase equilibrium assumed. The flowsheet is displayed in Figure 5. A separation rate (that is, the fraction of CO_2 absorbed) of 90% was set, and flows were adjusted accordingly. For temperature and salt analyses mass flows were: 1000 kg/s water, 50 kg/s flue gas and 9.3 kg/s NaOH. For the analysis of inlet pH, both the NaOH and water mass flows were varied in order to achieve 90% absorption of CO_2. The resulting parameters of interest was how much of inlet CO_2 that was absorbed, and the distribution of dissolved inorganic carbon (DIC), that is CO_2, HCO_3^- and CO_3^{2-}, in the liquid outlet stream.

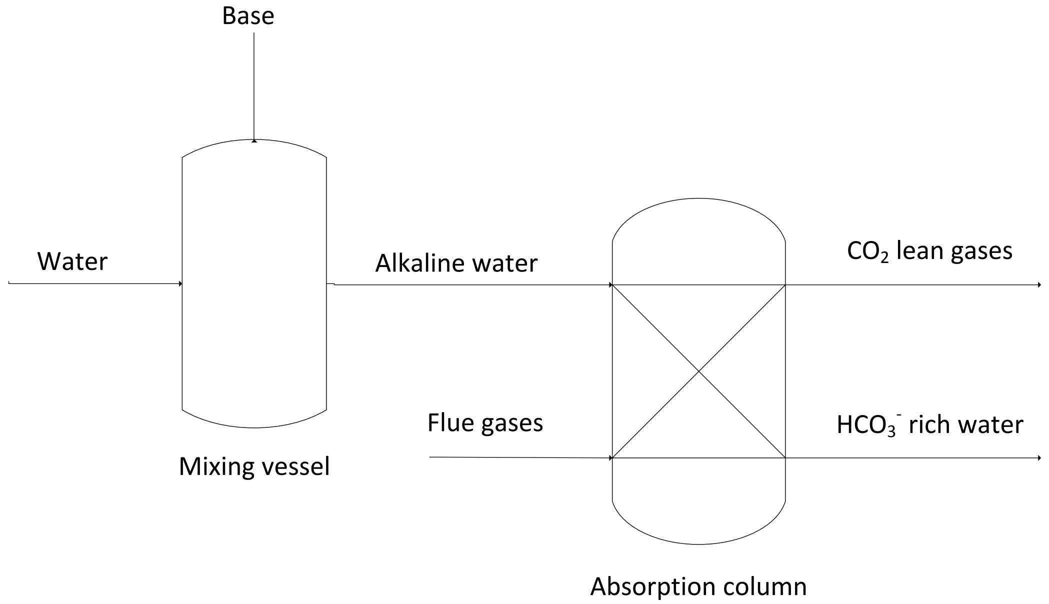

Figure 5: Flowsheet illustrating a CO_2 absorption column, with mixing of water and base (NaOH) for pH adjustment.

As a validation of the pH sensitivity analysis, curves showing the distribution of DIC at different pH values were simulated and compared to the theoretical reference distribution mentioned in Section 2.3. The mole flows of CO_2, ${HCO_3}^-$ and ${CO_3}^{2-}$ were obtained from the liquid outlet stream and plotted against pH. 90% absorption was not necessarily achieved at all data points The obtained curves are shown in Figure 1 and correspond well with theory [20]. Lastly, as a complement to NaOH, two other basic compounds were also evaluated as pH adjusters; Na_2CO_3 and $CaCO_3$.

3.3 Storage option: solid salt from precipitation

In cases where oceanic storage cannot be implemented other storage options should be considered. The conventional CCS storage of gaseous CO_2 is of course an option, but the problem with missing infrastructure and sourcing of aquifer locations is still limiting. Furthermore, this storage method is well researched and described in literature and was therefore not given much attention. Instead, the focus was on the concept of storing CO_2 in solid form. Ultimately, conversion to solid form is what happens with the gaseous CO_2 injected in aquifers, and CO_2 in oceans; it just takes longer and depends on mineral availability.

For the solid form storage option initial sensitivity analyses on precipitation were performed. The parameters that were thought to affect yields the most were the fraction of water removed (that is, the concentration of the solution), temperature and salt content (fresh water vs seawater). The salt that was formed most easily was according to literature $NaHCO_3$ and the dependent variable was how much of inlet DIC that formed this salt.

A simple model was constructed with a mixer, where a concentrated stream of salt ions could be diluted with varying water flow, and a unit for heating or cooling. Assumed flows were corresponding to the rates and thermodynamic study, with 1000 kg/s water and absorbed CO_2 (or rather HCO_3^-) from approximately 90% capture of 50 kg/s flue gases. The pressure was 1 bar. The temperature was adjusted to a constant 15°C with the heater/cooler, with the exception of the sensitivity analysis of stream temperature where the temperature range was 0-40°C. Fresh water, with no inherent ion or salt content, was used unless salt content was the varied parameter.

After parameter studies, possible separation techniques that could be used were evaluated. Evaporation and membrane filtration were selected for a closer examination. Evaporation was simulated with a flash that evaporated a certain fraction of the water. Resulting stream outlet compositions were studied. For membrane filtration, no simulations were performed, mainly because Aspen does not provide the appropriate model unit operations. Therefore, the discussion on membranes is kept on a theoretical level.

3.4 Process design and case application

Based on the results from the sensitivity analyses two process alternatives were designed. The difference between the alternatives was the location of the pH adjustment, before the absorption for alternative 1 and after absorption for alternative 2. For both process alternatives the minimum material flow ratios for 90% absorption were estimated, for example kg H_2O/kg CO_2, that allowed for comparison of the cases. The cases considered were the coal combined heat and power (CHP) plant Nordjyllandsværket (NJV) in Denmark, the CarbFix project at the geothermal CHP plant Hellisheidi in Iceland, the Yara ammonia factory in Norway, the coal power plant Lippendorf in Germany, and finally the waste CHP plant Lillesjö in Sweden. For some background information on these cases, see Appendix B. The relevant process data for the plants are presented in Table 8.

Table 8: Plant data for the five cases considered when estimating flows. * indicates estimated value/assumption, DH = district heating, NJV = Nordjyllandsværket.

Parameter	NJV	Lippendorf	Lillesjö	Yara	CarbFix
Plant type	Coal CHP	Coal condensing	Waste CHP	Ammonia factory	Geothermal CHP
Flue gas flow [kg/s]	370	1 000*	25	50*	0.4
Flue gas pressure [bar]	1	1	1	26	5
Flue gas inlet temp. [°C]	56	56*	50	50	20
Steam turbine condenser flow [kg/s]	13 400	21 400	- (DH)	-	36
Water inlet temp. [°C]	15	30*	- (DH)	10*	20
Mole% CO_2 in gas	21.4	14	14.6	18.9*	82.69
CO_2 flow [kg/s]	80	140*	3.65	9.45	0.33

Equilibrium calculations were preferred with regard to both chemistry and mass transfer, because the aim of the simulations was to determine mass flows rather than equipment dimensions. Furthermore, the study of kinetics and rates indicated that equilibrium could be reached within reasonable column sizes. The data for NJV, Lillesjö and CarbFix are verified figures from plant operation. Unfortunately, the data available for Lippendorf and Yara was incomplete, so assumptions and estimations were made in some instances, marked with a *. It should be noted that Lillsjö plant does not utilize cooling water, but district heating water for condenser cooling, therefore the water flow rate has been omitted. NJV and Lippendorf also have capacity to produce district heating, but these plants can also be run without production of district heating and therefore the cooling water flow rate is reported. For Yara, the flow rates were unknown, and given that their process is quite unique, no guess was made on the water flow rate.

Process alternative 1

The flowsheet for process alternative 1 is identical to the one in Figure 5, where pH was adjusted by NaOH-addition prior to absorption of CO_2. NaOH was selected mainly for simplicity but other bases with OH^- or CO_3^{2-} anions that readily dissolve can be considered. The increased pH allows CO_2 to react to HCO_3^- in the absorption column, with the pH of the liquid stream around 8.

Process alternative 2

Process alternative 2 uses pH adjustment after the absorption of CO_2. Because the pH is not raised prior to absorption, the pH in the liquid stream will be about 4, meaning that CO_2 will not react to HCO_3^- in the column. The flowsheet is shown in Figure 6.

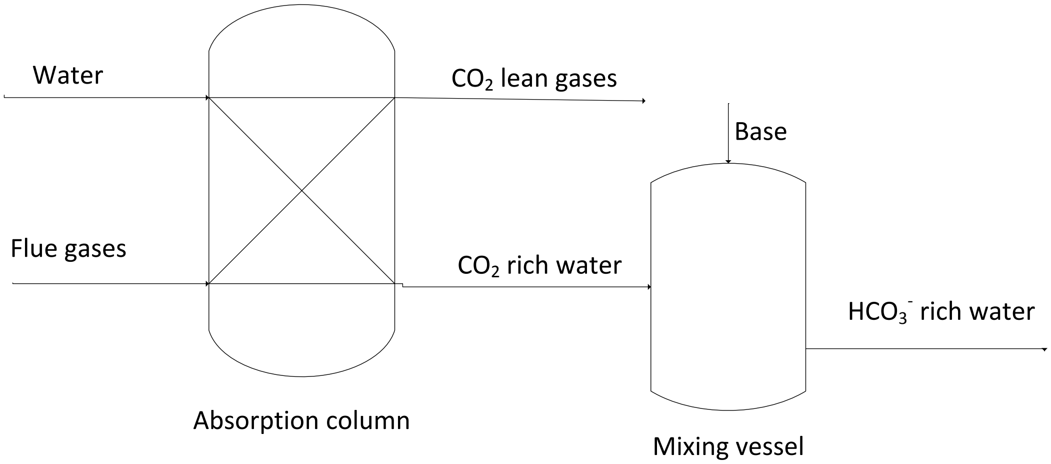

Figure 6: Flowsheet for process alternative 2 with pH adjustment after the absorption column.

The liquid stream enters a Gibbs reactor where $CaCO_3$ is added. NaOH could have been used in this alternative too, but $CaCO_3$ was selected in order to compare the use of other bases. Greater flows of water were expected for this alternative, which favours solubility of $CaCO_3$. Some of the $CaCO_3$ dissolves and reacts with the CO_2 to produce ${HCO_3}^-$ and Ca^{2+} ions according to Equations 14 and 15. The time taken for dissolution and reaction is neglected in this model, the theoretical equilibrium composition and conversion to ${HCO_3}^-$ were of higher interest.

$$\mathrm{CaCO_3\,(s) \rightarrow Ca^{2+}\,(aq) + {CO_3}^{2-}\,(aq)} \tag{14}$$

$$\mathrm{{CO_3}^{2-}\,(aq) + CO_2\,(aq) + H_2O\,(aq) \rightleftharpoons 2\,{HCO_3}^{-}\,(aq)} \tag{15}$$

Partial capture

The concept of partial capture was looked into and applied to process alternative 1 for the Lillesjö plant. Commonly, it is desirable to capture high fractions of inlet CO_2 (above 85%) since this will be required in the long term perspective for emissions reductions. However, in some cases lower percentage capture could be acceptable and this is what partial capture is about. For example, power plants that combust a mix of fossil fuel and biomass, perhaps waste, could use partial capture to sequester the fraction of CO_2 that corresponds to the fossil part of the fuel, and thus make the plant emissions net zero [21].

For the Lillesjö model, the desired fraction of CO_2 captured was varied from 10 to 90% and water and base mass flows were adjusted to achieve pH 8 in the liquid effluent. Trends in flow rate variability were determined by plotting the capture rate against mass flow. Equilibrium calculations were used in the model, although the column dimensions would likely be heavily dependent on the capture ratio and resulting flow rates.

Model validation

Plant data from CarbFix/Hellisheidi (where CO_2 absorption in water is used today) was used to validate Aspen model. The input data was: 36.00 kg/s inlet water, 0.40 kg/s inlet flue gases, inlet temperatures of 20°C and the pressure was 5 bar in all streams[22]. The inlet gas composition used was 82.69% CO_2, 12.77% H_2S and 4.54% N_2. The actual composition also includes small fractions of CH_4 and H_2 which were neglected in the model and represented as nitrogen. The plant absorbs 99% of H_2S and 78.5% CO_2.

Rate based phase transfer calculations and equilibrium reactions were used, because the phase equilibrium is of interest in this case where absorption (transfer of molecules from gas to liquid phase) is the main object. Reactions are not expected to occur to a great extent since pH is not adjusted, therefore equilibrium was assumed. The set up was equal to Figure 17 in Appendix B. Table 9 shows results from the validation simulation together with reference model data.

Table 9: Comparison of CarbFix plant data and results from model validation simulation

Stream	Liquid out	Vapour out
Reference model data		
Gas flow [kg/s]	36.27	0.13
Temperature [°C]	20.6	20.5
CO_2 absorbed [%]	78.5	
H_2S absorbed [%]	99	
Aspen model results		
Gas flow [kg/s]	36.29	0.11
Temperature [°C]	20.9	20.7
CO_2 absorbed [%]	72.8	
H_2S absorbed [%]	99.9	

The Aspen model results are similar to the reference data, although the absorbed CO_2 and temperatures differ slightly. However, it was not stated which gas inlet composition was used in the reference model, and composition appeared to affect the results markedly.

4 Results

The following sections present the findings and analyses of mass transfer and reaction rates, operating conditions, conversion to solid phase and lastly application of the process to industrial cases.

4.1 Mass transfer and reaction rates

As described in Section 3.2.1, three reaction paths from CO_2 to HCO_3^- were studied, using both equilibrium and kinetic/rate based calculations in simulations. The aim was to compare the reaction paths with regard to the time taken to reach equilibrium composition, and the corresponding column height. Furthermore, the rates of reaction and mass transfer were compared to determine if the absorption was controlled by diffusion or reaction.

Firstly, when chemical equilibrium was assumed (Reaction 2a), the results remained essentially unchanged no matter if phase equilibrium or rate based calculations were used. That is, phase equilibrium was established quickly and did not affect the fraction captured, indicating that the process is reaction controlled. The reaction path chosen (Reaction 2b-2d) did not influence establishment of phase equilibrium, which is sensible given that the reaction occurs in the liquid phase when the mass transfer is completed.

The establishment of chemical equilibrium showed greater variation with reaction path. The models where phase equilibrium and kinetics were employed yielded the approximate times to reach chemical equilibrium in the liquid phase, and are presented in Table 10. There is a distinct difference between the reactions, the catalyzed reaction (2d) is about 1 000 times faster than the non-catalyzed reactions (2b and 2c). Moreover, when both kinetics and rate based mass transfer calculations were used the effect of reaction path was evident in the required column height to reach equilibrium composition, also given in the table below, as well as illustrated in Figure 7.

Table 10: Approximate liquid residence time and column height to reach chemical equilibrium in the liquid phase for the three reaction paths considered.

Reaction	2b (OH^-)	2c (H_2O)	2d (enzyme)
Time [s]	0.5	5	0.0005
Height [m]	120	1 300	10

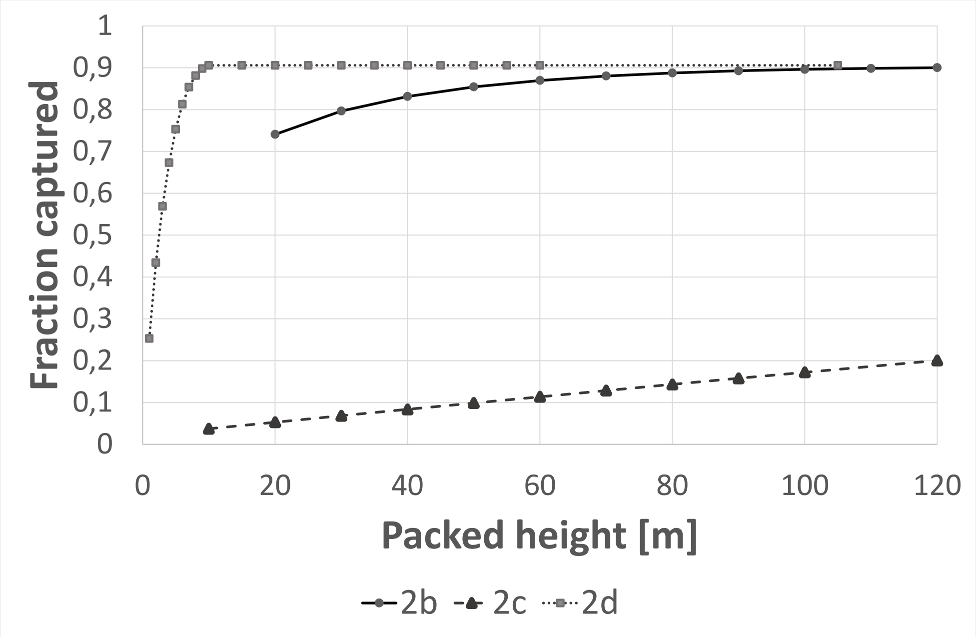

Figure 7: Packed column height affects the captured fraction of CO_2 for reactions that have relatively slow kinetics, as higher column translates to longer residence time. Column diameter was constant at 8 m.

It appears that the enzyme catalyzed reaction, 2d, reaches chemical equilibrium at low column heights (equilibrium is reached when no further increase in capture is seen), while the non-catalyzed reactions (2b and 2c) require 120 and 1 300 m packed height respectively. The slow rate of the H_2O reaction was expected; Penders-van Elk et. al. [23] reported that for 90% CO_2 capture, commercial column height approached 800 meters for the uncatalyzed H_2O reaction. If the enzyme is used the column height needed for adequate yield could be reduced. However, mass transfer resistance in the liquid phase applies for use of enzyme, but is not included in these models. This is further discussed in Section 5.1.

The H_2O and enzyme reaction applies for ${CO_3}^{2-}$ generating bases, such as Na_2CO_3 or $CaCO_3$, while OH^- corresponds to hydroxide bases, like NaOH. If enzymes are not available, choosing a hydroxide forming compound is the only option to reach chemical equilibrium in reasonable column height.

The column diameter was 8 m, the liquid velocity 0.02 m/s and the gas velocity was 0.78 m/s. The pH varies with column height and fraction captured; given that the inlet water is alkaline and has a high pH, at low column height when not much CO_2

has reacted and been captured, the pH is high, but when equilibrium composition is reached the pH decreases to approximately 8, which is desirable for the effluent.

4.2 Thermodynamic sensitivity analyses of absorption

Sensitivity analyses on thermodynamic parameters and pH were performed to determine operating conditions' impact on process performance. The parameters studied were pressure, water and gas inlet temperatures, salt content of water and amount of base added (pH value). Variation in pH, or mass flow of base, was combined with variation in partial pressure of CO_2 to produce Figure 8, illustrating the amount of water required to capture 1 kg CO_2 at different operating points.

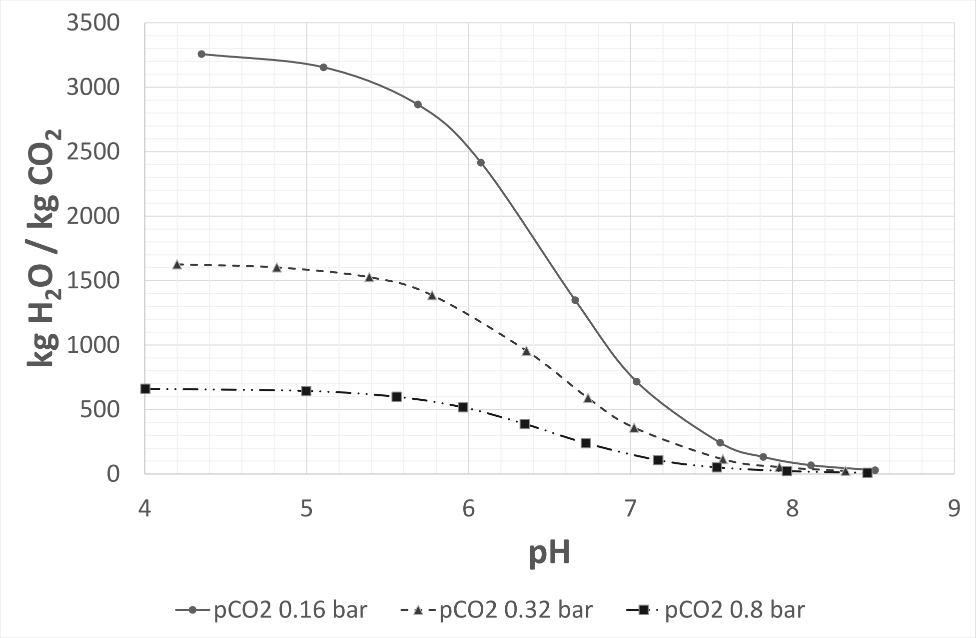

Figure 8: The mass flow ratio kg H_2O/kg CO_2 as a variation of pH in the outlet stream and inlet CO_2 partial pressure. 90% of incoming CO_2 is absorbed.

Figure 8 shows how the amount of water required to absorb 90% of CO_2 varies with pH for three inlet CO_2 partial pressures. Large amounts of water are required for 90% absorption rate, but the water flow rates are lowest, lower than 100 kg/kg CO_2, at pH above 8 where CO_2 is reacted to HCO_3^-. For low pH values the water mass flows are extreme, especially for the lowest partial pressure, 0.16 bar, where more than 3000 kg water/kg CO_2 is needed for 90% absorption. CO_2 flow rates vary greatly depending on plant, but typically the CO_2 mass flow is between 10-100 kg/s for a power plant, which would require a water flow rate of 30 ton/s or more for high capture rates at low pH. If the gas is highly pressurized to increase partial pressure the process could be feasible at low pH, but the high water flow rates could still be a limitation. The most efficient use of water occurs at high pressure and high pH.

Varying gas and water temperature did not affect the absorption significantly. It makes sense that gas temperature did not cause changes, since the gas mass flow was 20 times smaller than the water mass flow, and the low water temperature (15°C) caused the temperature difference between gas and liquid to be evened out rapidly. However, water temperature was expected to affect the absorption more, as the solubility of CO_2 increases with decreasing water temperature. On the other hand, the increase in solubility is likely in the order of magnitude of 0.1-0.01 g CO_2/kg water, so in a larger perspective the increase in captured fraction may not be more than marginal.

Increasing the salt content had a small impact on the absorption. The only noticeable effect was that when the pH was adjusted to 8 with NaOH, slightly more CO_2 and ${CO_3}^{2-}$ was held by the water due to the increased alkalinity that came with salt additions. The amount of ${HCO_3}^{-}$ remained unchanged. In addition to NaOH, two other bases were also tested for pH adjustment; Na_2CO_3 and $CaCO_3$. Use of NaOH and Na_2CO_3 yielded similar capture rates, with the only main discrepancy being the pH value of inlet water; slightly above 13 and 11 respectively. $CaCO_3$ resulted in lower capture of CO_2, and when both sodium bases completely dissociated in the water, a considerable amount of limestone remained in solid form, undissolved. Thus, solubility of the base seems to be important to achieve high absorption rates.

In sum, out of the parameters tested, pressure and pH clearly impact the absorption the most, given that a base with high solubility is used for pH control.

4.3 Storage of ${HCO_3}^{-}$ in solid form and precipitation

In addition to oceanic storage of ${HCO_3}^{-}$, storage in solid form was also considered. In order to make aqueous ${HCO_3}^{-}$ form a salt and precipitate, water must be removed to concentrate the solution. Analyses were performed to determine the amount of water that must be removed, and if temperature and salt content had a significant effect on precipitation. Results from the analysis of how water content affects salt formation are presented in Figure 9. The input data were 1 000 kg/s water and 237 mol/s DIC, corresponding to absorber effluent from 90% absorption of 50 kg/s flue gases.

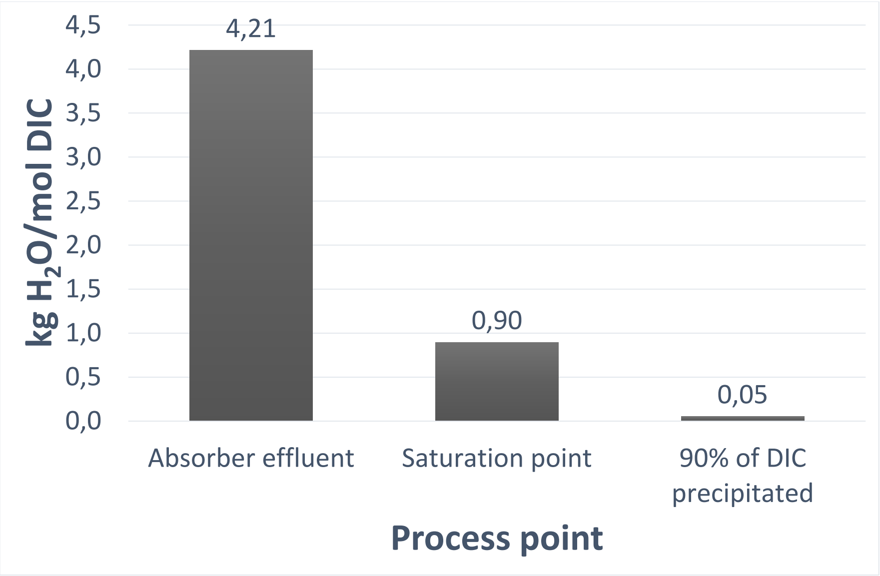

Figure 9: The ratio of water to dissolved inorganic carbon (DIC) at three points of the precipitation process.

Figure 9 shows the ratio of kg water to mol DIC at three steps in the precipitation process; the absorber effluent where no water has been removed, the saturation point where precipitation is about to start, and the point where 90% of DIC has been precipitated. It is clear that in order to achieve salt precipitation, a large fraction of the effluent water must be removed, about 80% to reach saturation and 99% of the water to reach 90% precipitation of DIC. When the saturation point has been reached, the fraction precipitated increases linearly with removal of water.

The variation of water temperature indicated that as temperature is decreased the precipitation yield is increased. For this sensitivity analysis 95% of inlet water was assumed to be removed and fresh water was used. The result was that at 0°C 80% of DIC precipitated, and at 40°C 63% precipitated. Thus, it could increase the efficiency of the precipitation process to add a subsequent cooler after water has been separated. The cooler should be placed after separation since the mass flow that is cooled is significantly lower, which minimizes utility costs.

When extra Na^+ was added, to simulate the use of seawater instead of fresh water, the precipitation yield increased slightly: from 74.5% with no added salt, to 78.3% with Na^+ addition corresponding to seawater levels. So, it is an advantage to use seawater rather than fresh water, although the effect of other ions and species present in seawater was not considered in this sensitivity analysis.

Separation techniques
The concentration techniques considered were evaporation and membrane filtration. Separation of water by evaporation proved to be of little use, as a large part of the dissolved CO_2, even if it was in HCO_3^- form, was desorbed from the liquid stream and lost together with the water vapour. This indicates that thermal methods are not appropriate as at high temperatures HCO_3^- is converted back to CO_2.

Membrane filtration could be more useful, although also more costly. Several membrane techniques are available, from forward or reverse osmosis to electrodialysis, but for high separation efficiency each option has its energy penalty. Reverse osmosis require high osmotic pressures, that is pressurized fluid, while electrodialysis consumes electricity in substantial amounts. Forward osmosis is a low-energy technology, but is the most efficient with dilute solutions where the desired concentration is relatively low, because a concentrated draw solution is needed to provide the separation gradient. Membrane filtration is further discussed in Section 5.2.

4.4 Process design and case application

The feasibility of the CCS process was determined by applying the CO_2 absorption process to five cases: coal power plants Nordjyllandsværket (NJV) and Lippendorf, waste CHP plant Lillesjö, Yara ammonia plant and Hellisheidi geothermal steam plant (labelled CarbFix). The two process alternatives are evaluated in this section based on results and mass balances from the case simulations.

Table 11 displays results from simulations of process alternative 1 and 2. The processes were designed to absorb 90% of incoming CO_2 in the water stream, and minimum water flow rates were adjusted accordingly. Chemical and phase equilibria were assumed. For alternative 1, the flow rate of NaOH corresponds to pH 8.016-8.088 in the liquid effluent. For alternative 2, the flow rate of $CaCO_3$ is the maximum amount that could be dissolved in the stream. Ratios of water or base per kg CO_2 are given for comparison of the cases. Figure 10 displays flowsheets for the process alternatives with stream numbering for aided interpretation of the flow rate results.

Table 11: Mass flows for 90% absorption of CO_2 with process alternatives 1 and 2. Numbers in parentheses correspond to streams in Figure 10.

Plant	NJV	Lippendorf	Lillesjö	Yara	CarbFix
Process alternative 1					
Minimum water flow rate [kg/s] (1)	6 200	19 700	400	350	5.5
NaOH flow rate [kg/s] (2)	64.4	114	2.97	7.8	0.32
kg H_2O/kg CO_2 in [kg/kg] (1/3)	78	141	110	37	17
kg NaOH/kg CO_2 in [kg/kg] (2/3)	0.81	0.81	0.81	0.83	0.97
Process alternative 2					
Minimum water flow rate [kg/s] (4)	240 000	1 020 000	16 700	11 500	44
$CaCO_3$ flow rate [kg/s] (5)	110	230	5.5	9	0.08
CO_2 converted to HCO_3^- [%] (6)	61.9	77.8	72.0	41.9	11.5
kg H_2O/kg CO_2 in [kg/kg] (4/7)	3 000	7 286	4 575	1 217	133
kg $CaCO_3$/kg CO_2 in [kg/kg] (5/7)	1.4	1.6	1.5	0.9	0.2

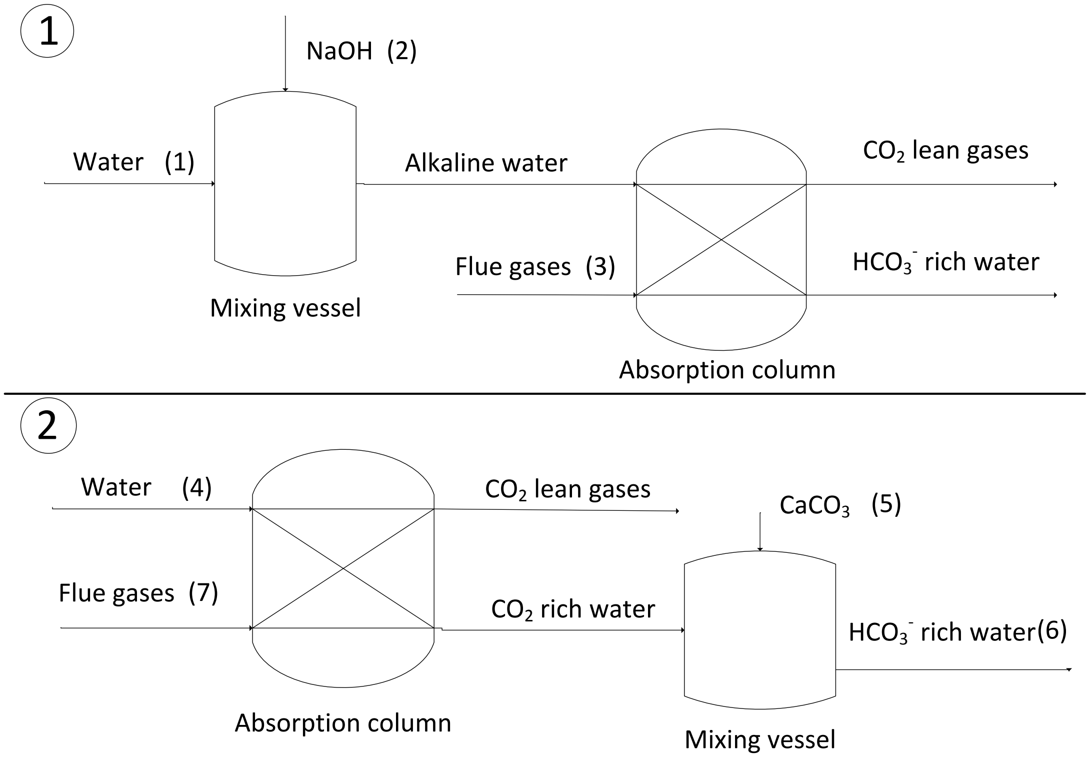

Figure 10: Flowsheet over process alternatives 1 (upper) and 2 (lower) with numbering corresponding to Table 11.

Water flow rate. There is a considerable difference in water flow rates between process alternative 1 and 2, but also between cases. For instance, for Nordjyllandsværket the water flow increases with a factor 38 from alternative 1 to 2. This is largely due to the lower pH of the water solution in alternative 2, which means less CO_2 is converted to HCO_3^-, and thus more water is required to absorb the equivalent amount of CO_2. Variations between cases can be explained by the operating conditions, where partial pressure of CO_2 is the most defining parameter. Water temperature also affects the water flow, which can be seen in a comparison between Lippendorf and Lillesjö; these cases have approximately equal partial pressures, but Lillesjö is assumed to have a lower water temperature, which results in a lower ratio of H_2O to CO_2.

The flow rates of water required for the larger power plants (NJV and Lippendorf) approach vast numbers, especially for alternative 2. As a comparison, the water flow rate of the Skellefte river in northern Sweden is 160 000 kg/s, so a required flow of 240 000 or even 1 020 000 kg/s is completely unrealistic. Not only would it be difficult to get hold of and manage such a large stream, but it would also be technically challenging to construct appropriate columns, as the column diameter approached 100 m, the maximum value allowed in Aspen, for Lippendorf. Steam turbine condenser flow rates are typically around 150 kg water/kg CO_2, so the water flow rates of alternative 1 are realistic. Figure 11 shows the water/CO_2 ratio in relation to the typical condenser equivalent for process alternative 1.

Base flow rate. The ratio of base to CO_2 is approximately the same independent of case, with the exception of CarbFix. For process 1, the value 0.8 kg NaOH/kg CO_2 makes sense based on stoichiometry; given that the molar mass ratio of NaOH to CO_2 is 40/44 = 0.9, and 90% is captured, so 0.9*0.9 = 0.81. For process 2, the ratio is more closely related to water flow rate and solubility; a higher water mass flow means more $CaCO_3$ can be dissolved, so the ratio is greatest for the cases with the highest water consumption. Figure 12 illustrates the correlation between water flow rate and CO_2 conversion for process alternative 2.

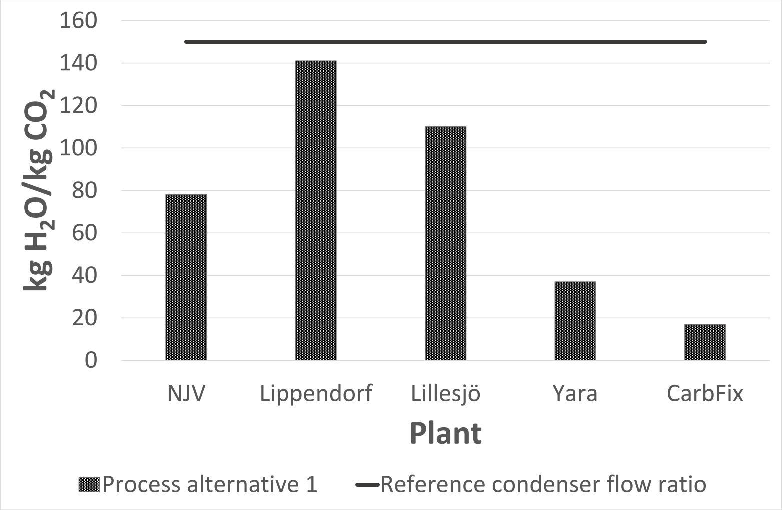

Figure 11: The water/CO_2 ratio for process alternative 1 compared to reference condenser ratio.

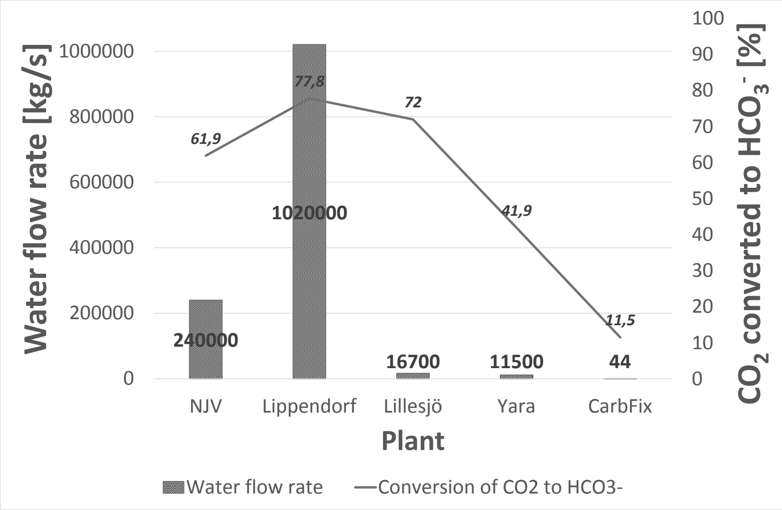

Figure 12: Water flow rates of process alternative 2, with % CO_2 converted to HCO_3^-.

Conversion to $\mathbf{HCO_3}^-$. The resulting yield of $HCO_3{}^-$ varies between process alternative 1 and 2. Process 1 has very high conversion to $HCO_3{}^-$ (more than 90%) in all cases. Process 2 has lower conversion, which is highly connected to base dissolution, $CaCO_3$ has much lower solubility in water than NaOH that dissolves completely in the given water flow. The equilibrium of the limestone dissolution reaction prevents higher conversion. Thus, it is not possible to capture and store all the absorbed CO_2 as $HCO_3{}^-$ with process 2 unless vast volumes of water are present.

Degassing. For process alternative 2, a pressurized column causes degassing of CO_2 from the liquid if the pressure is lowered in subsequent process steps. Due to the higher CO_2 partial pressure water will absorb more gas at high column pressure even if it is not reacted to $HCO_3{}^-$. When simulating pressure reduction, some of the dissolved CO_2 that was not reacted to $HCO_3{}^-$ was desorbed at 1 bar. For Yara, operating at 26 bar, 21.4% of DIC was degassed at 1 bar, and the fraction of $HCO_3{}^-$ decreased from 41.9 to 37.1%. This desorbing tendency was not observed with process alternative 1, the fraction of $HCO_3{}^-$ remained stable through pressure decrease.

Energy. The energy demand of the absorption process was not in focus, mainly because energy was not required for the capture process to be functional. Of course, temperatures could be adjusted with heating or cooling to optimize and increase efficiency of the absorption, but it is not critical. The energy requirements of the CCS process will likely manifest themselves in other parts of the process, such as production of base or regeneration of process water through membrane filtration, if applied.

Partial capture. When the fraction of CO_2 capture was varied between 10-90% for process 1, it was found that for a fixed gas flow, the factor that affected the capture ratio the most was the mass of NaOH added, while the flow of water merely had an impact on the resulting effluent pH. For the Lillesjö case, with a fixed flue gas flow of 25 kg/s, the required flow rates of NaOH and water appeared to be linearly dependent on the percent captured (in the interval 10-90%) according to Figure 13 and Equations 16 (NaOH) and 17 (water). y is the mass flow in kg/s and x is the percent captured, for example 50%.

$$y_{NaOH} = 0.033x \qquad (16)$$

$$y_{water} = 4.59x \qquad (17)$$

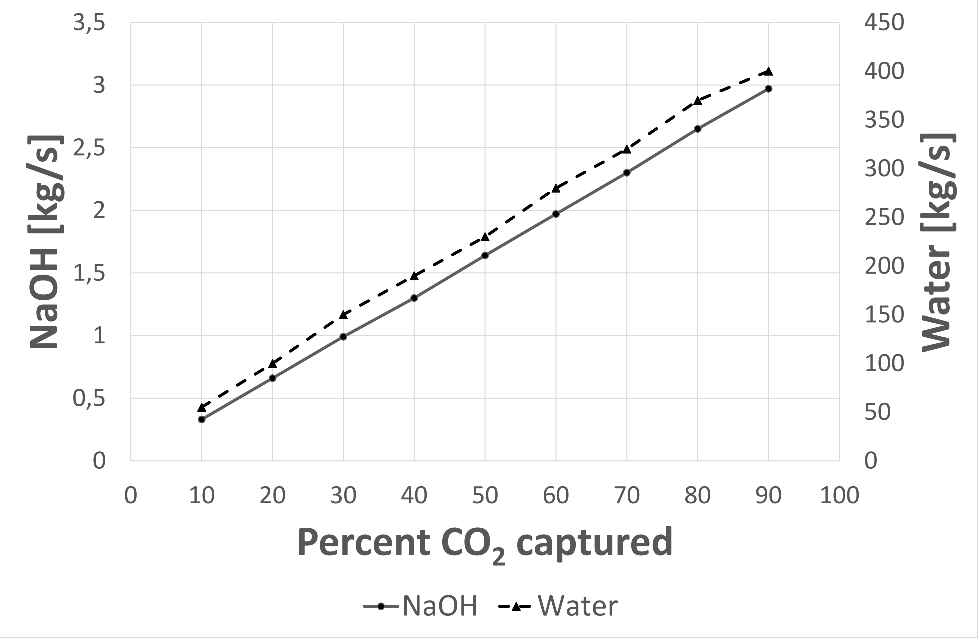

Figure 13: Consumption of NaOH and water as a function of the percent CO_2 captured at Lillesjö power plant.

The resulting effluent pH for these correlations will be about 8.05. Since the conversion of CO_2 to HCO_3^- is of great importance for the absorption capacity, it is reasonable that the availability of reactant - NaOH - is the main factor that controls the fraction of CO_2 absorbed. 1 mol base neutralizes 1 mol H^+ from 1 mol CO_2, which causes the linear relationship between capture and base mass flow. Again, the pH value is regulated mainly by the water flow rate, so variations in water flow will not affect the percent captured significantly, only the outlet pH.

It is not only resource demand that decreases in partial capture scenarios, the column packed height can also be reduced. The relation between height and capture rate can be recognized in Figure 7 where the captured fraction of CO_2 increases with packed height. However, the curves in Figure 7 should not be directly translated to the partial capture case since the independent and dependent variables are interchanged. So, instead of the $\sqrt{x}$ resembling curves in Figure 7 where capture rate is dependent on height, a graph for height dependent on capture rate should look more like a power function.

5 Discussion

As stated in the results section, there are many factors that affect the process to consider when determining the feasibility of this CCS technique. There are also parameters whose effect are not completely known or quantified as of yet and require further study. This section will discuss the factors that were identified as most important for process functionality and implementation; namely use of carbonic anhydrase for increased reaction rate, pH adjustment for optimal absorption and flow rates, and disposal of the effluent stream as a means of CO_2 storage.

5.1 Reaction rates and enzyme immobilization

The results of the kinetic and transport rates showed that using carbonic anhydrase greatly decreased the time taken to reach equilibrium for CO_2 absorption and conversion, and there is potential for reduced equipment sizes. However, the model used only takes into account the mass transfer of CO_2 from gas to liquid phase. For the case of enzymes immobilized in the column for catalytic effect, there is an additional mass transfer through the liquid phase to the solid surface where the enzyme is located. This transport is thought to be the limiting, rate determining, step in catalysis with immobilized enzyme [23, 9], but it has unfortunately not been included in any models. There are several techniques available for enzyme immobilization and the one chosen could possibly affect the transport time, but the liquid film thickness should be as thin as possible to minimize the transfer distance. Penders-van Elk et. al. [23] concluded that the average liquid film thickness around packing material is too large for the enzyme to be of much use and therefore immobilization of CA will not be a viable option for CO_2 capture.

If CA cannot be efficiently immobilized, the alternative is to have it dispersed in the liquid phase, which means that it will not stay in the column, but exit with the liquid outlet stream. For this option to be economically sound, the water with enzyme would have to be regenerated and recycled in some way, which brings increased process costs.

At this point it should be emphasized that it is only the reaction between CO_2 and H_2O that is catalyzed by CA, and that the enzyme is only relevant to use in combination with bases containing ${CO_3}^{2-}$. This conclusion is supported by literature, stating that CA is only functional in carbonate forming systems [24]. The practical implication of this is that if the enzyme activity is lower than assumed here, be it because of mass transfer resistance or denaturing, or if CA is not used at all, the absorption rate will be heavily dependent on the type of base used. It could even be that a OH^- producing compound will lead to a significantly higher rate and improved absorption than the case where a ${CO_3}^{2-}$ base is used together with immobilized enzyme.

Reaction wise, the kinetics do not pose a threat to the process feasibility; whether enzyme/CO_3^{2-} base or OH^- base is used the column height to reach equilibrium is realistic. A 120 m high column is no unusual feature of large plants.

Given the importance of reaction rates for process feasibility, the sensitivity of the results to the kinetics used must be evaluated. The activation energy of the enzyme is the parameter that is most likely to impact results. Various articles report measurements of the activation energy; for example 37 kJ/mol [25] for immobilized enzyme, and for free enzyme in solution 30 kJ/mol [25] and 51 kJ/mol [26]. The differences could be due to synthesis methods or the type of enzyme studied, so it is difficult to get an accurate and representative value. On the other hand, a lowering of activation energy from 61 (non-catalyzed reaction) to 50 kJ/mol is likely enough for the catalytic effect (based on a sensitivity analysis), compared to 37 kJ/mol that was used in simulations. The limitations of immobilization are more important to consider.

Lastly, carbonic anhydrase could still be of interest for other purposes and processes. Conventional CCS with absorption and stripper recycles the absorbing solvent, so use of enzyme in this context does not require immobilization. Rather, the enzyme can be dispersed in the solvent, which is more favourable for the reaction rate. A substantial amount of research has been ongoing in this area (for example [13]). Other solvents than the common MEA are required though, as CA is only effective in carbonate forming systems [24]. Currently, the energy demand for the stripper is the main drawback for post combustion CCS, but this could be overcome by using CA together with a lower-energy solvent.

5.2 Storage of HCO_3^-

The purpose of CCS technologies is to hinder anthropogenic CO_2 from reaching the atmosphere by storing it in a long-term stable way. So, if the present process is to have a place in climate change mitigation strategies, it must provide a means of storage. Solid and aqueous storage options have been the focus of this work but gaseous storage is briefly mentioned here, and this section discusses the challenges associated with these alternatives.

Oceanic storage
From a techno/feasibility point of view, storage of effluent HCO_3^- in oceans, where large amounts of the ion are already present, is favourable. It should be pointed out that this idea is not the same as concepts that discuss storage of gaseous CO_2 in the deep ocean (depths greater than 1 000 m), the present process converts CO_2 to the stable ion HCO_3^- for storage.

Presently the oceans contain approximately 38 000 Gton CO_2 [17], of which more than 90% is HCO_3^-, and most of the rest is CO_3^{2-}. The annual global emissions of CO_2 was approximately 32 Gton in 2010 [6], of which 46% was emitted by the industry and heat and power generation sectors. If the current levels of annual CO_2 emissions are assumed to remain constant, and all the 32 Gton of CO_2 are captured during the next 50 years, a total of 1 600 Gton CO_2 need to be stored. If they are stored in oceans, it would mean that the CO_2 content of the oceans increases with 4.2%. As a comparison, a 10% increase in atmospheric CO_2 leads to a 1% increase in oceanic CO_2. However, this line of thought assumes that the effluent is evenly spread in the entire ocean. This does not happen instantaneously, so there would likely be a higher percental increase on a local level that may cause problems for the marine climate.

To avoid harmful consequences to the local environment, a case study with focus on the Hoping plant in Taiwan stated that "To protect marine biota with narrow pH tolerance, human activities should not result in a change in environmental pH of more than 0.2 pH units from normally occurring values.", and that the outflow solution should be within spatial and temporal variations [16]. But the effluent impact need not only be negative, Marubini and Thake [27] found that addition of bicarbonate to oceans can lead to increased coral calcification rates and protection against nutrient enrichment.

Another consideration is that large amounts of cations, for example Na^+, would also be released in the effluent stream. Compared to CO_2, the percental increase of Na^+ would be 48 ppm, but it could mean that the ocean salinity increases slightly. Ocean salinity has been constant for a long time, and stability is important for most cells. Other species - pollutants - may also be released with the effluent that could have a biological impact. To conclude, it is difficult to predict if any severe environmental consequences or ecosystem imbalances would be caused or not, if large scale injection of effluent streams is implemented. More research is needed before any conclusions can be reached.

Solid storage

An option to oceanic storage is the possibility to form a solid salt of the aqueous HCO_3^-. The most promising dewatering technique to concentrate the solution is membrane filtration, but the high separation requirement for precipitation will demand considerable quantities of energy input.

The salt that is most easily precipitated is $NaHCO_3$ which requires that the base used contains sodium. Assuming that the solid storage form is implemented, this will result in vast amounts of the salt produced that require large volumes of storage space. For instance, Nordjyllandsværket emits 80 kg CO_2/s, and 90% capture would, assuming 8 000 hours of operating time per year, lead to 1.8 Mm^3 $NaHCO_3$ per year to store. To put this figure in perspective, the volume of the second largest excavated hole in the world - the Mirny mine in Russia - is approximately 582 Mm^3, which could hold solid material for several years from many plants. However, transport of material to suitable storage places could be an issue.

One possible disadvantage of storage of $NaHCO_3$ is that it can decompose to Na_2CO_3 at high temperatures (starting from 50°C):

$$NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \tag{18}$$

This implies that some of the captured CO_2 is lost to the surrounding air, which is of course not desirable. To avoid decomposition storage locations must thus be chosen with care.

In spite of the drawbacks of solid storage, with energy consumption and volume requirements, synergistic effects could add to the advantage of this option. In a scenario where drinking water is scarce, which is considered a growing problem globally, there will be a greater demand for desalination of seawater. From the process perspective, desalinated water is a byproduct from membrane filtration, and if this can be sold the incentives for solid storage benefit. Having a desalination plant at a power plant also has further potential; there is usually low-grade excess heat available that there is no use for. This heat could together with forward osmosis provide a filtration method with relatively low energy demand. Figure 14 illustrates the idea.

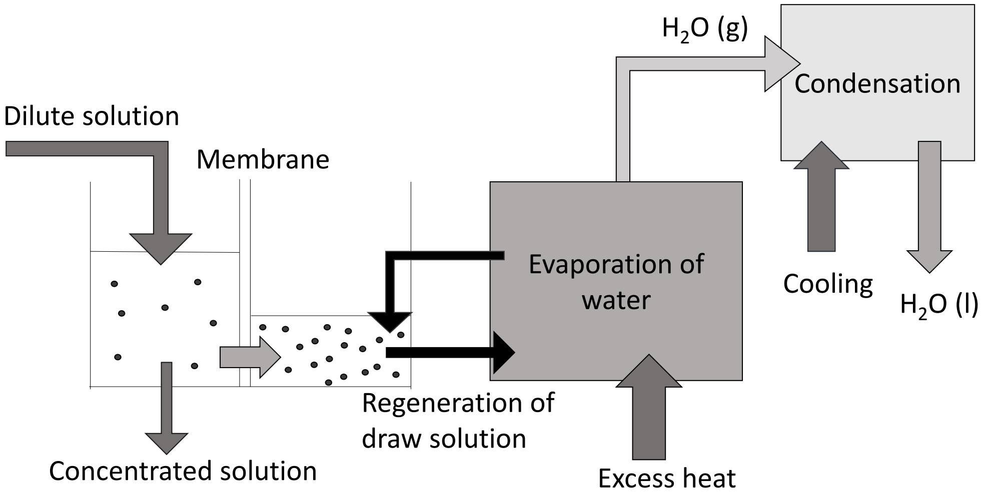

Figure 14: Membrane filtration coupled with fresh water production at a power plant for increased opportunities of solid storage.

Forward osmosis is membrane filtration where the driving force is provided by a draw solution that is more concentrated (has a higher osmotic pressure) than the stream that is being separated. Thus, no or little energy must be added to create a driving force for separation, but instead energy is used to regenerate the concentrated draw solution. In Figure 14 the idea is to regenerate the draw solution by evaporating water from it with excess heat from power production. The evaporated water can then be condensed and sold as fresh water. Seawater can be used as the cooling utility. This separation process utilizes low-cost, readily available resources, but a prerequisite is of course that sufficient supply of NaOH can be arranged for the CO_2 capture.

Gas storage
The most common idea of how to store CO_2 is in gaseous form, injected into deep-lying aquifers. There are great amounts of research concerning gas storage. Since the aim of this CCS water absorption process is to convert CO_2 to HCO_3^-, in a way it defeats the purpose to convert the HCO_3^- back to CO_2 for gaseous storage, but it could be a way to solve the problem with suitable HCO_3^- storage. Moreover, there is potential for CA-based processes to replace the energy demanding stripper conventional in MEA cycles. This idea was briefly mentioned in Section 5.1, with combination of CA and carbonate forming solvents.

A problem with using CA to catalyze both formation and consumption of HCO_3^- in cyclic processes is that the reactions (forward and backward) are pH dependent, which means that the pH in absorber and stripper need to be controlled; with a high pH in the absorber and low pH in the stripper. At a first glance, no obvious technical solution comes to mind on how to manage this pH control. In this work, pH was raised by addition of base, and pH could of course be lowered with addition of acid, but for a cyclic process, this entails accumulation of material, most noticeably cation from base and anion from acid, that could eventually cause problems with precipitation of salt that harm equipment. Therefore a better solution to control pH must be found before gaseous storage can be applied to the water absorption and reaction process.

An alternative is to not convert CO_2 to HCO_3^-, but only absorb CO_2 and let it be dissolved in water until it is desorbed in the stripper or by pressure reduction. This idea is similar to the CO_2 water absorption that Yara utilizes (flowsheet in Appendix B), and also process alternative 2 but without the addition of base after absorpion. Yara reports that the resulting CO_2 stream has very high purity, so it would be simple to store the gas without further treatment other than compression and transportation, and no chemicals are used. However, the water demand would be a great deal higher for such a process than the scenario where CO_2 reacts to HCO_3^-. For realistic water flow rates, the flue gases must be pressurized, which was seen in the case results for process alternative 2, Section 4.4. Pressurization of flue gases at power plants is not economically feasible, compression is expensive, so niche applications such as Yara are the main target plants for this version of the capture process.

5.3 Feasibility of the capture process

So far, the discussion has been focused on the theoretical and technical aspects necessary for the process to work, and the results indicate that the process is functional.

However, in order to be of use in industrial settings other factors, such as resource consumption and economics, play an important role. This section will evaluate the process feasibility based on the case simulation results.

First of all, from simulation results it is evident that great amounts of material are consumed in the capture process, both water and base. At power plants, process alternative 1 will be the only reasonable option due to the unrealistic water flow rates of process alternative 2. Process alternative 2 could have some application potential at plants where gases are pressurized, such as Yara, and perhaps in combination with partial capture to reduce water demand. For a power plant the water requirements can probably be fulfilled by using condenser cooling water. However, the consumption of base presents a challenge, and this was also concluded in the Hoping case study [16], which states that the feasibility of the process is dependent on the availability of base and seawater. For process alternative 1, a base with high solubility is important for high capture rates. In addition, if a solid salt should be formed for storage it is beneficial if the base contains Na^+ anions. Thus, NaOH and Na_2CO_3 are left as the two most promising options. Reaction wise, since NaOH can be used without aid from enzymes, this base is the focus of the continued discussion.

Assuming an annual operating time of 8 000 hours, the annual flow of NaOH required for 90% capture of CO_2 at Nordjyllandsværket is 1.85 Mton/a. The annual global production of NaOH is about 60 Mton, so only one power plant would demand a considerable share of the global production if the process was implemented. As an option, the plant could produce its own NaOH using the chlor-alkali process[2]. If this is applied at Lillesjö plant the corresponding electricity cost for production of NaOH would be 80.7 MSEK/a, or 815 SEK/ton CO_2[3]. Now, electricity constitutes about 50% of operation and maintenance costs in NaOH production, so the calculated cost should be roughly doubled for total production cost.

On the other hand, these costs should be compared to alternative CCS techniques for a fair evaluation. Conventional CCS based on MEA cycling and storage of gaseous CO_2 requires energy in the stripper and for compression, and the gas transportation network will also have its costs.

Due to the large material demands and costs associated with production of NaOH, it might be difficult for large scale power plants that emit around 1 Mton CO_2/a to implement this CCS process. The demands on capture are likely to be high for these plants, in the vicinity of 90% capture, so the enormous material consumption cannot be

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[2] The chlor-alkali process entails electrolysis of NaCl to produce NaOH, H_2 and Cl_2, and is electricity intensive. To produce 1.1 ton NaOH (with 1 ton Cl_2 and 0.03 ton H_2 as byproducts) 2.79 MWh electricity and 0.18 MWh steam are required [28].

[3] Assuming an electricity price of 0.3722 SEK/kWh (Spot price 26/4 2017 [29]); and 90% absorption of CO_2 emissions resulting in a demand for NaOH of 85.5 kton/a.

avoided. On the other hand, smaller plants, emitting approximately 100 000 tons/a of CO_2 might be better suited for the process if partial capture can be applied. Furthermore, the simplicity of the process with only two necessary reactants - water and base - avoids handling of chemicals that is necessary with conventional amine based capture processes. Another advantage is that plants in remote locations can avoid construction of the system for transportation and storage of CO_2 that is required for conventional storage of CO_2 in gaseous form. In Sweden, the water absorption process could be of special interest for waste or biomass combusting plants that allow for BECCS.

Although the process is theoretically realizable, some issues still need to be solved before practical application is considered. The challenges and opportunities of the process are summarized in 12.

Table 12: Challenges, opportunities and unknowns for the CO_2 water absorption process.

Challenges and unknowns
- Resource efficient pH adjustment methods - Ecosystem consequences for marine life if ${HCO_3}^-$ is stored in oceans - Mass transfer limitations associated with enzyme immobilization
Opportunities
- Use enzyme for conventional CCS with amine or carbonate buffered solution - Combine precipitation for solid storage with desalination and evaporation for fresh water production - Small scale plants with partial capture and BECCS

6 Conclusion

The investigated CCS process with absorption of CO_2 in water followed by reaction to HCO_3^- has proven to be technically feasible to use in power plants or industries, but is challenged by its high demand for base, and especially the associated production cost of base. Out of the two process alternatives considered, the first one with pH regulation prior to absorption is the most promising, given the manageable water mass flows.

The results indicate that pH regulation is not only important, but critical, to process performance. Without pH control through addition of base the reaction from CO_2 to HCO_3^- does not occur, and the required water flow rates escalate. Carbonic anhydrase significantly increased the reaction rate of the CO_2 conversion, and has the potential to reduce column height. However, satisfying results were also obtained without use of enzyme catalyst, through addition of a hydroxide base which yielded acceptable column heights.

To keep costs and resource demand low, small scale plants that can benefit from partial capture are best suited to use the water absorption process. Although the storage options of the process require further research before they are applicable, the diverse possibilities could be advantageous for plants that want to avoid the transportation network associated with conventional storage of gaseous CO_2.

A Estimation of kinetic parameters for enzyme catalysed reaction

The rate of a reaction

$$\mathrm{a\,A + b\,B \rightleftharpoons c\,C + d\,D} \tag{19}$$

is commonly given by the expression

$$r = k_+[\mathrm{A}]^a[\mathrm{B}]^b \; - \; k_-[\mathrm{C}]^c[\mathrm{D}]^d \tag{20}$$

where r is the reaction rate [mol dm^{-3} s^{-1}], k_+ is the forward reaction rate constant, k_- is the reverse reaction rate constant (unit adjusted depending on rate expression), and [X] is the concentration of species X [mol dm^{-3}]. To calculate the rate of reaction the rate constants must be provided. Many reaction rate constants can be calculated using the Arrhenius equation which includes temperature dependency, this is the convention used in Aspen:

$$k = Ae^{-E_a/RT} \tag{21}$$

A is called the pre-exponential factor, E_a is the activation energy [J/mol], R is the ideal gas constant (8.3145 J/mol K) and T is the temperature [K]. By providing values for A and E_a Aspen will calculate k at the appropriate temperature.

Given that a specific reaction follows the Arrhenius rate law, the parameters can be estimated from plots of ln(k) at various temperatures (plotted as 1/T). The y-intercept of such a plot gives ln(A), and the slope represents (-E_a/R).

The reaction involving CO_2 and H_2O does unfortunately not follow the Arrhenius equation, but literature provided correlations for the rate constants as a function of temperature [30, 31]. These correlations were used to plot the rate constant in the relevant temperature interval, and a trendline was fitted to the data points to calculate Arrhenius parameters, Figure 15. The fit was good in the interval, $R^2 = 0.9947$. For reactions outside the selected temperature interval the estimations of k will be less accurate due to curvature in the correlation.

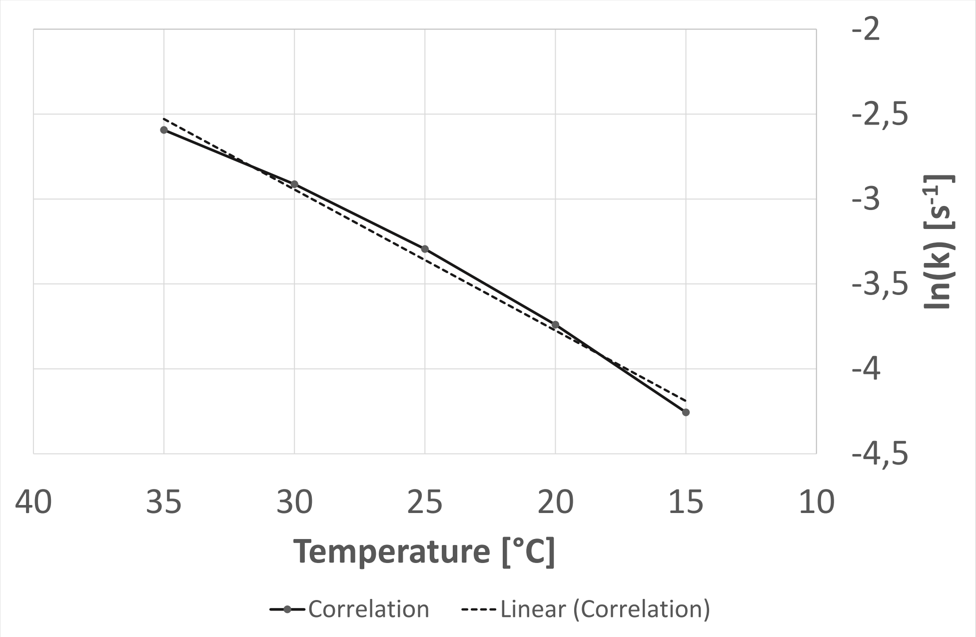

Figure 15: Plot of ln(k) versus temperature, based on correlations from Johnson [30]. The dotted trendline is used for estimation of kinetic parameters.

The reverse rate constant was based on a correlation from Roy [31]. The same type of graph was plotted for the reverse reaction as well, with good fit in the interval, $R^2 = 0.9906$. The values obtained for A and E_a are summarized in Table 5 together with the estimated activation energy for the enzyme catalyzed reactions. The enzyme activation energy was taken from Chandra [25], where the activation energy for immobilized enzyme was reported as 8.9 kcal/mol, which corresponds to approximately 37 kJ/mol. For the reverse reaction the activation energy was decreased with the same factor as the forward reaction:

$$E_{a,reverse} = \frac{37}{61.39} * 45.86 = 27.64 \tag{22}$$

The reverse activation energy is merely a rough estimation and lacks experimental backing. However, without a lowering of reverse reaction activation energy, the simulation results were unrealistic and did not correspond well with theory.

B Potential industrial applications of CO_2 water absorption

There are several cases where CO_2 absorption in water for carbon capture could be implemented. Five of these cases are explored in this thesis, each with its own point of view of how the process could be of use. The cases are described in the following sections.

Combined heat and power plant Nordjyllandsværket in Denmark

Nordjyllandsværket is a coal combusting combined heat and power plant situated in northern Jutland, Denmark, by the Limfjord. The operation of the plant can be varied to production of electricity only (400 MW), or to production of both power and district heating (340 MW el + 420 MW heat). The coastal location grants plentiful access to turbine condenser cooling water, although the shallow waters in the Limfjord places restrictions on the effluent water temperature. Therefore cooling water flow is higher than for other similar power plants.

The cooling water flow is constant at 13 400 kg/s, independent of cooling duty. The inlet and outlet water temperatures vary with season and cooling duty respectively. The flue gas composition from the boiler is presented in Table 13. The mass flow of flue gases to the stack is 370 kg/s with a temperature of 56°C.

Table 13: Flue gas composition from boiler at Nordjyllandsværket. "Other" constitutes of sulfur and nitrous oxides, and argon.

Compound	Mass%
N_2	68.9
CO_2	21.4
H_2O	5.4
O_2	3.1
Other	1.2

Given the flows of water and flue gas, the amount of cooling water available for capture of 1 kg CO_2 is:

$$\frac{\text{kg H}_2\text{O}}{\text{kg CO}_2} = \frac{13400\,\text{kg/s}}{0{,}214 * 362{,}3\,\text{kg/s}} = 172{,}83 \tag{23}$$

Coal power plant Lippendorf in Germany

Lippendorf power plant is one of the largest and most modern in Europe, with two blocks of some 900 MW el each with an efficiency of 42.5%. Situated 15 km from Leipzig, it supplies the town with some district heating (maximum 330 MW). The fuel is lignite, and the fraction of CO_2 in flue gases is 14%. The plant is located inland with limited availability of water for cooling. Instead, a natural draft cooling tower is used. In comparison to Nordjyllandsværket, the cooling water is allowed to heat to a higher temperature, approximately 30°C.

Waste CHP plant Lillesjö in Sweden

Lillesjö is a waste combustion CHP plant that produces a total of 42 MW in the boiler. It supplies 2/3 of Swedish city Uddevalla with district heating. The district heating flow is 153 kg/s, and is used to take up heat from the condenser cooling cycle, with no need for extra cooling water. The flue gas flow is 25 kg/s of which 14.6% is CO_2, 73.7% is N_2, 7.2% O_2 and 4.5% H_2O. The annual CO_2 emissions from the plant is approximately 110 000 ton per year. The waste fuel consists of partly fossil material, so partial capture could be interesting in this context to make plant emissins net zero.

Yara ammonia plant in Norway

The Yara ammonia plant in Porsgrunn, Norway, is one of the three CO_2-emitting industries identified by the Norwegian government as suitable for full scale CO_2 capture in Norway [32]. Yara uses a water wash process to separate CO_2 from the process gas, cold fresh water is used and recirculated. No other chemicals than water are used and the product obtained has a very high purity. The absorpion is carried out at 26 bar, and the water is regenerated by lowering the pressure so that CO_2 is desorbed, followed by air stripping. The process flow sheet is shown in Figure 16.

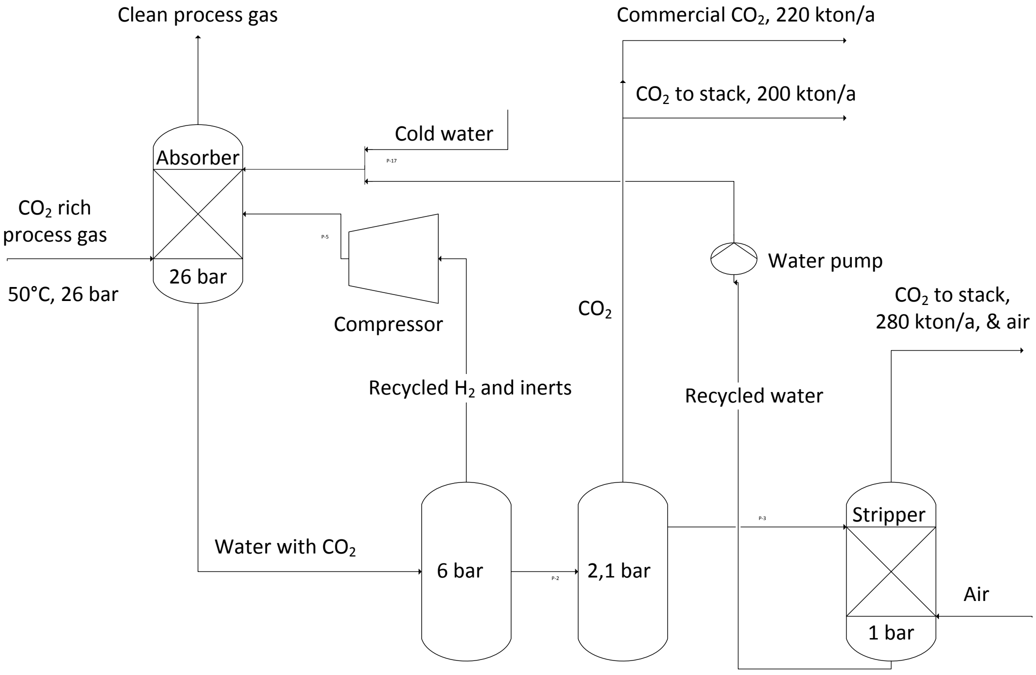

Figure 16: Process schematic of CO_2 separation at Yara ammonia plant [32].

Four parallel absorption columns are utilized in the factory. Process gas at approximately 50°C and 26 bar is introduced to the absorber from the bottom. 8°C water is entered counter-currently at the top. The CO_2 saturated liquid stream leaving the column is treated in three steps where the pressure is lowered in stages. Firstly, hydrogen and inert compounds are removed and recycled in a flash at 6 bar. Then a second flash, at 2,1 bar, desorbs about two thirds of the CO_2 with a purity of 96%. Lastly, the remaining CO_2 is removed from the water in an air stripper, and the water is recycled to the column.

In total, the plant emits about 1 Mt/a CO_2, where 400 kt/a are flue gases from a reformer and 700 kt/a are absorbed and separated from process gas in the water wash. Out of the absorbed CO_2, 220 kt/a is sold for food grade purposes, the rest is vented to the atmosphere.

Hellisheidi/CarbFix in Iceland

The Hellisheidi geothermal steam plant outside Reykjavik is a combined heat and power plant, with seven turbines delivering a total of 300 MW el and 130 MW heat, where the geothermal steam consists of not only pure water, but also CO_2, H_2S, H_2, N_2 and CH_4. After turbine expansion, the steam in the gas is condensed for district heating purposes, leaving an acid gas stream. The mass flow of geothermal steam to the plant is shown in Table 14. The non-condensed gas composition from turbines vary between 58-83% CO_2, 13-40% H_2S with H_2, N_2 and CH_4 making up the remaining part [22].

Table 14: Geothermal steam mass flow to Hellisheidi plant [22].

	H_2O	CO_2	H_2S	Remaining gas	Total
Mass flow [kg/s]	1177,67	1,61	0,67	0,05	1180,0

Tests of acid gas removal were carried out in the projects CarbFix and Sulfix, where CO_2 and H_2S is removed from the acid gas in a water absorption column, see Figure 17. The captured CO_2 and H_2S were then re-injected into basalt rock formations 400-800 meters underground [22]. The basalt rock is rich in minerals that causes the CO_2 to mineralize almost completely in less than two years [33]. Injection of CO_2 into basalt formations thus provides a promising option for long term storage of CO_2 in a solid form that has no risk of leakage.

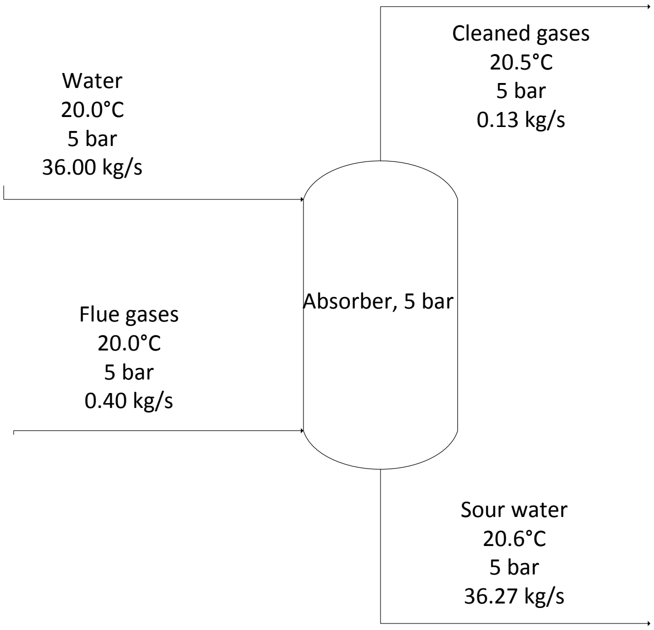

Figure 17: Process schematic of CO_2 and H_2S absorption at Hellisheidi plant [22].

The aim of the SulFix project was to capture 99% of H_2S and 78,5% of CO_2. The ratio of water to gas used in the column is:

$$\frac{\text{kg } H_2O}{\text{kg } CO_2} = \frac{36\,\text{kg/s}}{0{,}4\,\text{kg/s}} = 90 \tag{24}$$

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