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Ex-ante Life Cycle Assessment of carbonating Green Liquor Dregs for CCUS

An early assessment on the prospects of using direct aqueous carbonation on green liquor dregs from the pulp industry for carbon capture, utilization and storage

Master's thesis in Industrial Ecology

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Gothenburg, Sweden 2024
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Abstract

Since pre-industrial time, the temperature on earth has risen with over 1°C due to human activities. To limit the temperature rise to less than 2°C there is a need of Carbon Capture, Utilization and Storage, CCUS, technologies that collect and store or use CO_2 from the atmosphere. However, the existing CCUS technologies are either expensive or ineffective, therefore there is a need to develop new CCUS technologies.

This thesis aims to show the possible prospects for CCUS by direct aqueous carbonation of green liquor dregs, GLD, using flue gas from pulp mills. With data from lab experiments and from Smurfit Kappa mill in Piteå, a scaled-up model was built to evaluate the maximum yield of sequestered CO_2, electrical energy needed to run the carbonation process and the possible avoided emissions from product replacement using the carbonated GLD, cGLD. The results was then scaled up to the total GLD production in Sweden in 2022.

Three scenarios were studied, 1.The cGLD was only filtered and assumed to be land-filled, 2.The cGLD was dried and used to substitute clinker and 3.The cGLD was dried and used to substitute gravel. The results show that scenario 2 has the highest negative emissions of -0.756 ton CO_2 per ton of input GLD, compared with roughly -0.176 ton CO_2 per ton input GLD for both scenario 1 and 3, using Swedish electricity mix for the emissions from electricity generation. The most energy intensive process step was drying, which in case 2 and 3 stood for 96% of the electricity use. When scaled up to incorporate carbonating all GLD produced in Sweden in 2022, the maximum negative emissions for the 2nd scenario summed up to 0.31% of all emissions from Sweden and 24% of the emissions from the total Swedish pulp and paper industry. A sensitivity analysis was performed by changing the electricity generation to be from general EU-mix. The impact on scenario 1 was minimal but for scenarios 2 and 3, the electricity mix had significant impact with total negative emissions of -0.627 and -0.005 ton CO_2 per ton input GLD respectively, due to the high energy use in the drying step.

Since this is a novel technology, no earlier studies regarding carbonation of GLD has been published. This report should therefore only be viewed as an indication that there could be noteworthy benefits of carbonating GLD for CCUS, with significant negative emissions of 0.31% of Sweden's total emissions.

Keywords: Green liquor dregs, carbonation, direct aqueous carbonation, carbon capture and storage, ex-ante life cycle assessment, pulp, material flow analysis.

Acknowledgements

Firstly, I would like to express my deepest appreciation to my supervisor, postdoc Gulnara Shavalieva, my examiner, Professor Henrikke Baumann and PhD Student Emmanouela Leventaki for providing data, important and helpful feedback and insights during the thesis work. I am also extremely grateful to Jeanette Bergstedt, Environmental Manager and Urban Lundmark, Manager power and recovery plant from Smurfit Kappa Piteå for their generous contribution of data and knowledge needed to make this model.

I would also like to give a special thanks to Anna Asplund, Environmental Manager and Sofie Semstrand, Environment and Energy Engineer from Nordic Paper Bäckhammar for their contributions to data and insights about the pulp industry. I am also grateful to Christian Kugge, R&D Specialist at SCA for his data contribution.

Lastly, I would like to thank my friends and family for their support through this process, especially my partner Elise, without whom I could not have completed this thesis work.

Harald Olivegren, Gothenburg, October 2024

List of Acronyms

A list of acronyms used in this thesis is presented below in alphabetical order:

CC	Carbon Capture
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Utilization
CCUS	Carbon Capture, Utilization and Storage
$CO_{2,eq}$	Carbon dioxide equivalent
EEA	European Environment Agency
EU	European Union
EU ETS	EU Emission Trading System
FU	Functional unit
GHGs	Greenhouse gases
GLD	Green liquor dregs
cGLD	Carbonated green liquor dregs
GML	Global Monitoring Laboratory
GWP	Global Warming Potential
IPCC	International Panel on Climate Change
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
MFA	Material Flow Analysis
SKP	Smurfit Kappa Piteå

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Introduction

According to the International Panel on Climate Change, IPCC [1], the temperature has risen over 1°C relative to 1850 due to human activities. The temperature rise is primarily due to release of greenhouse gases, GHGs, into the atmosphere. The most discussed GHG is carbon dioxide, CO_2, and according to the Global Monitoring Laboratory, GML [2], the global mean concentration of CO_2 was 416 ppm as of October 2022. That can be compared to the concentration of CO_2 before the industrial revolution which was approximately 280 ppm around year 1750 [3]. In their sixth assessment report, IPCC states [4] with high confidence that the climate sensitivity lies between 2.5 and 4 °C for a doubling of concentration of GHGs in the atmosphere. Thus, for the mean value, an end concentration of roughly 410 ppm have to be reached to limit the global warming to 1.5 °C, and 450 ppm to limit it to 2 °C. Consequently, to be able to reach the goals of limiting the global warming to 2 °C and preferably 1.5 °C [5], there is a need of both lowering current emissions and also having negative emissions. One way of doing this is with carbon capture technologies but it is uncertain to which extent they really can draw down the concentration of CO_2 in the atmosphere.

1.1 Background

1.1.1 Carbon Capture, Utilization and Storage

To be able to have negative emissions there is a need of Carbon Capture, CC, technologies. There most discussed technologies are so called Carbon Capture and Storage, CCS. The carbon, generally in the form of CO_2, is captured and stored underground and thus is taken out of the carbon cycling in the atmosphere [6]. However, there are many obstacles that hinder the application of these technologies. In general the technologies are either very expensive or very ineffective. They require large amount of both space and resources which makes them very expensive to build and run. Most of the technologies has only been tested in small research scale and only a few has been employed at large scale and thus needs more research before being adopted for use. Another obstacle that has hindered the application of CCS is public skepticism to the geological storing of CO_2, due to potential leakage that could have negative effects, such as contamination of water supplies [7].

Instead of storing captured CO_2 in underground storage spaces, it can be utilized as a raw material for production of other products such as fertilizers, fuels and in building materials [8]. The captured carbon can thus have an economic value compared to the case in CCS where it only is stored. The added economic value may be an incentive for investing in carbon capture technologies. For some cases, such as when it is used in fertilizers and fuels, the captured carbon will not be permanently stored but instead utilized and thus only replace emissions of fossil carbon into the atmosphere and it therefore called Carbon Capture and Utilization, CCU. For cases where the carbon is used in products with longer life span, such as building materials, the captured carbon is stored during the life span of the material and for some cases in its end of life storage as well, which is called Carbon Capture, Utilization and Storage, CCUS [8].

As of today, most of the ways to conduct CCS, CCU or CCUS are either very expensive, ineffective or both [9]. To be able to have a fighting chance to reach the goals of the Paris agreement there needs to be a continued development of new ways to capture and store carbon. According to Lebling et al. [10], approximately 45 million tons of CO_2 is captured each year by CCS-technologies which is equal to 0.1% of the worlds emissions of GHGs.

1.1.2 CCUS via carbonation

Another way of storing CO_2 may be by producing solid minerals by carbonating alkaline materials, mainly oxides, with CO_2 from flue gas. The process follows the natural chemical weathering of alkaline rocks, where CO_2 and H_2O(g) from the atmosphere reacts with silicate rocks to in the end form a carbonite, e.g calcium carbonite, $CaCO_3$(s). Naturally, the carbonation process is very slow, which in the case of using carbonation for CCU or CCUS needs to be sped up [11], [12]. For the cause of CCUS or CCUS, not only silicate rocks can be used to store CO_2 from flue gas. The carbonation can be done on other alkaline compounds including magnesium or sodium as well as calcium, such as waste and by-products from industry. According to Emmanouela Leventaki [13], carbonating these kinds of materials with high pH using CO_2 lowers the pH of the material.

Generally there are three different ways to perform carbonation on alkaline materials for CCU or CCUS. The main ways are direct gas-solid carbonation, direct aqueous carbonation and indirect aqueous carbonation.

In the direct gas-solid carbonation the flue gas containing CO_2 reacts with alkaline oxides to form carbonites. The chemical process is slow and happens at high temperatures, between 500 and 700°C [14]. The process is therefore both energy ineffective and slow.

In the direct aqueous carbonation, the reaction is performed in water or in water vapor. The presence of water or water vapor enhances the kinetics and lowers the pressure and temperature needed so that the reactions can occur at ambient conditions. In direct aqueous carbonation the CO_2 from the flue gas is solved into water which through multiple reactions ends up as HCO_3^-(aq) and CO_3^{2-}(aq) + H^+(aq).

There will be a balance between the two alternatives and the increase of free H^+ will lower the pH and make the solution acidic. The acidic environment will allow the alkali to be released from the mineral as e.g. Ca^{2+} or Mg^{2+}. The positive alkali cations reacts with the anions to form precipitation in the form of metal carbonate, such as $CaCO_3(s)$ or $MgCO_2(s)$. However, this reaction is favoured in a higher pH. An additive can therefore be added at this step to increase pH and thus enhance the precipitation, this is a so called *pH-swing* [15], [16].

In the indirect carbonation the alkali cations are extracted from the feedstock, which could be minerals such as serpentine or alkaline by-products and waste streams such as steelmaking slag [17], [14]. The extration is done using acids, molten salts or sodium hydroxide. For acids and molten salts, they are not consumed in the process and can be used multiple times where the sodium hydroxide is consumed by the reaction [16]. The extracted alkali ions can then in a later step be carbonated using CO_2 to produce carbonates. The carbonates produced in this manner, with only the cations present for the carbonation, will have less impurities than for the case of direct carbonation where the whole mineral is present. The process can reach high effectiveness in carbonation with high purity carbonates. However, for all the various ways of dissolving the mineral into alkali ions, there are large energy penalties, thus they require large amounts of energy. For the molten salts alternative the salts corrosive properties may also pose problems for large scale usage and for the sodium hydroxide, the consumption of it while dissolving the minerals will cause large amounts of it would be required [15], [16].

1.1.3 GHG emissions in Sweden

In the last decade, the GHG emissions in Sweden has declined with roughly 30% from approximately 69 million tons of CO_2-equivalent in 2010 to 49.523 million tons during 2022 [18], which could be lowered even more using CCS and CCUS technologies. According to the Swedish Environmental Protection Agency [19], the emissions from the Swedish pulp and paper industry (including printing) was 648 001 tons of CO_2-equivalent GHGs in 2022, which is accounts for 1.31% of the total emissions in Sweden that year. It should be noted that the global warming potential of the GHGs is set at the time frame of 100 years, GWP100, as recommended by the United Nations Framework Convention on Climate Change [20].

1.1.4 EU Emissions Trading System

A large part of the EU's climate policy to limit emissions and promote industries and companies to lower their emissions of GHGs is the EU Emission Trading System, the EU ETS. In the EU ETS some sectors, such as industries and aviation get free emission rights for their operations which then is distributed among the companies within that sector. If the companies emit more GHGs than they have emission rights for, they have to buy more emission rights at market price within the EU ETS. For companies that emit less than their allowance, they can either be saved up or sold at market price within the EU ETS [21]. The market price on the emission rights fluctuate and in 2022 and 2023 the price on GHG emissions has varied between 65 and 105 euro per ton GHG [22]. In 2022 the Swedish pulp and paper industry were given emission rights for 2.9 million tons of $CO_{2,eq}$ [23].

1.1.5 Kraft cycle

In the pulp and paper industry, a technology called the Kraft cycle is used to produce pulp that then can be turned into paper. In the Kraft cycle, wood chips are digested in a liquid called white liquor which is strongly alkaline with sodium hydroxide and sodium sulfide as main components. In the digestion process, the wood fibers is extracted from the wood chips to then be separated as pulp. The remainder after pulp separation is called black liquor. The black liquor has a high pH and consists of lignin and carbohydrates from the wood, together with residues from the white liquor such as water, sodium and sulphur. Water is evaporated from the black liquor that then is burned in a Recovery boiler that creates steam and electricity [24]. The remaining smelt is then blended with weak white liquor which creates Green liquor with dregs [25]. The green liquor is separated from the dregs and then added to a recausticizing plant. In a lime kiln, lime mud is converted into lime, mainly calcium oxides, using heat from a burner. Other than lime, flue gases is produced at the lime kiln. The lime produced at the kiln is then added to the recausticizing plant together with the green liquor, which produces white liquor that can be used in the first step together with wood chips. A schematic flowchart of the Kraft cycle is shown in Figure 1.1.

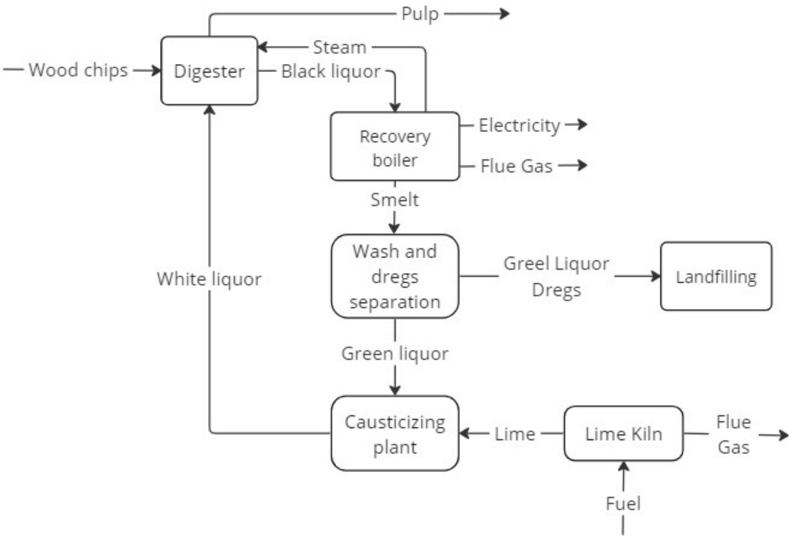

Figure 1.1: Schematic flowchart over the conventional Kraft cycle

1.1.6 Green Liquor Dregs

The dregs that are separated from the green liquor are called green liquor dregs, GLD. GLD are a highly alkaline sludge with a general pH between 11 and 13. The dregs can be separated from the green liquor using several different methods such as clarification via sedimentation and several different filtration techniques. According to Golmaei et al. [25], filtration techniques are more prominent for newer pulp mills due to a higher efficiency. GLD have a high content of calcium carbonate, $CaCO_3$ and Sodium carbonate, Na_2CO_3 [26], however GLD also contains other minerals with alkalis [27] and has a relatively high content of heavy metals such as cadmium, lead and zinc [28]. The high concentration of alkali in GLD makes it suitable for capturing carbon via carbonation.

As of today, there are two main ways of handling the dregs after they are separated from the green liquor, land-filling it or using it as a covering layer on landfills. In Sweden, GLD is since 2004 excluded from the ban of landfilling according to the Swedish Environmental Protection Agency regulations NFS 2004:4 [29]. According to the Swedish Tax Agency, landfilling GLD is granted a tax exemption due to the fact that there are no other viable options to landfilling to date [30], for other wastes the taxation is 725 kr/ton waste [31]. In 2023 however, the Swedish Environmental Protection Agency proposed an update to the regulations concerning GLD where the the Swedish Environmental Protection Agency eventually wants to have a restriction on landfilling and have recycling of organic wastes such as GLD [32], [33].

1.1.7 Earlier studies on carbonation of GLD

In the available literature there are very limited sources discussing alkaline waste materials from the pulp and paper industry for CCS via carbonation. In those articles calcium mud and slaker grits are the most prominent waste streams that are discussed with high possibility of being suitable for CCS via carbonation [34], [35]. Regarding the alkaline GLD, no sources was found that investigated the possibility of carbonating GLD for CCS except for the study by Leventaki [13] that this thesis is based on. According to Leventaki no earlier studies has been published regarding this topic.

1.2 Aim and Research questions

This thesis aims to investigate and show the potential prospects for CCUS by carbonation of green liquor dregs, GLD, a byproduct or waste stream from the Kraft cycle used at pulp mills. The purpose of the report is to give an early indication on if there could be enough environmental benefits to continue with the development of capturing, storing and utilizing carbon via direct aqueous carbonation of green liquor dregs.

The research questions for the thesis were:

1. How much CO_2 can be sequestered in the yearly Swedish production of GLD?
2. How much emissions of $CO_{2,eq}$ can be avoided by product replacement using carbonated GLD in conventional products?

3. Does the sequestration of CO_2 and avoided emissions of $CO_{2,eq}$ outnumber the emissions from producing the electricity needed to run the carbonation process?
4. What is the total emissions from carbonating GLD, including sequestration of CO_2, emissions from electricity generation and avoided emissions from product substitution?

2

Methods

In this chapter a general description of the methods used in this thesis is presented in sections 2.1-2.3 and the application of these methods is defined in section 2.4. To answer the research questions presented in section 1.2, an LCA on carbonating GLD for CCUS and a simple material flow analysis to estimate the scale and significance of potential CO_2 reduction via carbonation of the yearly Swedish production of GLD, was conducted.

2.1 Life Cycle Assessment

The framework for LCA is established through ISO 14044:2006 and consists of four steps, Goal and scope definition, Inventory analysis, Life cycle impact assessment and Interpretation [36], as shown in Figure 2.1.

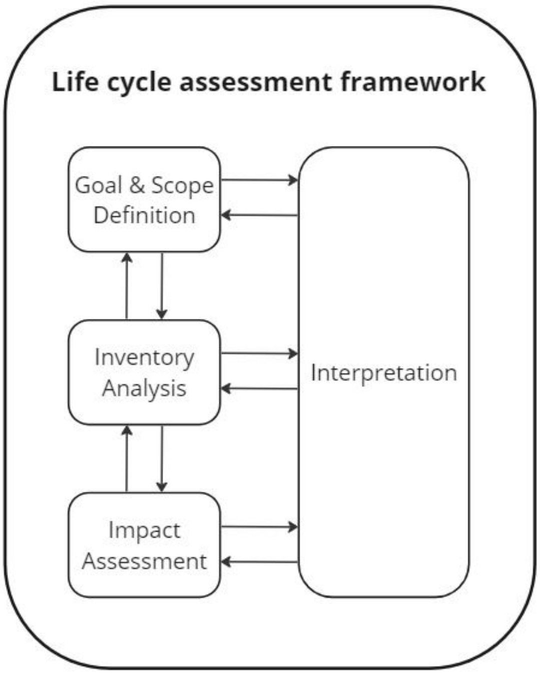

Figure 2.1: LCA framework according to ISO 14044:2006

In the first step, Goal and Scope definition the objective of the study is presented together with the research questions that the study is based on. Included in the objective of the study, the use of the study is presented. In this section the scope of the study should be presented. The scope should include the functional unit, an initial flowchart, the environmental impacts that are being considered, the system boundaries and allocation strategy [37].

It is in the Inventory analysis the model of the subject under study is formed. The Inventory analysis generally consists of three different steps. The first step is to create a more detailed flowchart of the model compared to the initial one, which shows the activities of the model and the flows of energy and materials. The next step is data collection, where the data needed to calculate the flows is gathered. The third step is the calculation of the used resources and the flows of products and emissions within and leaving the system. The flows are also calculated in relation to the functional unit that was chosen in the Goal and scope definition.

The third step is called the Life cycle impact assessment, LCIA. In the LCIA the flows of emissions are used to evaluate the environmental impacts they might have on the environment. Generally, the LCIA is divided into steps. The two main and compulsory steps are *Classification* and *Characterisation* [37]. In the classification step the midpoint environmental impacts are set, such impacts can be for example acidification potential, eutrophication potential and global warming potential, GWP. It is important to note that the emissions calculated in the inventory analysis step can impact multiple midpoint environmental impacts [38]. In the Characterisation step the different emissions in each midpoint category is calculated to have a joint base to show the relative impacts of each emission. The mass of the emissions are multiplied with a midpoint characterisation factor specific for the emitted substance [38]. This gives each emission in a given midpoint impact category the same base and can thus be compared. The LCIA can also be extended with additional steps such as Normalisation, Grouping and Weighting to be able to compare and rank the different impact categories. Doing this can give a one-dimensional index of the environmental performance of the system under study. It is important to note that normalising and weighting the different impacts is subject to subjective values [37].

The last step of the LCA is the Interpretation where the results of the LCA is reviewed. Even though the Interpretation step is placed at the end of this list, it should be performed iteratively during the whole process of the LCA [37] as shown in Figure 2.1. The Interpretation step gives the LCA analyst a tool to analyse and present the results from the two previous sections of the LCA and make suggestions and draw conclusions. This step can be used to show the hot spots of emissions within the system, where in the life cycle most of the emissions are released. In the Interpretation, a crucial step is to perform a sensitivity analysis to determine the influence of the different parts of the model by changing the parameters. In the Interpretation, limitations of the study and suggestions to aid with decision making should also be presented [37], [38].

2.2 Ex-ante LCA

Conventionally, LCAs are most commonly used on products and services that already exist. However, to be able to predict the environmental impacts of not yet developed technologies something else needs to be done. This is called a prospective LCA, where the time frame for the analysis is set at a future stage. Specifically, if the technology under study at present time is in the beginning of development but at the time frame for analysis is assumed to be a mature technology the study is called an Ex-ante LCA [39]. According to Cucurachi et al. [40], some of the biggest problems with Ex-ante LCA is the lack of primary data since the technology under study is not yet fully developed. To cope with this problem, Cucurachi et al. proposes that learning curves, secondary data and assumptions can be used.

According to van der Giesen et al. [41], a way of handling lack of data when doing LCAs for technologies in early development is to use data from current similar technologies to make assumptions on how the technology under investigation could work at a larger scale.

However, it is not only the availability of data that is a main problem. For the data available from the early stage development, scaling it up to the extent of where the fully developed technology may lead to some major uncertainties. There are a few different ways of scaling data for use in Ex-ante LCAs. In this study, the scale up framework by Piccinno et al. [42] will be used together with formulas from chemical engineering regarding momentum and mass transfer [43] to model the technology at industrial scale.

2.3 Material Flow Analysis

Material Flow Analysis, MFA, is an assessment tool which determines and quantifies the flows of materials within a specific system. The system is in a defined boundary in terms of time and space. Within the system boundaries material balances are implemented with the law of conservation of matter. The material balances shows the connections of the inputs, flows and outputs of the system [44]. MFAs can be used together with LCAs to widen the boundaries of the LCA [45], which for example could be used to scale up the results from an LCA to a larger scale.

2.4 Performing the LCA and the simplified MFA

This thesis consists of an Ex-ante LCA study on the specific case of carbonating GLD from the paper and pulp industry in Sweden for CCUS. This LCA was performed by making a model over the presumed process steps needed for carbonation. The model was made with values from a lab experiment done by Emmanouela Leventaki [46] and scaled up using the Piccinno framework [42] to the production of the Smurfit Kappa pulp mill in Piteå. It was then scaled up using a simplified MFA approach to take the LCA results showing emissions per functional unit and scale it to total emissions for Sweden. To explore the potential for carbon capture via carbonation of GLD, different scenarios were evaluated to identify what type of solutions could generate the greater negative GHG emissions.

3

Goal and scope definition

In this chapter, the goal and scope of the study will be presented according to Chapter 2.1.

3.1 Goal

The goal of the study was to make an early and general evaluation of carbonating GLD for CCUS for a possible future scenario with a large scale application of the technology. The LCA investigates three scenarios in relation to utilization:

1. Landfilling the carbonated GLD
2. Using the carbonated GLD for substitution of clinker
3. Using the carbonated GLD for substitution of gravel

It intended to help show if the technology shows promise and thus should be further investigated or not. To be able to do that, the study aims to answer the research questions stated in section 1.2.

3.2 Scope

In this section the scope of the study will be presented. The scope includes the functional unit, system boundaries, an initial flowchart, assessment method and impact categories, data acquisition and allocation method.

Functional unit

The function of the technology is to store carbon from flue gas in green liquor dregs. To be able to compare different uses for the carbonated GLD the functional unit, FU, was set to 1 ton uncarbonated GLD. This also allows for easy scaling to the national level.

Geographical boundaries

The geographical boundaries of the study is set to Sweden. However, for the carbon intensity for the products chosen for substitution, no values from Swedish production were available within the used data set. For these values the geographical boundaries had to be extended to include Europe to be able to get data.

Temporal boundaries

As the first research question is chosen as *How much CO_2 can be sequestered in the yearly Swedish production of GLD?*, the temporal boundary is set to one year. It is important to note that it is a calendar year and not production year since many industries have yearly production stops. Since the study is an Ex-ante LCA, the time frame is set to an arbitrary future where the technology is assumed to be matured and implemented into the Swedish pulp and paper industry.

Flowchart

The initial flowchart, shown in Figure 3.1, was used in the modelling in the Inventory analysis as a base to build around. It shows the assumed addition to the conventional Kraft cycle ass the carbonation step. The red dashed box shows where the boundary for the LCA was set.

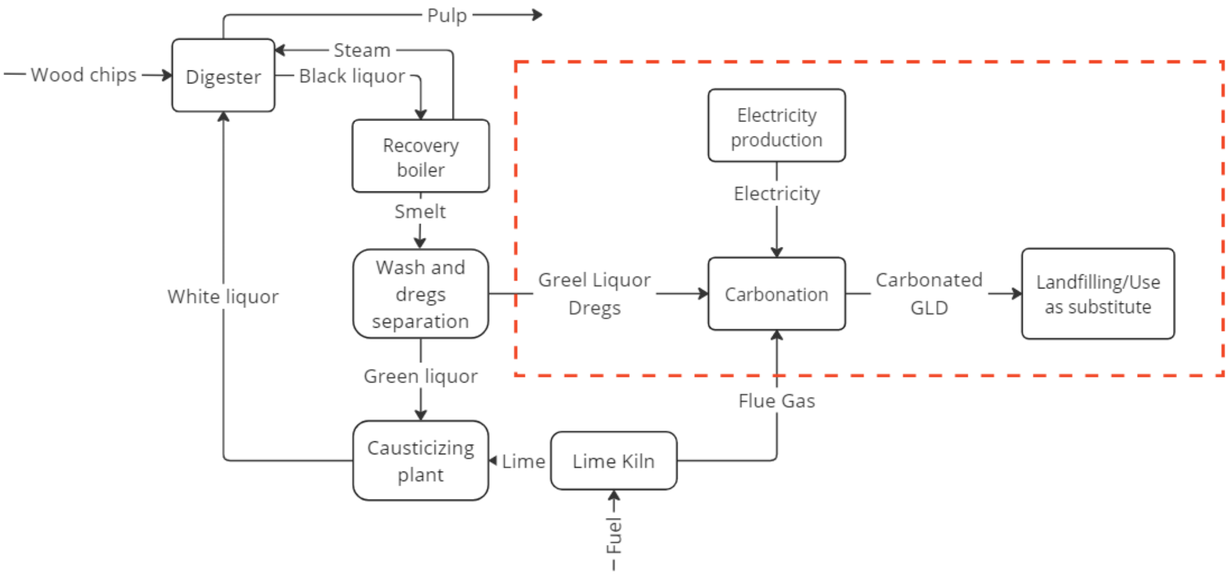

Figure 3.1: Initial flowchart over the study

Data acquisition

The model of the assumed future state of the technology was build and calculated in Microsoft Excel. Data acquisition for the background data, which was carbon intensity, was collected from the European Energy Agency for the carbon intensity of electricity generation in Sweden [47] and by using OpenLCA and ecoinvent 3.9.1 cutoff database for the carbon intensity of production of the materials that was assumed to be substituted. The foreground data was received through the experimental group at the chemical engineering department at Chalmers University of Technology, literature search and through the pulp industry, specifically interviews with representatives from the pulp industry and given data sheets.

Impact category and assessment method

As impact category for the study, only climate change with global warming potential over 100 years, GWP100, was chosen. That was since the purpose of the study was to show the potential negative emissions by CCUS via carbonation of GLD. With that as the only impact category, the assessment method was chosen as IPCC 2021 method through the ecoinvent 3.9.1 database in OpenLCA.

Allocation method

Since the green liquor dregs are a waste or by product from the pulp industry and the comparative analysis only concerns its carbonation or not, only the emissions related to the implementation of the carbonation technology are included in the LCA. To be able to compare different scenarios for the use of the carbonated GLD system expansion was used. With the system expansion it was possible to calculate the avoided emissions from replacing a conventional product with the carbonated GLD. Clinker and gravel were chosen as potential products that could be substituted.

4

Inventory analysis

In this section, the methods used to gather the data and form the model will be presented. The inventory analysis for this study consisted of a literature study, interviews and e-mail contact with representatives from industry, and modelling.

4.1 Lab data

The base to model around was lab data from labs by Emmanouela Leventaki [46]. In the data from Leventaki, data for the reaction time to full saturation and capture yield of CO_2 $[gCO_2/gGLD]$ was presented for five different concentrations of GLD in water, 5wt%, 10wt%, 15wt%, 20wt% and 25wt%. The result of the different mixtures is presented in Table 4.1.

Table 4.1: Lab results for the five scenarios

Concentration [%]	**Sample size** [g]	**Reaction time** [min]	**Captured CO_2** [g]	**Capture yield** [$gCO_2/gGLD$]
5	3	24	0.53	0.177
10	6	36	0.69	0.115
15	9	48	0.79	0.088
20	12	52	0.96	0.08
25	15	80	1.08	0.072

The scenario with 5wt% GLD in water was used as base for the modelling due to the fact that it had the highest capture yield combined with the lowest required time for full carbonation.

To gain homogeniety, the mixtures were stirred before carbonation. Leventaki tested three stirring scenarios, 1 hour, 1 day and 2 days. For the 1 hour scenario the capture yield were $0.063 gCO_2/gGLD$ and for both 1 and 2 days the capture yield was $0.177 gCO_2/gGLD$, therefor it was decided that 1 day of stirring would be used in the modelling.

In the lab setup a 60 ml bubble column reactor was used and the gas that was used for carbonation was 30% CO_2 and 70% N_2 which were flowing through the reactor at a flow of $200 ml/min$. Both the temperature and pressure were ambient and thus assumed to be 25°C and 1 atm.

4.2 Data from industry

To be able to gather data regarding the processes at the current pulp industry interviews and conversations over e-mail with representatives from three different pulp mills, Smurfit Kappa Piteå, Nordic Paper Bäckhammar and Östrands massafabrik. The main goal of the contact with the industry was to answer the questions

- How much pulp is produced per year at the specific mill?
- How much GLD is produced per year at the specific mill?
- How is the GLD handled at the specific mill?
- How much flue gas is produced at the mill?
- How is the flue gas handled?
- Is the production running 24 hours per day? How many production days do you have per year?

4.2.1 Smurfit Kappa

The representatives from Smurfit Kappa Piteå, Urban Lundmark and Jeanette Bergstedt, were both present at an interview and supplied info and data sheets through e-mail. In the interview they answered that at their mill, 540 000 tons of pulp and roughly 10 000 tons of GLD is produced each year with a mean dryness of 45% (weight% of dry material, the rest is assumed to be water). The mill has a production stop of a week, seven days, each year and thus has 358 production days per year with production 24 hours per day.

The GLD produced at Smurfit Kappa Piteå is used as material for construction of covering layers at external landfills not owned by Smurfit Kappa themselves. Therefore the GLD they produce is not classified as being put on landfill as waste. Even though GLD is excluded from the taxation of land filling, there are costs for handling the GLD, both for putting it on landfill and as in their case another company that handles the GLD to be used in a covering layer.

In the interview, Lundmark describes how the flue gas is first cleaned from particulate matters to be used in the mill to dry sawdust that then is used as fuel in the lime kilns. This lowers the temperature of the flue gas to approximately 110°C. The last step before the flue gas is released is in a heat exchanger before being released at approximately 70°C.

Bergstedt provided report sheets from their 2022 analyses and measurements of the flue gas from their lime kilns, their recovery boiler and their combined chimney [48]. The data sheets showed that the concentration of CO_2 in the flue gas from the recovery boiler after electrical flue gas filter was 15.06%. For the lime kilns, the report sheet had data for two different fuels, wood powder and bio-oil with the CO_2

concentration at 27.61vol% and 24.23vol% in the flue gases for the respective fuel [48].

4.2.2 Nordic Paper Bäckhammar

The representatives from Nordic Paper, Anna Asplund and Sofie Semstrand were both present at an interview. In the interview they stated that the production of pulp and GLD over 2022 were 222 000 and 3 887 tons respectively. In the interview they stated that their GLD is blended with ash among others to be used as a covering layer on top of landfills approximately 1 km from the mill. For their lime kilns, the main fuel that is used is bio oil and wood powder. However, at the start up of the lime kilns fossil fuel is used but according to Semstrand only 2% of the fuel used in the lime kilns is from fossil sources. For the flue gas produced at Nordic Paper Bäckhammar, no flows or CO_2-concentrations were provided. It was given though that the flue gas is cleaned and its heat is used in the process so when the flue gas is released it holds a temperature of 50-55°C.

4.2.3 Östrands massafabrik

The representative from Östrands massafabrik, Christian Kugge, did not attend an interview but gave answers to the second and third questions through e-mail. In the e-mail he states that they produce 15 000 tons of GLD per year with a wetness of 44%. In the e-mail he states that the GLD produced at Östrands massafabrik is landfilled. To complete the information needed about production of pulp a search showed that the production of pulp at Östrands massafabrik is approximately 900 000 ton/year [49].

4.3 Modelling

The modelling of the system was done based on the Scale-up framework by Piccinno et al. [42]. At first, the laboratory data provided by Leventaki was used to make a flowchart over the lab process, see Figure 4.1. The flowchart was then combined with the flowchart of the Kraft process showed in Section 1.1.5 to create flowcharts over the model of the carbonation of GLD in the Kraft cycle. Figures 4.2 and 4.3 show the flowcharts for the model in two scenarios, one where the carbonated GLD is landfilled after filtration and one where the carbonated GLD is dried to then be used as substitute for clinker or gravel.

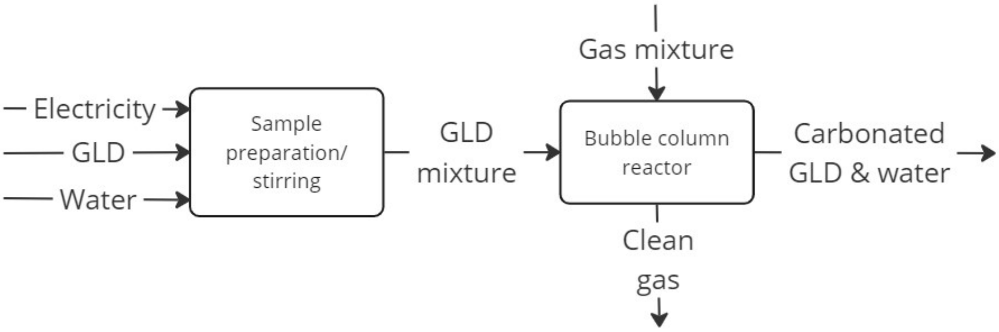

Figure 4.1: Flowchart over lab setup

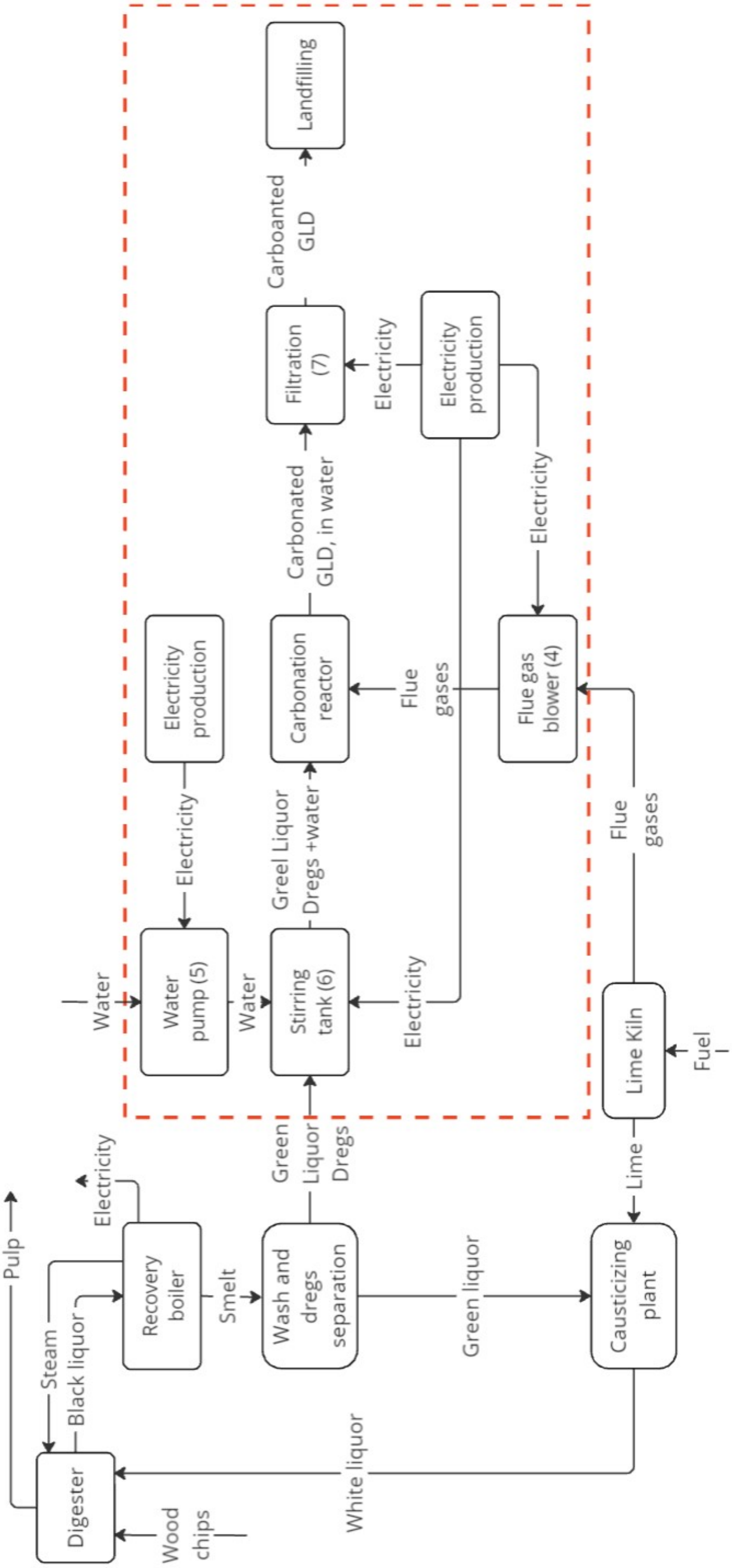

Figure 4.2: Flowchart over model with landfill as endpoint

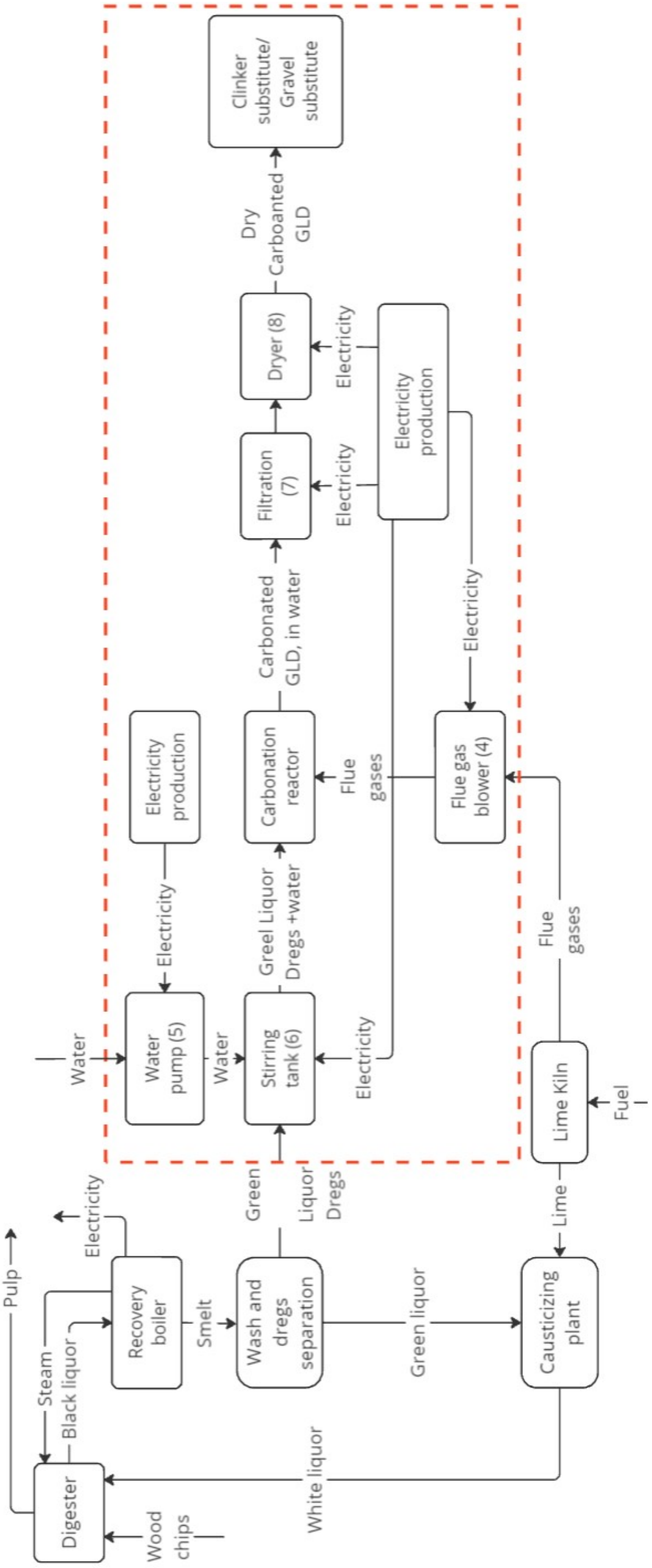

Figure 4.3: Flowchart over model with substitution in clinker or gravel

In Figures 4.2 and 4.3, the red box shows the boundary set to the LCA.

Following the Scale-up framework [42], the different process steps were scaled up separately to later on be linked together to get a full result of the scaled up process. To be able to, in a relatively easy and straightforward way, scale up the data from the lab results it was determined that the scaled up model would be using carbonation in batches instead of carbonation in a continuous reactor. Therefore, the energy consumption for each process was first calculated for one batch. The calculated energy consumption per batch were then multiplied with the estimated number of batches that was to be run each day and then with the assumed number of operating days per year, the energy use was converted to electricity consumption in terms of $kWh/year$ according to equations A.1-A.3 in Appendix A [50]. In that way, the electricity consumption for each process over a span of a year was calculated to then be linked with the other processes. The modelling was first done to model a single pulp mill to then be expanded through extrapolation to encompass a scenario where all GLD produced in Sweden over a year was carbonated. The modelling was therefore based on the data from Smurfit Kappa Piteå since they provided the most complete data.

The different process steps that were modelled were *Reaction time(1)*, *Batch size(2)*, *Flue gas flow(3)*, *Flue gas pumping(4)*, *Headloss from pumping water(5)*, *Stirring(6)*, *Filtration(7)* and *Drying(8)*. The resulting need of electricity for each step is presented below. The calculations of each modelling step are described in more depth in Appendix A.

4.3.1 Reaction time (1)

An assumption was made that the reaction time would be linearly dependent on the concentration of CO_2 in the flue gas. It was assumed that for half the concentration from the lab setup, which would be 15%, the reaction time for full reaction would be doubled. Since the flue gas from the lime kilns had a higher concentration of CO_2 than the flue gas from the recovery boiler, it was chosen to be used in the modelling. At this stage it was assumed that the flow was large enough and at a later stage the flow was investigated to make sure that it was sufficient for the carbonation. As described in section 4.2.1, there were data for two different fuels used. For the modelling a mean of these values was used, which resulted in 25.92% CO_2 in the flue gas. Given that concentration, the reaction time was calculated to be 30.53 $min/batch$.

4.3.2 Batch size (2)

It was chosen that for the model, multiple reactors would be used so that there would be a continuous start and end of batches. With that the amount of batches per day could be calculated with the reaction time from the earlier step, which resulted in 47.17 batches per day. With the yearly production of GLD and the amount of production days per year, the size of each batch could be calculated to be 0.592 $tonGLD/batch$. With an assumed concentration of GLD in water of 5wt%, the need of water per batch was calculated according to equation A.6 in Appendix A to be 11.29 $m^3/batch$.

4.3.3 Flue gas flow (3)

The assumption made in Section 4.3.1 that the flow of flue gas was sufficient needed to be tested. Using the flow of gas in the lab setup with a flow of $200 ml/min$ for 3 gram of GLD, the required flow was first extended in terms of $m^3/(h * tonGLD)$ and then matched with he calculated batch size from Section 4.3.2 which gave a required flow of 2 369 m^3/h. In the report sheet provided by Bergstedt [48], the flow of flue gas from the lime kilns were presented for gas flow of wet, hot gas at low pressure, wet gas at normal state (273 K and 1 atm) and dry gas at normal state. To compare with the lab data, the needed flow of flue gas for carbonation was compared with the flow of dry gas at normal state. The mean value of flue gas flow, for the two fuels, was then 30 979.5 m^3ndg/h, where ndg stands for dry gas at normal state. Thus the flow of flue gas is much larger than the needed flow and thus sufficient for full carbonation.

4.3.4 Flue gas pumping (4)

Modelling the energy needed for pumping flue gas to the reactor from the lime kilns it was assumed that only the needed flow of 2 369 m^3/h would be pumped and that the gas would be in dry and normal state.

The modelling of the energy use from blowing flue gas was based on an energy analysis and life cycle assessment on Post-combustion Carbon Capture technologies by Zhang et al. [51]. That is due to difficulties in finding a proper model to use for energy consumption from blowing flue gases. In the assessment from Zhang et al. [51], both the flow of the blown flue gas and the energy consumption of the blower is stated as 781.8 $kgfluegas/s$ and 8.2 MJ/s. To model the energy consumption for the blower a formula for energy consumption per gas flow was derived from the values from Zhang et al. according to Equation 4.1.

$$\frac{8.2\ MJ/s}{781.8\ kg/s} = 0.01049\ MJ/kg \tag{4.1}$$

Together with the needed flow and with the density of the dry flue gas at normal state presented in the emission reports from Smurfit Kappa Piteå [48], the energy use for pumping the flue gas was calculated to be 35.95 MJ/h. Assuming that the pumping is done 24 hours per day for 358 days per year, the yearly energy use was calculated to be 308 882.86 $MJ/year$, which was converted to be 85 808 $kWh/year$.

4.3.5 Headloss from pumping water (5)

Due to a high need for water in the carbonation process the energy needed for pumping the water had to be modelled. It was assumed that the pumping of water would be constant and with $11.29m^3/batch$ and 47.17 batches per day, the flow would be $532.3m^3/day$ or $0.00616m^3/s$.

To gather the relevant information regarding the modelling parameters regarding the pumping of water several assumptions had to be made. The needed parameters were distance that the water needed to be pumped, the height the water needed to be pumped, the diameter of the tubing, the fittings and bends of the tubing and the efficiency of the pump that would be used.

Using Google Maps measurement tool, several pulp mills were measured. With the assumption that the general mill was in a circular shape the mean radius of 300m was used as length of the tube. Assuming the reactor to be cylindrical with a height of 4 meters standing on the same level as the pump, the height was assumed to be 4m. Test of the effect of the diameter of the tube together with fittings and bends due to different turbulence scenarios was done according to equations A.10-A.14 in Appendix A [43], [52], [53]. The conclusion was that a standard tube with an inner diameter of 0.1m would be used with two 90° bends and no other fittings than pipe entrance and tank inlet. According to Piccinno et al. [42], the efficiency of the pump could be assumed to be 85%.

With these parameters, the power needed to pump the water was calculated to be $0.284kW$ following equation 4.2 [43].

$$P = \frac{\dot{Q} * H * g * \rho}{\eta_{pump}} \tag{4.2}$$

Where g is the gravitational constant 9.82 m/s^2 and ρ is the density of the water at the assumed 25°C, which is $0.997ton/m^3$ [54]. With the needed power of $0.284kW$, the yearly electricity consumption for pumping the needed water would be 2 $440kWh/year$.

4.3.6 Stirring (6)

For the modelling of the stirring of the mixture, 5wt% GLD in water, for 24 hours, the formula from the Scale-up framework by Piccinno et al. [42], was used. From the Scale-up framework it was chosen that the stirrer would be a stirrer with axial flow. Following the framework, with a density of dry GLD from dos Santos et al. [26] and an assumed content of 55% water in the wet GLD, the energy needed to stir the mixture could be calculated as shown in Appendix A.6. The calculation gave that the needed to mix one batch for 24 hours would be $9.237kJ/batch$, which for a production year would use 43 $333kWh/year$ in electricity.

4.3.7 Filtration (7)

The modelling steps above describes the processes before carbonation, but after the carbonation is complete the carbonated GLD, cGLD, needs to be separated from the water in the mixture. For that it was assumed that it would be done through filtering because that is how GLD conventionally is separated from green liquor in the pulp mills according to the representatives from Smurfit Kappa Piteå. No data regarding the electricity consumption from filtering out the GLD was given from Smurfit Kappa Piteå, so the Scale-up framework was used. According to the Scale-up framework by Piccinno et al. [42], the energy needed for filtration can be estimated between 1 and 10 $kWh/ton\ Filtrate$ depending on particle size. Due to limited data and knowledge on the particle size of the cGLD, the highest value was chosen. However, as a parameter for sensitivity analysis a mean value of 5.5 $kWh/ton\ Filtrate$ was also tested.

In the lab data by Leventaki [46], it was assumed that all added weight after carbonation was due to added CO_2. Therefore it was assumed that the amount of water in the filtered cGLD would be the same as for the GLD added to the mixture before carbonation. Thus, the mass of filtrate after each batch was calculated according to Equation 4.3.

$$m_{cGLD} \ = \ m_{GLD} \ + \ m_{CO_2} \tag{4.3}$$

Where m_{cGLD} is the mass of filtrate, m_{GLD} is the mass of GLD in each batch before carbonation and m_{CO_2} is the mass of CO_2 that has been bound to the GLD in the carbonation.

Given the calculated mass of filtrate per batch, batches per day, operating days per year and the two scenarios 5.5 and 10 $kWh/ton\ Filtrate$, the electricity consumption from filtration of the cGLD was calculated to be 64 735$kWh/year$ and 117 700$kWh/year$ respectively.

4.3.8 Drying (8)

For the cases where the cGLD were to be used as substitution in clinker or gravel it was assumed that the cGLD had to be dry before being transported from the pulp mill. Therefore a drying step had to be modelled. The calculations for the energy use for drying the cGLD was done according to Equation 4.4 below, from the Scale-up framework by Piccinno et al. [42].

$$Q_{dry} \ = \ \frac{C_{p,cGLD} * m_{cGLD} * (T_{boil} - T_0) \ + \ \Delta H_{vap} m_{vap}}{\eta_{dry}} \tag{4.4}$$

Where Q_{dry} is the energy needed, $C_{p,cGLD}$ is the specific heat capacity for cGLD, m_{cGLD} is the mass of moist cGLD, T_{boil} is the boiling temperature for the water, T_0 is the initial temperature, ΔH_{vap} is the heat of vaporisation for the water that is to be evaporated, m_{vap} is the mass of the water that is to be evaporated and η_{dry} is the efficiency of the dryer, which was assumed to be 80% as per the Scale-up framework.

With that, the energy needed for drying a batch of cGLD to 0% wetness was calculated to be 1 072 768.85 $kJ/batch$ and would thus use 5 032 521 $kWh/year$ worth of electricity.

The assumptions made and values of the parameters used to calculate the energy is presented in Appendix A.7.

4.3.9 Summary of model

After each process step was modelled and their respective electricity consumption was calculated, they were connected as described in Piccinno et al. [42]. In this step the electricity consumption, for each step and total, was also calculated in terms of functional unit. Thus, the yearly electricity consumption for the model of Smurfit Kappa Piteå was divided with their annual production of GLD. In Table 4.2, the electricity consumption for each process step is presented with summaries with and without drying for two scenarios of filtration.

Table 4.2: Electricity consumption, for Smurfit Kappa Piteå and per functional unit

Process step	**Yearly electricity consumption** $[kWh/year]$	**Electricity consumption per functional unit** $[kWh/tonGLD]$
Flue gas pumping	85 808	8.581
Headloss	2 440	0.244
Stirring	43 333	4.333
Filtration, mean value	64 735	6.474
Filtration, high value	117 700	11.770
Drying	5 032 521	503.252
Total, mean filtration and without drying	196 316	19.632
Total, high filtration and without drying	249 281	24.928
Total, mean filtration	5 228 836	522.884
Total, high filtration	5 281 801	528.180

For the analysis of sensitivity based on the value of filtration energy, the following four charts in Figure 4.4 can be used. The charts shows that when analysing the emissions from electricity generation, the value for filtration energy makes a significant impact for the case where there is no drying but with a drying process step added the impact of the value makes maximum 1% difference. However, when comparing the emissions from using the two values of filtration compared with the amount of sequestered CO_2 it can be seen that both measures up to less than 0.05% compared to the negative emissions from the sequestration. The higher value of filtration energy is therefore chosen for further calculations.

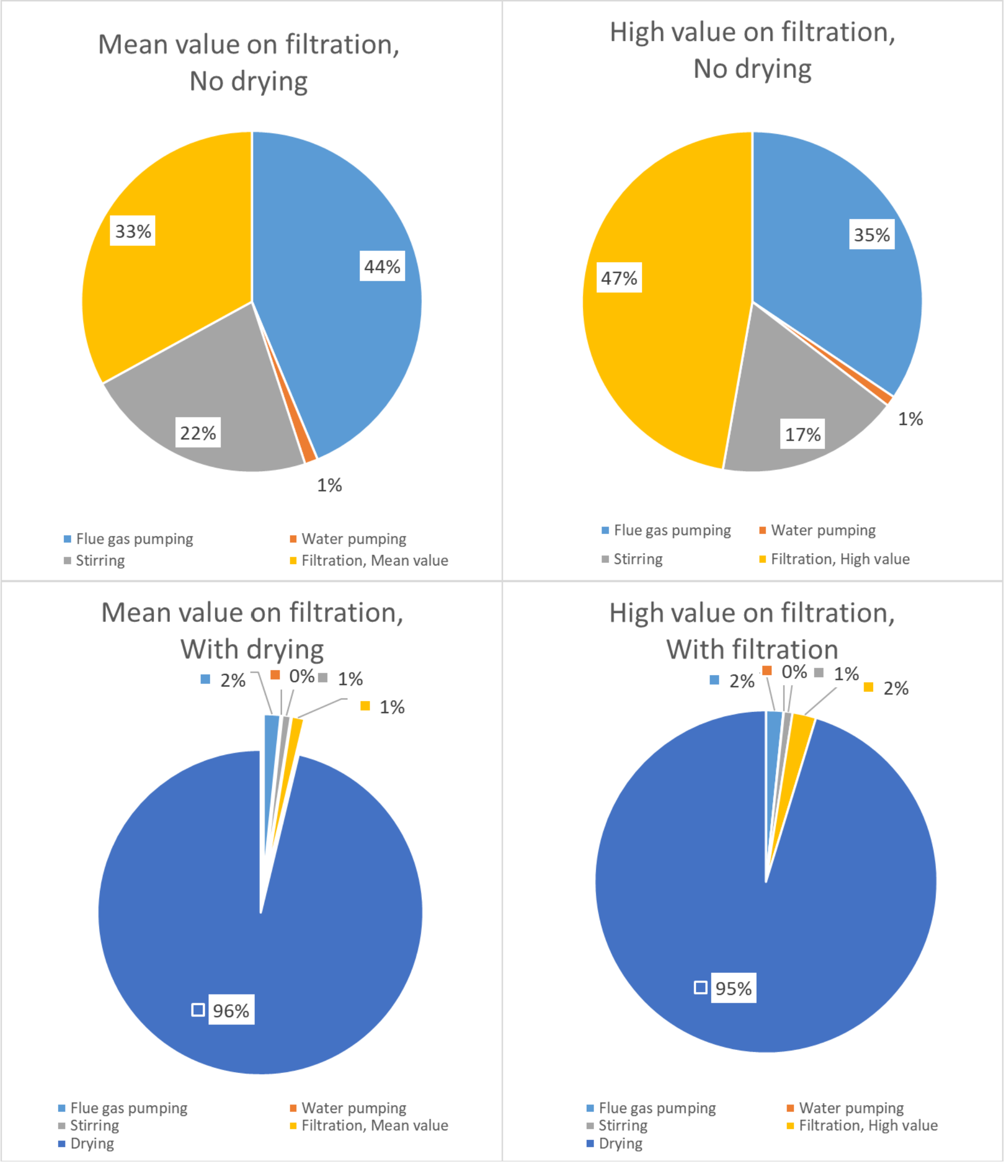

Figure 4.4: Chart over partial emissions for each process step

4.3.10 Product substitution

As described in Sections 4.3.8, it was assumed that for use as substitution, the cGLD had to be dried. To calculate the avoided emissions, the mass of dry cGLD had to be calculated. As the added weight was assumed to be due only to sequestrated CO_2, the weight of the dried cGLD could be calculated according to Equation 4.5.

$$m_{cGLD,dry} = m_{GLD}(1 - u_{GLD}) + m_{CO_2seq} \tag{4.5}$$

Where $m_{cGLD,dry}$ is the mass of the dried cGLD, m_{GLD} is the mass of GLD input, u_{GLD} is the water content in the input GLD and m_{CO_2seq} is the mass of the CO_2 that is sequestrated in the carbonation, which can be expressed in terms of input GLD as $0.177 * m_{GLD}$. Adding 10 000 tons of input GLD per year with a water content of 55% ($u_{GLD} = 0.55$) gives an amount of 6 270 tons of dry cGLD produced each year at Smurfit Kappa Piteå. Relative to the functional unit, the amount of dry cGLD is 0.627 ton dry cGLD per ton input uncarbonated GLD.

Due to the high content of calcium carbonates in GLD, and with the assumption that the sequestered CO_2 would contribute to an even higher content of calcium carbonates cement was investigated as a possible product that could be substituted. According to Quina and Pinheiro [27] and also Martínez-Lage et al. [55], GLD is not suitable as substitution for produced cement for use in concrete. However, Quina and Pinheiro [27], claim that it is feasible to use GLD as a substitution for up to 10% of clinker in the production of Portland cement and can after washing be used as aggregate in road pavement construction. Thus, the products that was assumed to be replaced with the cGLD was chosen to be clinker and gravel, due to its use as aggregates in pavement constructions such as asphalt.

4.4 Emissions

As described in Section 4.1, the yield of CO_2/GLD of 0.177 together with the yearly production of GLD 10 000 tons of GLD at Smurfit Kappa Piteå, the yearly sequestration of CO_2 would be 1 770 ton CO_2 per year for Smurfit Kappa Piteå. Relative to the functional unit, the sequestration would be 0.177 $tonCO_2/tonGLD$.

From the European Environment Agency, EEA [47], the carbon intensity of electricity production in Sweden was 7 grams of CO_{2eq} per kWh ($7*10^{-6}$ $tonCO_{2eq}$/kWh). Combing the carbon intensity with Table 4.2 gave the resulting emissions of each process step for the modelled case based on Smurfit Kappa Piteå and per functional unit. The result is presented in Table 4.3.

Table 4.3: Emissions from electricity generation, for Smurfit Kappa Piteå and per functional unit

Process step	**Yearly emissions** $[tonCO_{2eq}/year]$	**Emissions per functional unit** $[tonCO_{2eq}/tonGLD]$
Flue gas pumping	0.601	$6.01*10^{-5}$
Headloss	0.017	$1.71*10^{-6}$
Stirring	0.303	$3.03*10^{-5}$
Filtration, mean value	0.453	$4.53*10^{-5}$
Filtration, high value	0.824	$8.24*10^{-5}$
Drying	35.228	$3.5228*10^{-3}$

As stated in Section 4.3.10, clinker and gravel was used as potential products that could be substituted up to 10% with cGLD. Using OpenLCA software, datasets within Ecoinvent 3.9.1 cutoff database for clinker production and gravel production processes could be identified and the environmental impact from producing 1 ton of respective product could be calculated with IPCC 2021 Impact assessment method within OpenLCA.

For clinker, a dataset for clinker production in Europe without Switzerland and Austria [56], was used. It was chosen due to difficulties with finding datasets within the Ecoinvent database for production in Sweden. Using the dataset the carbon intensity of producing 1 ton of clinker was calculated to be 0.929595 $tonCO_{2eq}/tonClinker$.

For gravel, a dataset for production of crushed gravel in Switzerland [57], was used. As for the clinker, it was chosen due to difficulties with finding datasets within the Ecoinvent database for production in Sweden. Using the dataset the carbon intensity of producing 1 ton of crushed gravel was calculated to be 0.00354128 $tonCO_{2eq}/tonGravel$.

With the amount of produced dry cGLD of 6 270 tons per year for Smurfit Kappa Piteå and 0.627 ton per FU, the avoided emissions from replacing production of the two products could be calculated. The results are presented in Table 4.4.

Table 4.4: Potentially avoided emissions from product substitution

Substituted product	**Avoided yearly emissions** $[tonCO_{2eq}/year]$	**Avoided emissions per functional unit** $[tonCO_{2eq}/tonGLD]$
Clinker	-5 829.6	-0.58296
Gravel	-22.2	-2.22*10^{-3}

To check the robustness of the model and the influence of the emissions from electricity generation, a parameter that was checked in the sensitivity analysis was the carbon intensity of electricity generation. The carbon intensity of Sweden's electricity generation was in 2022 one of the lowest in EU according to the EEA [47]. Thus, the mean carbon intensity for electricity generation in EU was chosen, which according to the EEA was 251 grams of CO_{2eq} per kWh (251*10^{-6} $tonCO_{2eq}$/kWh) in 2022 [47]. With that value for carbon intensity the resulting emissions from electricity production for each step would be as presented in Table 4.5.

Table 4.5: Emissions from electricity generation for Smurfit Kappa Piteå and per functional unit. With mean carbon intensity for electricity generated in EU

Process step	**Yearly emissions** $[tonCO_{2eq}/year]$	**Emissions per functional unit** $[tonCO_{2eq}/tonGLD]$
Flue gas pumping	21.54	2.15*10^{-3}
Headloss	0.61	6.12*10^{-5}
Stirring	10.88	1.09*10^{-3}
Filtration, mean value	16.25	1.62*10^{-3}
Filtration, high value	29.54	2.95*10^{-3}
Drying	1263.16	1.26*10^{-1}

4.5 Scale-up to Sweden

To scale up the results from the model based on Smurfit Kappa Piteå to Sweden, the yearly production of GLD in Sweden needed to be estimated. To do that a general ratio of how much GLD is produced per ton pulp produced was calculated for the three mills. Using the data presented in Section 4.2, it was calculated that the mean ratio was 0.0176 $tonGLD/tonPulp$. From the Swedish Forest Industries (Skogsindustrierna) [58], it could be gathered that the production of pulp in Sweden in the year 2022 was 11.7 million tons, which with the ratio above gave an estimated production of 205 507 ton GLD in Sweden in 2022.

A ratio of GLD production in Sweden over GLD production at Smurfit Kappa Piteå was used to scale up the results from the model of carbonation of GLD at Smurfit Kappa Piteå. The ratio was calculated to be 20.55074 and with that the result shown in Table 4.6 was calculated.

Table 4.6: Emissions from process steps, sequestration of CO_2 and product substitution if all GLD produced in Sweden over a year is carbonated

Process step/ Product replacement	**Yearly emissions** $[tonCO_{2eq}/year]$
Sequestered CO_2	-36 375
Flue gas pumping	12.3
Headloss	0.4
Stirring	6.2
Filtration, mean value	9.3
Filtration, high value	16.9
Drying	724.0
Clinker production	-119 781
Gravel production	-456

5

Results and Interpretation

In this section, the results and interpretation of the LCA will be presented. The results will be presented in form of an LCIA. Due to the scope of this study, the only impact category analysed is Climate change and the results that is presented in this section is therefore only the emissions connected to electricity generation, storage of CO_2 and avoided emissions of CO_2 via product substitution. Since only one impact category is analysed, no normalization, grouping or weighting was needed. Table 5.1 shows the summed up emissions for the three scenarios, Figure 5.1 and 5.2 shows the contributions to the climate change potential for the three emission points within each scenario and Figure 5.3 shows the emission points when the EU-electricity mix is used.

5.1 Climate change

The results presented in Table 5.1, shows that the scenario where the cGLD could be used as a substitute for clinker, for use in production of portland cement, has the highest negative emissions with a total of over -0.756 tons of CO_{eq} per ton input GLD. For the scenario where the cGLD would be landfilled or used as cover for landfills and the scenario where the cGLD would be dried and used to replace gravel, the negative emissions were similar with -0.177 and -0.176 tons of CO_{eq} per ton input GLD respectively.

With the result shown in Figure 5.1 the first, second and third research questions stated in Section 1.2 can be answered. Assuming that in a future time setting, defined by the time frame stated in Section 3.2, where all of the GLD that is produced in Sweden is carbonated, a total amount of 36 375 tons of CO_{2eq} could be sequestered by aqueous carbonation according to the model. For the scenario with substitution of clinker production, the maximum avoided emissions would be equal to 0.31% of the total emissions of Sweden in 2022 and 24% of the emissions from the Swedish pulp and paper industry in the same year. For the other two scenarios, the maximum avoided emissions could sum up to 0.07% of Sweden's emissions in 2022.

Table 5.1: Total emissions from carbonating GLD for CCUS with three scenarios

Scenario	**Total yearly emissions** $[tonCO_{2eq}/year]$	**Part of Swedens total emissions 2022** [%]	**Emissions per FU** $[tonCO_{2eq}/tonGLD]$
1. Landfilling/ cover layer	-36 339	0.0734	-0.17683
2. Replacing clinker	-155 396	0.3138	-0.75616
3. Replacing gravel	-36 071	0.0728	-0.17552

In Figures 5.1 and 5.2, the different impacts of the emission points are shown. For all scenarios, the emissions from electricity generation, assuming Swedish electricity mix, is significantly less than the negative emissions from sequestering CO_2 in the GLD during the carbonation. For the two scenarios with product substitution, the added process step where the cGLD is dried increase the emissions from electricity generation with 2019% from $0.000174 tonCO_{2eq}/tonGLD$ to $0.0037 tonCO_{2eq}/tonGLD$.

For the case where the cGLD can be used to substitute gravel, the avoided emissions from the substituted gravel production are smaller than the emissions from the added electricity generation.

For the case where the substituted product is clinker, the avoided emissions from the substituted clinker production are roughly 165 times larger than the emissions added by the drying step and 3.3 times larger than the negative emissions from the sequestration of CO_2.

With these result, it can be shown that considering climate change, the benefits from further processing the carbonated GLD for product substitution heavily depends on the material it is substituting. For the case with substitution of gravel there were no benefits in terms of climate change potential but for the case with substitution of clinker, with a high carbon intensity, there were large benefits with the extra process steps. It is important to note that in these calculations, no emissions from transportation of the dry cGLD was included in the calculations. Including transportation could make the scenario 3 even less beneficial in terms of climate change potential.

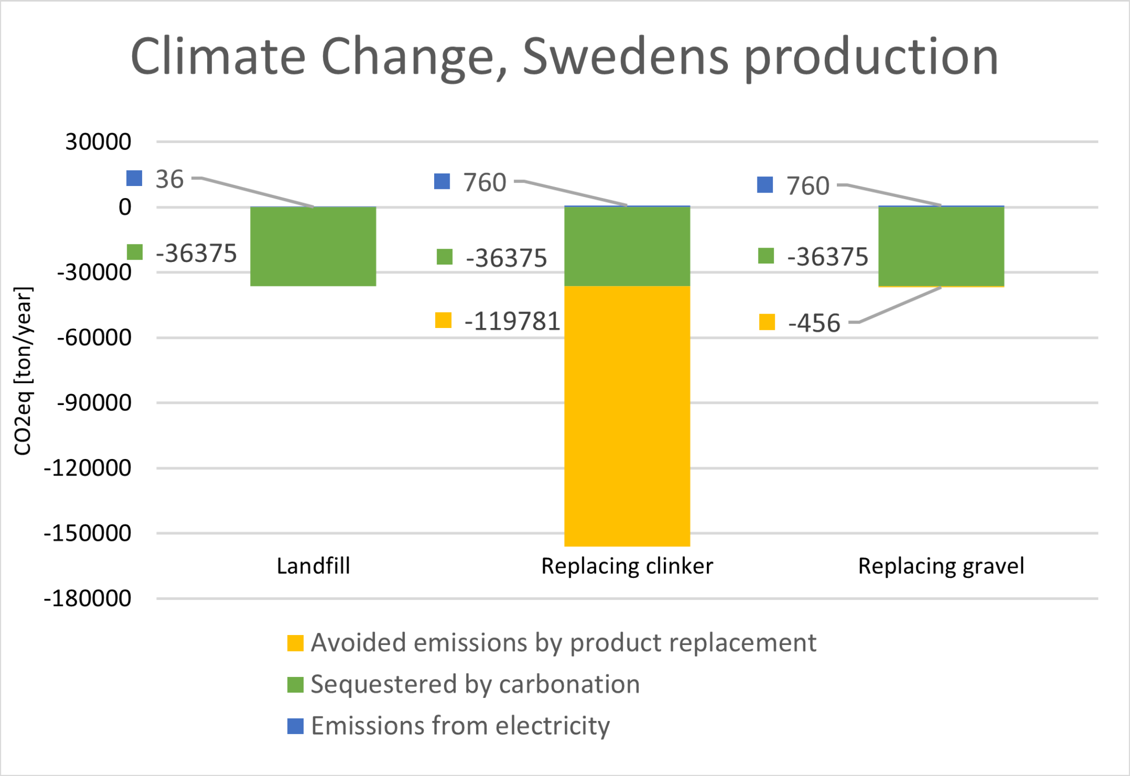

Figure 5.1: Climate change potential from the Swedish yearly production of GLD for the three scenarios of handling the cGLD: Landfilling, Replacing clinker and Replacing gravel

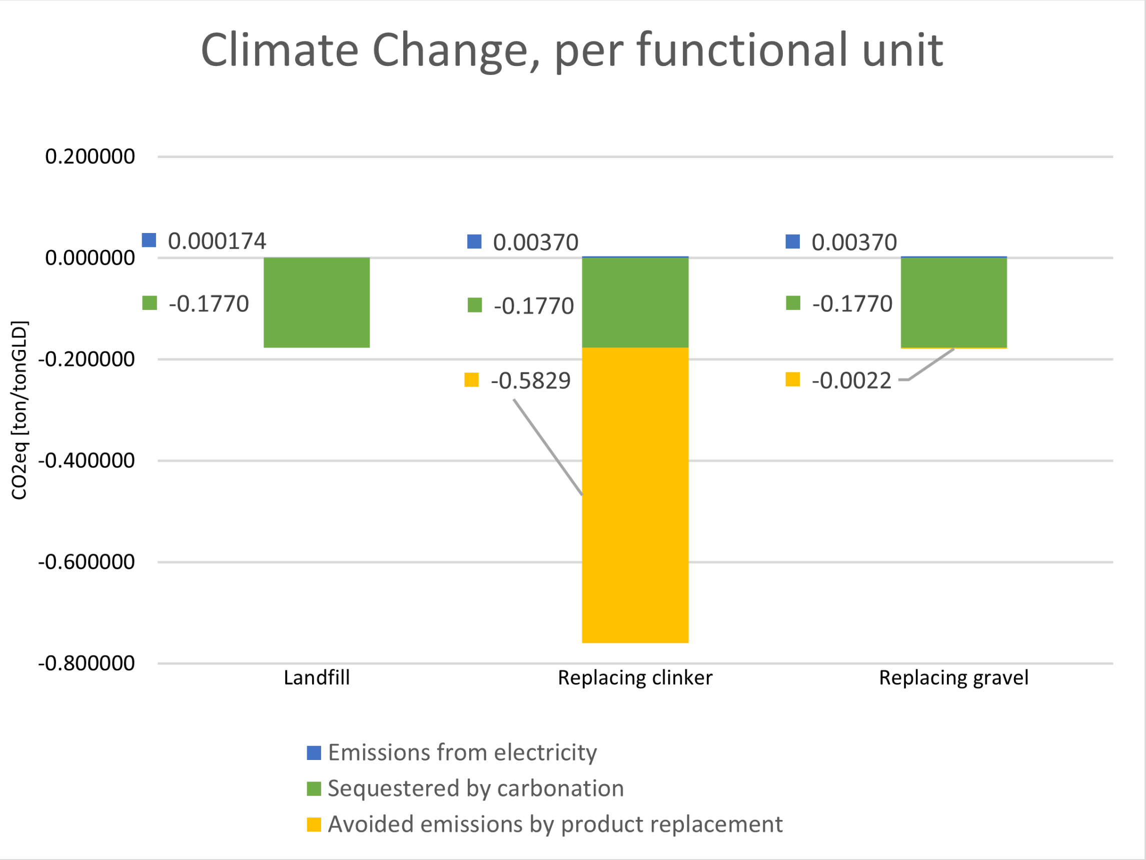

Figure 5.2: Climate change potential per ton uncarbonated GLD for the three scenarios of handling the cGLD: Landfilling, Replacing clinker and Replacing gravel

5.1.1 Sensitivity

Since it was determined early on that one of the parameters for sensitivity analysis, the value of filtration energy, did not have a large impact it was determined in an early step that the higher value would be used. For the other parameter that was chosen for sensitivity analysis, the carbon intensity of electricity generation, the impact was much larger. For such a case, the emissions from generating the required electricity for carbonation would be 36 times higher with EU-electricity mix than Swedish electricity mix. As can be seen in Figure 5.3, the higher carbon intensity for EU electricity gives that for the base case, without drying and product substitution, the emissions from electricity generation is still considerably less than the negative emissions from the CO_2 sequestration. For the case with drying and where the cGLD replace clinker for cement production, the avoided emissions from clinker production is over 4 times larger than the emissions from electricity generation. For the last case, with drying and where the cGLD replace gravel, the avoided emissions from gravel production is almost 60 times smaller than the emissions from electricity generation.

Thus, even though the carbon intensity of the electricity generation has minimal impact on the results for the first scenario it is clear that the impact is significant on the two scenarios with added electricity use for drying the cGLD before product substitution.

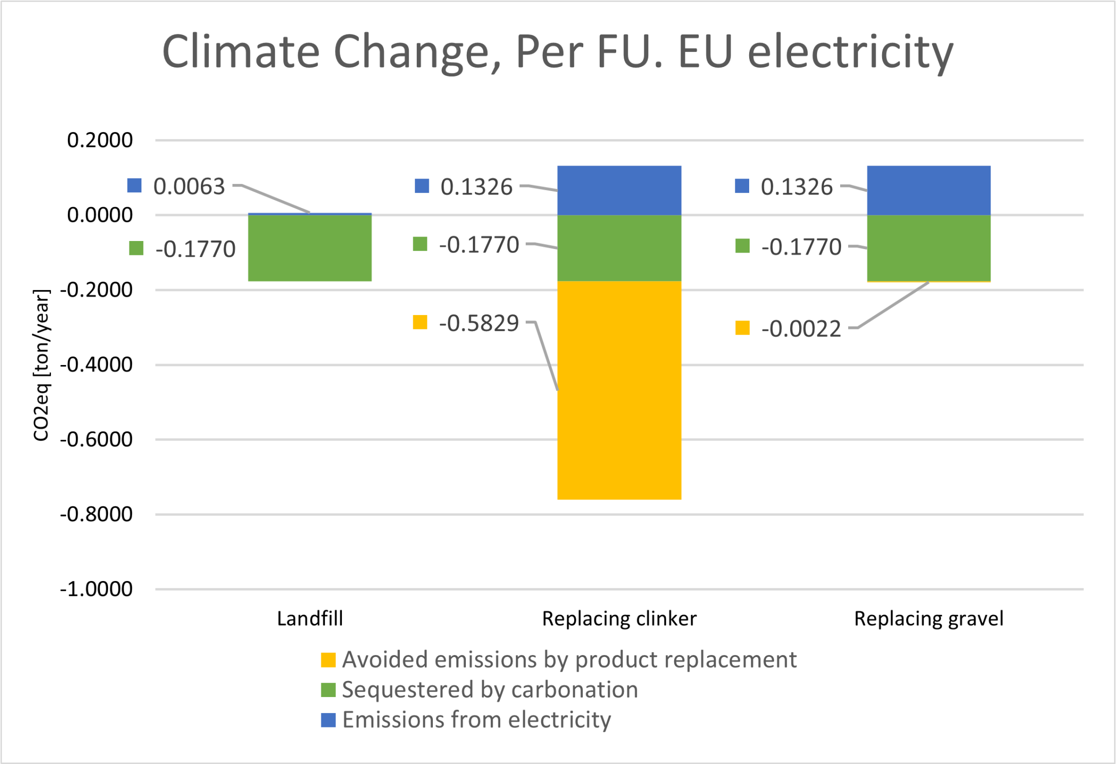

Figure 5.3: Climate change potential per ton uncarbonated GLD for the three scenarios of handling the cGLD: Landfilling, Replacing clinker and Replacing gravel. With EU-electricity

6

Discussion

In the discussion, the result of the study, limitations of the modelling, and a comparison to the available literature and earlier studies are analysed to provide context, assess the reliability of the study, and highlight areas for future research.

6.1 Result of the study

The aim of the study was to make an early indication on the possible benefits of carbonating GLD for CCUS using a scaled up model of the technology using the provided lab data as base. With the results and chosen research questions, the study clearly shows that carbonation of GLD could be an effective technology for CCUS, depending on the application of the cGLD. The sensitivity analysis with emissions from electricity generation as variables shows that the results can vary depending on relatively small changes in the input variables. As the sensitivity analysis showed that there are sensitivities within the model, together with the many assumptions made, the results should not be taken as facts but only a rough indication of the possible prospects for the technology.

An incentive for continuing the research on this technology and later on the implementation of it in the industry is the discussion regarding the tax exemption for landfilling GLD [32], [33]. If the exemption is removed, there could be benefits for the pulp industry with carbonation of GLD, if the cGLD can be categorized as a by-product that also could be sold and thus generate profits. Another incentive that could make this technology beneficial for the pulp and paper industries are that the negative emissions lowers their total emissions of fossil CO_2. With less emissions of fossil CO_2 the industries could make also profit from selling the freed up emission rights.

6.2 Earlier studies

In the literature study, no earlier studies were found that evaluated or further tested CCS or CCUS via carbonation of GLD. However, there were studies that discussed the possibility of using carbonation of alkaline waste materials for CCS and CCUS [34] [35], which would include GLD that has potential due to its high alkalinity. The results from this LCA shows that GLD, as discussed in the paper by Leventaki [13], could possibly be a viable option for carbonation. This study therefore contributes to increase the knowledge regarding using alkaline wastes, specifically GLD, as a source for storing and utilizing CO_2.

In the few studies that tested the possibility of using GLD as a substitute or additive to conventional products such as clinker, cement or gravel [27], [55], the GLD that was used was regular uncarbonated GLD. As the carbonation increase the amount of carbonates in the GLD, the physical properties of cGLD may vary from regular GLD. Thus should further studies on the possible uses of GLD in conventional products also be done using cGLD to see if the possible product range for substitution increases.

6.3 Limitations

Due to the fact that this is a study on a new way of conducting CCUS, there were a lot of limitations in the development of the model, such as lack of data. To handle the lack of data, some data from the current and conventional pulp and paper industry was used as well as assumptions. Many assumptions were made to be able to scale-up the lab data to industrial scale, which makes for uncertainties with the result. The assumptions were based on the scale-up framework by Piccinno et al. [42], information from the literature study and expertise from the industry. The impact of some assumptions was tested, such as the sensitivity analysis on the assumed electrical consumption from filtration and the choice of electricity production. Furthermore, important additions to the emissions from this technology such as transportation and construction of the needed infrastructure is not included which needs to be taken into account.

As discussed above, there are only a few studies that have looked at and tested the possible implementation of GLD as substitute for conventional products [27], [55], where all of them were using conventional uncarbonated GLD. The studies were also done in small scale so a limitation to this study is the uncertainty to which extent carbonated GLD can be used as substitute in reality. The assumption that the cGLD can be used as a substitution in clinker or gravel needs to be further confirmed.

Some other limitations of the study are the exclusion of emissions from transportation of the carbonated GLD and that the calculations are based on a best case scenario where all GLD produced in Sweden would be carbonated, which is a very optimistic assumption made to show the full potential of the technology.

It should also be noted that this study does not take into consideration the potential leaching of heavy metals and such which has to be addressed in further studies.

Due to the limitations in this study, the results should not be viewed as facts but as a rough indication on how carbonation of GLD could work as a technology for CCUS.

7

Conclusions

This Ex-Ante LCA aimed to provide early insights into the possibilities of implementing carbonation of GLD for CCUS on an industrial scale. The results show that the technology shows promise and in the case where the cGLD can substitute products that emit large amounts of GHGs when produced, such as clinker for Ordinary Portland cement production, this study shows that it can contribute with avoidance of large emissions. In this study, the calculations show that if all GLD produced in Sweden in a year is carbonated and used to substitute clinker, the avoided emissions could sum up to 0.31% of all of Sweden's and 24% of the Swedish pulp and paper industry's yearly emissions, based on the emissions in 2022.

It can be seen that the most energy intensive part of the technology is the drying of the cGLD for easier transport and use as substitutes. The energy required for drying is that large, so for the avoided emissions to be larger than the emissions from the electricity production, the substituted product need to be CO_2 heavy products. For the case without drying the largest electricity consumption comes from filtration of the dregs after carbonation followed by the pumping of flue gas.

The choice of electricity mix showed that the emissions from generating the electricity needed can mainly for the case with drying have a big effect the total amount of negative emissions and thus needs to be taken into account.

7.1 Further studies

With the result, the technology shows promise and should therefore be further studied. For future studies some design parameters could be made more efficient. Since the highest emissions within the system comes from drying, other possibilities or routes for drying should be assessed. It should be investigated if excess heat from the pulp mill could be used to dry the cGLD and thus lower the electrical energy use. The possibility of reusing the water needed for the aqueous carbonation should be investigated, that could thus possibly lower the need of energy in pumping the water and also be more resource efficient. This model is based on a simple case where the carbonation is done in batches, in further studies a more realistic scenario where the carbonation process would be continuous should be investigated.

To further establish the possibilities for using cGLD for substitution, studies should be made on the physical properties of cGLD, both by itself and mixed in potential subjects for substitution such as asphalt and cement. The physical properties of cGLD mixed with those products should be compared with the case with regular uncarbonated GLD to assess if the carbonation increases the stability and structure of GLD.

In further studies, other impact categories should be considered to get a full understanding of the possible impacts from carbonating GLD and possibly using it as substitution in conventional products. Impact categories that could be interesting to investigate are Resource use, Eutrophication and Acidification. As well as other impact categories, transportation of cGLD to be used as substitute should be included in further studies. The impact of transporting the cGLD if dried should be compared with transporting it without drying. In that way it can be studied if the drying step could be excluded and thus significantly lower the emissions from the electricity needed within the carbonation system.

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A

Appendix A

Conversion equations to calculate electricity consumption is presented in equations A.1-A.3.

$$1\ kWh\ =\ 3.6 * 10^6\ J \tag{A.1}$$

$$1\ kWh\ =\ 3.6 * 10^3\ kJ \tag{A.2}$$

$$1\ kWh\ =\ 3.6\ MJ \tag{A.3}$$

A.1 Reaction time

In the lab experiment, the time needed for full reaction was 24 minutes [46] when using a 30% CO_2 mixture of gas with a flow of 200 ml/min. To be able to roughly model the needed time for reaction with another composition it was assumed that the required reaction time was linearly dependent on the percentage of CO_2 in the gas flow, given that the flow rate was sufficiently above the need if 30% CO_2. The modelling of the needed flow of flue gas is described in Section A.3. The linearity was assumed as such that with 15% CO_2 the reaction time would be double compared to the lab case with 30%.

A.2 Batch size

It was chosen that for the model, multiple reactors would be used so that there would be a continuous start and end of batches. The assumption is that only one batch would be effectively active at a time but that once a reaction in a reactor was done the next one would start directly. That would make the time needed to fill and emptying of the reactors could be neglected. With that assumption it could be calculated how many batches there would be per day according to equation A.4.

$$Batches/day\ =\ \frac{24}{t/60} \tag{A.4}$$

Where t is the reaction time in *min/batch* 24 is hours per day and 60 is minutes per hour. With the assumed production days and the yearly produced amount of GLD according to Lundmark and Bergstedt [59], the amount of GLD that was to be carbonated in each batch could be calculated according to equation A.5.

$$m_{GLD}[ton/batch] = \frac{ton\ GLD\ produced/Operating\ days}{Batches/day} \tag{A.5}$$

Where m_{GLD} is in ton per batch, *GLD produced* is in tons per year and *Operating days* are per year. The resulted batch size is shown in section 4.3.2.

A mix of 5wt% GLD in water gives that for each ton of GLD there needs to be 19 tons of water. Using the amount of GLD per batch, the mass of water per ton of GLD and the density of water that at 25°C is 0.997 ton/m^3[54], the volume of water needed per batch was calculated according to equation A.6.

$$V_{H_2O} = m_{GLD} * \frac{19}{\rho_{H_2O}} \tag{A.6}$$

Where ρ_{H_2O} is the density of water.

A.3 Flue gas flow

For the modelling of the gas flow it was first chosen which source of flue gas from the Smurfit Kappa Piteå mill would be most preferred according to the assumed linear time dependence stated in Section 4.3.1, assuming all sources had a sufficiently large flow. The given data sheets on flue gas flow from the mill included reports on the recovery boiler, lime kilns and the combined flue gas flow from both. For the lime kilns, there were two data sets depending on the fuel used. One was when using wood powder and one was when using bio oil. It was chosen that the modelling of the flue gas would be based on a mean value of the flow and composition of the two fuels in the lime kilns. That is because both the recovery boiler and the lime kilns produces an abundance of flue gas and the concentration of CO_2 was higher in the flue gases from the lime kilns than the recovery boiler. In the emission report the gas flow is presented in three states, first the actual state right after the lime kilns, then one for if the gas is in normal state (273 K and 1 atm pressure) and one for if the gas is dry and in normal state, m^{3}ndg/h. Since the the modelled carbonation is aqueous and the carbonation in the lab experiment used dry gas and carbonation at atmospheric pressure, the last one was used. It is also coherent with the values for the concentration of CO_2, which is presented in volume percent for dry gas, vol%dg. To check if the flow of flue gas from the lime kilns were large enough the flow of gas in the lab experiment by Leventaki needed to be normalized and then expanded. In the lab setup a flow of 30% CO_2 and 70% N_2 was used, where the percentages are assumed to be volumetric. The flow in the lab experiment was 200 mL/min of gas for 3 grams of GLD sample. The flow of gas in the lab experiment was first normalized to be dependent of the amount of GLD in grams and minutes to then be extended to m^3 of gas per hour and ton GLD. 200 mL/min for three grams was in that way extended to 4000 $m^3/h/ton\ GLD$. The needed flow per ton of GLD was then multiplied with the amount of GLD that was modelled to be carbonated per batch, to get the needed minimum flow $\dot{Q}_{fg}$. The minimum flow was then compared with the given data on flow of gas from all sources the Smurfit Kappa mill to check that the requirements in terms of flue gas flow could be met.

A.4 Flue gas pumping

To model the energy use from pumping the needed flue gas through the GLD was not straight forward.

The section of the model regarding the energy consumption from blowing flue gas from the boiler through the reactor is based on an energy analysis and life cycle assessment on Post-combustion carbon capture technologies by Zhang et al. [51]. That is due to hardships in finding a proper model to use for energy consumption from blowing flue gases. In the assessment from Zhang et al. both the flow of the blown flue gas and the energy consumption of the blower is stated as 781.8 kg fluegas/s and 8.2 MJ/s. To model the energy consumption for the blower a formula for energy consumption per gas flow was derived from the values from Zhang et al. according to equation A.7

$$\frac{8.2\ MJ/s}{781.8\ kg/s} = 0.01049\ MJ/kg \tag{A.7}$$

Together with the gas flow, $\dot{Q}_{fg}$ modelled in section A.3 and the density of the flue gas presented in the emission reports, the energy consumption for blowing the flue gas was calculated. In the emission reports the density of the flue gas was presented in three different conditions, kg/m^3, kg/m^{3}n and kg/m^{3}ndg. Because the earlier used data from the reports were for dry gas at normal state, ndg, the last version was used for calculating the energy consumption for pumping flue gas. It is assumed that only the needed amount of flue gas will be used pumped through the carbonation reactor and not the excess.

A.5 Headloss

The energy needed to pump the water was modelled through equation A.8 [52]

$$P = \frac{\dot{Q} * H * g * \rho}{\eta_{pump}} \tag{A.8}$$

Where P is the power needed to pump the water in $[W]$, $\dot{Q}$ is the volumetric flow of the liquid in $[m^3/s]$, H is the head in $[m]$, g is the gravitational constant 9.82 m/s^2, ρ is the density of the liquid in $[kg/m^3]$ and η_{pump} is the assumed efficiency of the pump. According to Piccinno et al. [42], the efficiency of a pump can be assumed to be 85%, thus was η_{pump} set to 0,85. The head, H, consists of static head h_S and dynamic head, h_D according to equation A.9.

$$H = h_S + h_D \tag{A.9}$$

Static head is the physical height the water needs to be pumped and the dynamic head is the pressure loss from friction to the inside of the pipe and from pressure losses due to fittings and turns of the tube. Due to assumed volume, height and type of reactor, the static head was assumed to be 4 meters. The dynamic head consists of headloss from friction inside the tube, h_L and headloss due to fittings,

h_F. According to Welty et al. [43], the headloss from friction can be calculated according to equation A.10.

$$h_L = 2f_f \frac{L}{D}\frac{v^2}{g} \tag{A.10}$$

Where f_f is the friction factor, L is the lenght of the tube, D is the inner diameter of the tube, v is the velocity of the liquid and g is the gravitational constant. The length of the tube was assumed to be 300 meters due to general measurements of pulp mills using Google Maps measurement tool. The friction factor depends on if the flow inside the tubes is laminar or turbulent and the roughness on the inside of the tube. To conclude if the flow inside the tubes would be laminar or turbulent the Reynold's number was used through equation A.11[52].

$$Re = \frac{vD}{\nu} \tag{A.11}$$

In equation A.11, the v denotes the speed of the liquid in $[m/s]$, D denotes the inner diameter of the tube in meters, ν denotes the kinematic viscosity of the liquid in m^2/s and Re denotes the Reynold's number for which Re<2300 shows that the flow is laminar and for Re>2300 shows that the flow is turbulent.

During the modelling and dimensioning of the pipes, all dimensiones gave Re=2199, thus laminar flow. Due to a laminar flow, the friction factor f_f can according to Welty et al. [43] be calculated acording to equation A.12

$$f_f = \frac{16}{Re} \tag{A.12}$$

For the pressure loss due to fittings, h_F, equation A.13 was used[43].

$$h_F = (\sum K_i)\frac{v^2}{2g} \tag{A.13}$$

Where K_i is a coefficient dependent on the fitting i. The coefficient, K_i, is also depending on the flow properties of the liquid flowing inside the tube where $K_{i,1}$ is the coefficient value for fitting i at $Re = 1$ and $K_{i,t}$ is the coefficient value for fitting i for turbulent flow. For turbulent flow, $Re < 2300$, the coefficient can be approximated using the Hooper approximation below.

$$K_{i,Re} = \frac{K_{i,1}}{Re} + K_{i,t} \tag{A.14}$$

For the modelling of the piping, only the pumping of water to the reactor was included. For simplicity, the pipe was assumed to be straight with two 90° turns, one to make the pipe go vertically by the side of the reactor and one for the pipe to face the reactor. It was assumed that the other fittings was only a pipe entrance and a tank inlet into reactor. A table containing the coefficients $K_{i,1}$ and $K_{i,t}$ [52][43][53] is presented below in Table A.1. Using the coefficients from Table A.1, equation A.14 and Re=2199, the coefficients presented in Table A.2 was calculated.

Table A.1: Pressure drop coefficients for laminar and turbulent flow

Fitting	$K_{i,1}$	$K_{i,t}$
90°bend	800	0.7
Pipe entrance	0	0.05
Tank inlet	160	0.2

Table A.2: Pressure drop coefficiants for Re=2199

Fitting	**K**
90°bend	1.06
Pipe entrance	0.05
Tank inlet	0.27
$\sum(K_i)$	2.45

Combining equations A.8-A.14and the values in Table A.2, the power needed to pump the needed water for one batch into the reactor could be calculated.

A.6 Stirring

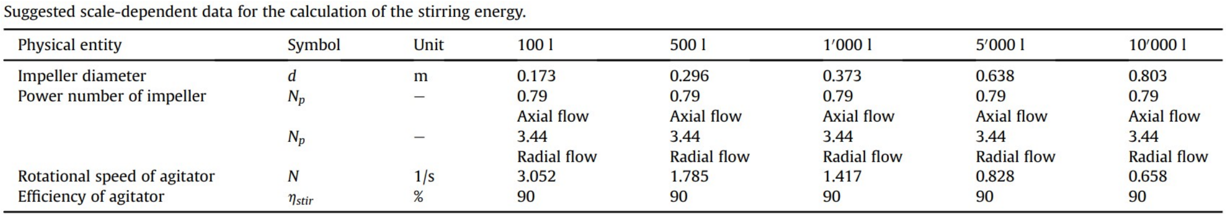
In the lab experiments by Emmanouela Leventaki [46] the mixture of GLD in water was mixed for 24 hours in the case with maximum carbonation of the GLD. It was therefore assumed that a stirring time of 24 hours would be applied to each batch as well, and therefore the energy needed to drive the stirrer had to be modelled. Two ways of modelling were first assessed, using the measured energy use for stirring the lab experiment and scaling it up to the needed size for the Smurfit Kappa mill and using a formula with some assumed constants as done in the scale-up framework by Piccinno et al. [42]. Since the stirrer in the lab environment is very different from industrial stirrers, the formula from the scale-up framework was used. In the framework the energy needed for stirring could be modelled according to equation A.15 [42].

$$E_{stir} = \frac{N_P * \rho_{mix} * N^3 * d^5 * t}{\eta_{mix}} \tag{A.15}$$

Where E_{stir} is in [J], N_P is a dimensionless number depending on if it is an axial or radial stirrer, ρ_{mix} is the density of the mixture in [kg/m^3], N is the rotational speed of the agitator in [1/s], d is the diameter of the impeller and η_{mix} is the efficiency of the agitator. In the framework, a table is shown with suggested data on N_P, N, d and η_{mix} related to different volumes of the tank ranging from 100 l to 10,000 l, which is shown in Figure A.1. For N_P, values for both axial flow and radial flow was presented of which the axial flow was chosen since the value was significantly lower than for radial flow. Since the modelled batch size somewhat exceeded 10,000 l, the values from the table were linearly extrapolated from the values at 5,000 l and 10,000 l. To calculate the density of the mixture the total volume of water and GLD needed to be calculated. According to dos Santos et al. [26], the density of dry GLD

(0% water) is 2498.1 kg/m^3 which combined with the assumed water content of 55% and the density of water gave a density of the wet GLD, ρ_{GLD}, at 1672.5 kg/m^3. Combining the mass of GLD per batch calculated according to section 4.3.2 with the density of wet GLD gave the volume of the GLD used in each batch. That was added to the volume of water needed, V_{H_2O}, to get the total volume of the mixture, V_{mix}. To get the density of the mixture, the mass of the mixture was divided with the total volume of the mixture according to equation A.16.

$$\rho_{mix} = \frac{V_{H_2O} * \rho H_2O + m_{GLD}}{V_{mix}} \tag{A.16}$$



Suggested scale-dependent data for the calculation of the stirring energy.

Physical entity	Symbol	Unit	100 l	500 l	1'000 l	5'000 l	10'000 l
Impeller diameter	d	m	0.173	0.296	0.373	0.638	0.803
Power number of impeller	N_p	–	0.79 Axial flow	0.79 Axial flow	0.79 Axial flow	0.79 Axial flow	0.79 Axial flow
	N_p	–	3.44 Radial flow	3.44 Radial flow	3.44 Radial flow	3.44 Radial flow	3.44 Radial flow
Rotational speed of agitator	N	1/s	3.052	1.785	1.417	0.828	0.658
Efficiency of agitator	η_{stir}	%	90	90	90	90	90

Figure A.1: Table showing data for calulation og stirring energy, from Picchinno et al.

A.7 Drying

It was assumed that for substitution in cement, concrete or gravel, the carbonated GLD needed to be completely dry. Therefore it was needed to model the energy needed to dry the filtered cGLD. As written in section 4.3.7, it was assumed that the bound CO_2 did not add any water to the cGLD after filtration compared to the GLD added to the batch from the beginning. Since the water content, u_{GLD}, was assumed to be 55% in the GLD before aqueous carbonation the amount of water needed to be removed by drying for each batch was calculated by multiplying the weight of the uncarbonated GLD with the assumed water content. To model the energy consumption from drying the carbonated GLD, Q_{dry}, the equation A.17 can according to the Scale-up framework by Picchinno et al.[42] be used.

$$Q_{dry} = \frac{C_{p,cGLD} * m_{cGLD} * (T_{boil} - T_0) \ + \ \Delta H_{vap} m_{vap}}{\eta_{dry}} \tag{A.17}$$

Where m_{cGLD} is the mass of the cGLD after filtration, $C_{p,cGLD}$ is the specific heat capacity of the cGLD after carbonation, T_{boil} is the boiling temperature of the water that is to be dried off, T_0 is the temperature before the drying process start, ΔH_{vap} is the heat of vaporization for the water that is to be evaporated, m_{vap} is the mass of the water that is to be evaporated from the bulk and η_{dry} is the efficiency of the dryer which is assumed to be 80% as recommended by Piccinno et al.[42]. The boiling temperature is that of water, which is 100°C at atmospheric pressure and the initial temperature T_0 is assumed to be 25°C. It is assumed that m_{vap} is equal to all water in the cGLD after filtration and the enthalpy of evaporation for water at T_{boil} is 2256.4 kJ/kg [60].

In the literature there is no data on the specific heat capacity of GLD, so to make a rough estimation some assumptions had to be made. As stated before it was assumed that the bound CO_2 did not add any more water to the GLD compared to before the carbonation. Therefore the water content after carbonation, u_{cGLD}, was assumed to be calculated according to equation A.18.

$$u_{cGLD} = \frac{u_{GLD} * m_{GLD}}{m_{cGLD}} \tag{A.18}$$

It was assumed that the bound CO_2 for most part had formed calcium carbonate, $CaCO_3$, and that most of the dry material of the cGLD therefore also consisted of calcium carbonate. It was therefore assumed that the dry material of the cGLD had the specific heat capacity of calcium carbonate, which according to The Engineerign ToolBox is 0.76 kJ/(kg*K)[61]. For water at 25°C, the specific heat capacity is 4.1816 kJ/(kg*K)[62]. To estimate specific heat capacity of the wet cGLD it was assumed that the heat capacities of the water and solids could be added together according to equation A.19.

$$C_{p,cGLD} \;=\; u_{cGLD} * C_{p,H_2O} + (1 - u_{cGLD}) * C_{p,dry\ cGLD} \tag{A.19}$$

The calculated heat capacity for the carbonated and filtered cGLD could then be put into equation 4.4 to get the estimated energy consumption for drying one batch of carbonated GLD to 0% water content.

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